A STUDY OF LUMINESCENT SI-BASED MATERIALS THROUGH X-

RAY SPECTROSCOPIES

A STUDY OF LUMINESCENT SI-BASED MATERIALS THROUGH X-RAY

SPECTROSCOPIES

By

TYLER RICHARD ROSCHUK

B. Sc. (University of Saskatchewan) 2002 M.A.Sc. (McMaster University) 2005

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AUTHOR: Tyler Richard Roschuk (McMaster University)

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Abstract

Light emitting silicon nanostructures are of significant interest for photonics due to their potential to act as the source material for a monolithically integrated Si-based light source. This thesis reports on the experimental characterization of such luminescent structures formed in silicon nitride, oxynitride, and rare earth doped silicon oxide thin films. Changes in the electronic structure of the materials have been analyzed using soft X-ray spectroscopy by probing the constituent elements at their absorption edges. The observed near edge structure at these edges is related to the local atomic bonding environment of the probed atoms. Specifically, changes in the near edge structure at the Si *K* and $L_{3,2}$ absorption edges can be related to the coordination of silicon atoms within the films.

In the silicon nitrides the Si-clustering process has been observed to onset at different anneal temperatures, dependant on film composition. In films that have a small amount of excess Si higher anneal temperatures are required before a significant Si-Si bonding signal is observed. In samples with high concentrations of excess Si this clustering process is observed to occur at temperatures as low as 700 °C. In silicon oxynitride samples only a small fraction of the excess Si forms into clusters within the films. Rather, in these samples the formation of distinct silicon oxide and silicon nitride phases is observed, with strong absorption related to the formation of the oxide phase being observed after annealing at high temperatures ($T \ge 1000$ °C). The nanoclusters

were determined to be amorphous in nature, rather than nanocrystalline, through the use of high-resolution, energy filtered, and scanning transmission electron microscopy. This behavior was seen even for samples with high excess Si concentrations and annealed at high temperatures. This contrasts with the behavior of silicon-rich silicon oxide thin films were nanocrystals are clearly observed after similar treatments, indicative of the influence of the nitride host matrix on the cluster formation process.

Changes in the electronic structure at these edges have been correlated with changes in the bonding structure within the films, as analyzed through Fourier transform infrared spectroscopy, and with the photoluminescent behavior of the films.

X-ray excited optical luminescence (XEOL) has been used for the study of rare earth doped silicon oxides, allowing for site specific excitation of the films in order to analyze the origin of luminescence in the films. In O-rich samples the luminescence of the films has been observed to be strongly excited at O-related absorption edges while in Si-rich samples XEOL is observed at Si-Si bonding absorption energies. The results indicate the presence of different sensitization pathways towards luminescence in the films, including the formation of oxide or silicate phases.

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Because this work has been primarily experimental I've been fortunate to work closely with a number of people with whom I've had many fruitful and stimulating

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List of Abbreviations

<i>a</i> -Si-nc	Amorphous silicon nanocluster
c-Si-nc	Crystalline silicon nanocluster/silicon nanocrystal
CLS	Canadian Light Source
CMOS	Complementary metal oxide semiconductor
CVD	Chemical vapour deposition
DOS	Density of states
ECR	Electron cyclotron resonance
EELS	Electron energy loss spectroscopy
EFTEM	Energy filtered transmission electron microscopy
FLY	Fluorescence yield
FTIR	Fourier transform infrared spectroscopy
HREM	High resolution (transmission) electron microscopy
ICP	Inductively coupled plasma
ITRS	International Technology Roadmap for Semiconductors
LED	Light emitting diode
MQW	Multiple quantum well
ORSO	Oxygen rich silicon oxide
PDOS	Partial density of states
PECVD	Plasma enhanced chemical vapour deposition
PES	Photoelectron spectroscopy
PL	Photoluminescence
QC	Quantum confinement
QCE	Quantum confinement effects
QD	Quantum Dot
QW	Quantum well
RBM	Random bonding model
RE	Rare earth
REXS	Resonant elastic x-ray scattering
RIXS	Resonant inelastic x-ray scattering
RMM	Random mixture model
Si-nc	Silicon nanocluster

SiON	Silicon oxynitride
SL	Superlattice
SRSN	Silicon rich silicon nitride
SRSO	Silicon rich silicon oxide
STEM	Scanning transmission electron microscopy
TEM	Transmission electron microscopy
TEY	Total electron yield
XANES	X-ray absorption near edge structure(s)
XAS	X-ray absorption spectroscopy
XRF	X-ray fluorescence
XEOL	X-ray excited optical luminescence

Chapter 1: Introduction

1.1 Microelectronics, Optical Interconnects, and Silicon Photonics

Silicon is the dominant material in microelectronics. The processing abilities available for fabricating integrated electronic circuitry based on silicon are currently unmatched by any other material system. The continued application of Moore's Law to microprocessor design has led to increasingly faster and complex integration schemes. Roughly stated, Moore's Law¹ says that the number of transistors that can be placed on an integrated circuit doubles every two years [1]. This trend is illustrated in Figure 1.1. Furthermore, the regular availability of the International Technology Roadmap for Semiconductors² (ITRS) has ensured that key technological requirements for the continuation of this trend are indentified [2]. Major difficulties and perceived roadblocks for future generations on integrated circuits are also addressed in the ITRS, along with information on the current status of potential solutions to these problems.

¹ The original statement by Gordon Moore is "The complexity for minimum component costs has increased at a rate of roughly a factor of two per year...", and was primarily an economic consideration [1]. Complexity is generally equated with transistor count.

 $^{^{2}}$ Editions of the ITRS are released biennially, with updates in the interim years. This ensures that the industry is continually aware of and updated on the status of current technologies and its ability to meet foreseen problems.

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Figure 1.1: Moore's Law. The number of transistors on an integrated circuit has historically increased exponentially, doubling \sim every 2 years (Source: Intel Corporation [3]).

One of the major challenges currently faced by microelectronics is the interconnect bottleneck. While the continued scaling of transistor sizes leads to faster clock speeds and switching times, the same is not true for the metallic wiring that connects the transistors. As the scale of these interconnects is decreased parasitic RC time delays become the dominant factor in how fast microprocessors can perform. This issue is illustrated in Figure 1.2 [4]. The problem is aggravated by the increasing length of interconnects required on a single chip in order to connect the increasing number of transistors³. This length (per unit area) is currently on the order of kilometers⁴. While

³ A press release by Intel celebrating the anniversary of Moore's Law in 2005 illustrates the Dual Core Itanium® processor having over a billion transistors.

⁴ There are further problems related to the current generation of interconnects. The multiple layers of interconnects required also lead to problems with cross-talk and RL or RLC delays. Moreover, power consumption and heat dissipation are resulting in thermal power densities on the order of rocket nozzles with the expectation that this density could reach that of nuclear reactors within several years.

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solutions to this problem have been found in the past through a switch in the material system for the interconnects to Cu and low- κ dielectrics, currently, there are no known manufacturable solutions to address this problem in subsequent generations. This is anticipated to have significant impact as the industry approaches the 45 nm (2010) and 32 nm (2013) processing nodes. It is, therefore, necessary to consider alternate paradigms in order to meet the demands for increasing processing speeds, as well as to accommodate the increased bandwidth requirements that accompany this.





A proposed solution to the issue of interconnect delay is the conversion from a traditional metal-dielectric interconnect scheme to optical interconnects. This would directly integrate photonic elements alongside complementary metal oxide semiconductor (CMOS) microelectronics. The 2003 ITRS identifies three key requirements for the development of optical interconnects [5]:

• A high efficiency, high switching rate laser source, monolithically integratable into Si CMOS, (at low cost) needs to be developed.

• A low power modulator, monolithically integratable into Si CMOS, (at low cost) to be used in conjunction with an off chip continuous laser.

• Low power, high efficiency, small size optical detectors monolithically integratable into Si CMOS (at low cost).

To date it is not possible to meet all these requirements. The 2007 edition of the ITRS reiterates the need for cost-effective, CMOS-compatible low power devices, listing these requirements as the current challenges for the implementation of optical interconnects [6]. In particular, the need for progress in the areas of modulators, light sources, and couplers (if an off chip light source is to be used) is identified.

In essence, the goal of optical interconnects is the miniaturization and integration of those components currently used in long-distance optical (telecom) networks with the added stipulations of requiring low-cost and low-power, barriers not historically faced in the telecom market. It is worth noting that photonics is a relatively immature field in comparison with microelectronics. However, advances in optical technologies have

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shown exponential growth, in terms of their performance to cost ratio, at greater rates than that of microelectronics, doubling every ~ 9 months⁵ [7]. The potential for optoelectronic and photonic technologies to advance and play an important role in computing technologies and to grab a significant portion of this >200 billion dollar market is great.

One of the key problems for optical interconnects (and integrated photonics in general) is that optoelectronics and photonics have seen no one dominant material for integrated applications. Light sources have traditionally been manufactured using III-V materials, such as GaAs and InP, waveguides may be made of silicon or silica, modulators fabricated in lithium niobate, and detectors made from a variety of materials, including silicon. The results are costly, complex, non-CMOS compatible integration schemes trying to accommodate these different material platforms. Further problems then arise with the different array of processing tools needed to meet these schemes.

Ideally, one wants a single material platform upon which these different components may be manufactured, with Si CMOS compatibility being obtained by attempting to fabricate everything on silicon. This is the goal of silicon photonics [8-10]. Using the same material platform as microelectronics, silicon photonics would also have access to the large infrastructure available for CMOS processing. This access provides additional advantages for the fabrication of Si-photonic devices not aimed at integrated

⁵ This was, at least, the case prior to the decline in the telecom market in the early 2000s. The potential for such continued growth remains and requires only renewed industrial interest and investment, as appears to have been occurring over the past few years.

applications (e.g. lighting and display applications). Optical interconnects are, however, one of the primary targeted areas for silicon photonics. Si-based photonic components would be implemented alongside current CMOS circuitry, providing board to board and chip to chip communications. In further instances silicon photonics would eventually seek to replace the on-chip interconnect system, beginning with the global interconnect in integrated circuits. This would enable the logic processing through the electronic circuitry and signal transmission and processing through the photonic circuitry. In the long-term it is possible to conceive that silicon photonics may mature in such a manner as to provide all-optical computing, however, such a development is likely decades away. Figure 1.3 highlights one initial potential integration scheme, as proposed by the Silicon Photonics Lab at Intel⁶ while Figure 1.4 illustrates the necessary components for this scheme.



Figure 1.3: An integration scheme for Si photonics. The scheme combines microelectronics for logic processing with photonic components for board to board or chip to chip communications. Reproduced with permission from Intel [11].

⁶ Now a part of the Intel Tera-Scale Computing Research Program.



Figure 1.4: The necessary components for silicon photonics. A Si-based light source remains the key missing component for the implementation of all Si-photonics. Reproduced with permission from Intel [11].

The optical components outlined in the above scheme; light sources, waveguides, modulators, and detectors, form a standard basic set for all integrated photonic circuitry [12]. Si-based waveguides [13, 14], modulators [15], and detectors [16] have all been demonstrated⁷. More detail on these components may be found in [9] and [17].

A Si-based light source suitable for integration is the key component that remains lacking. While recent reports have demonstrated the ability to get lasing in silicon through the Raman Effect [18-20], such a laser still requires a high powered external laser for its operation. While the results from this work are interesting, the lack of electrically driven excitation and the need for an external laser source make the silicon Raman laser

⁷ This includes detectors capable of operating at sub-bandgap wavelengths. This is necessary for processing data transmitted through optical fibres, for which the transparency windows are 1.3 and 1.55 μ m.

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 unsuitable for the development of wholly Si-based integrated photonics. The device does,

 however, carry the notable banner of being the first silicon laser.

Another recent development is the so-called hybrid silicon laser [21, 22]. This laser uses III-V materials, which act as the electrically driven gain medium, bonded to a Si ridge waveguide. It is not yet clear that such a device can be implemented in a CMOS-compatible manner, both from a processing and economic standpoint. A more detailed discussion on CMOS compatible integration has recently been given by J. Milgram [23].

The problem with using silicon itself as the light emitting material for silicon photonics arises from its electronic structure, in that silicon is a so-called indirect bandgap material. This means that the minimum of the conduction band and the maximum of the valence band are offset in momentum space. Electron-hole recombination in silicon is, therefore, a three body process, requiring the simultaneous interaction of a phonon for the conservation of momentum and the emission of a photon in order to conserve energy. The phonon interaction process is long in comparison with alternative non-radiative recombination pathways, which makes bulk silicon an inefficient light emitter. A more detailed discussion of the subject is reserved for Chapter 2.

Once the dimensions of silicon are taken down to the nanoscale, however, its behavior begins to be dominated by quantum confinement effects (QCE). QCE result in the localization of electrons and holes within the nanoclusters. This spatial confinement leads to a broadening of the electron (or hole) wavefunctions in momentum space. When

there is sufficient overlap of the electron and hole wavefunctions the need for phonon interaction is relaxed, and light emission becomes a more efficient process. An exact understanding of the observed emission spectra from silicon nanoclusters often requires further considerations regarding the interface of the nanoclusters, which can present localized surface defects through which recombination can occur.

Light emission from silicon nanostructures has been an intense area of research for nearly two decades, beginning with the observations of luminescence from porous silicon by L. Canham in 1990 [24]. The efforts devoted to this research can be attributed to the immense potential of a Si-based light source, particularly a Si-based laser for integrated photonic applications⁸. The observation of gain in the emission from Sinanocrystals formed in silicon oxide thin films has served to bring the possibility of a Silaser closer to reality and spurred further research in this field [25]. As mentioned, other applications of Si-based light sources can also be found in the areas of displays and solid state lighting.

In spite of the vast amount of research that has gone into this area, many unresolved issues still present themselves, both in terms of the understanding of the materials, including their luminescent properties, and the details of nanocluster formation as a function of deposition and processing parameters, and in the engineering of a light

⁸ The ISI Web of Knowledge returns a combined total of just under 15,000 results for a search of the terms porous silicon and silicon nanocrystals. Canham's paper itself has nearly 4,500 citations. To put this number into perspective A. Fern shared $\frac{1}{2}$ of the 2007 Nobel Prize in Physics for his part in the discovery of giant magnetoresistance (considered the birth of spintronics). Fern's paper has just fewer than 4,000 citations. If a silicon light source suitable for integration is developed using quantum confined silicon the prediction of a Noble Prize in Canham's future would not be unreasonable.

source itself. One of the key difficulties in the understanding of light emission from Sibased materials relates to the relative contributions to the luminescence process of quantum confinement and defects in the host material, particularly at the nanoclusters interface. The emission range of porous Si is tunable from the blue to the near-infrared, however, the oxidation of porous silicon has been shown to limit the observed emission to the red-near infrared emission range due to the presence of Si-O related states [26]. More recently, silicon nitride based materials have drawn increased interest. In the nitrides, however, several defect levels may be present which can pin the observed emission energy [27], although it may be considered advantageous in some cases that these defects lie at higher energies, allowing access to more of the visible spectrum. Silicon nitrides also have a lower barrier for carrier injection and may be better suited to the development of electrically pumped devices. Light emitting diodes based on nanoclusters embedded in silicon nitrides have already been fabricated [28].

The incorporation of rare earth elements in silicon nanocluster embedded materials provides localized defects to which the nanoclusters may transfer energy leading to light emission characteristic of the rare earth elements [29]. This behavior can be exploited when specific emission wavelengths are desired. Erbium is by far the most intensively studied rare earth for such applications, due to its emission at the silica fiber transparency window of 1.54 μ m. The visible emissions of other rare earths may be suitable for display and lighting applications. The nature of the energy transfer process, defect related coupling mechanisms, and details of rare earth incorporation into these

<u>PhD Thesis – T. Roschuk</u><u>McMaster University– Engineering Physics</u> materials are not yet clear. In fact, although it often seems that in the literature the rare earths are discussed in the same breadth, it is not necessarily clear that the details of the excitation and energy transfer process are the same for the different rare earths, particularly with varying compositions of the host matrix.

Details of nanocluster formation and the role of the surrounding dielectric in this process remain an active area of research, both for undoped and rare-earth doped systems. This thesis focuses on certain aspects within this area and a literature review and discussion of the subject is given in Chapter 3. It is worthwhile to note that the study of these materials encompasses a huge parameter space, including silicon rich silicon nitrides (SRSN), silicon rich silicon oxides (SRSO), oxygen rich silicon oxides (ORSO), nitrogen rich silicon nitrides (NRSN), silicon oxynitrides, and rare earth doped versions of any of the preceding systems. The parameter space is further expanded by considering the annealing treatments to which these films are subjected in terms of environment, temperature, and duration. The issues related to understanding these films are compounded because the films can show drastically different behavior with composition. Silicon rich silicon oxides require annealing at temperatures greater than 1000 °C before luminescence is typically observed, while silicon rich silicon nitrides often show their best behavior at ~700 °C. Some samples may or may not emit any luminescence depending on their growth rates, regardless of subsequent annealing conditions. As materials science related issues are slowly becoming better understood, however, our

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 ability to develop more efficient materials increases, in turn increasing the probability of fabricating a silicon-based light source.

Finally, two practical aspects related to the above discussion merit consideration. First, quantum confined silicon systems are not the sole contender for developing CMOScompatible light sources. Alternative luminescent Si-based systems, such as high purity, float zone silicon have been used to fabricate efficient Si-based light emitting diodes (LEDs) [30, 31]. The structure of such devices is, however, currently quite complicated. Other groups have explored the use of band-structure engineering in Si/SiGe nanostructures and superlattices [32, 33]. Although using a Si-based material is desirable, it is not a necessity provided that another material system can be readily incorporated in a CMOS processing workflow without resulting in contamination. Given the almost immediate applicability of a CMOS-compatible device it is quite likely that the first successful approach will rapidly dominate the field. Although it is not yet clear which material will be used for the development of a CMOS-compatible emitter, the work of Joel Milgram presents some of the first efforts at integrating luminescent Si-nanocrystal based systems (fabricated at McMaster University) with Si-based waveguides with promising results for the integrability of the material systems discussed in this work [23, 34]. Other groups have also reported on the fabrication and behavior of Si-nanocrystal based field-effect light emitting devices [35].

Second, while the development of a Si-based light source would provide the final component necessary for silicon photonics another compatibility issue remains when one

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considers the long term applications of silicon photonics; that of the size mismatch between the current generation of electronics, where transistors are now being manufactured on scales less than 100 nm, and photonic components, which have sizes on the order of the wavelength of light (at least hundreds of nm). This size mismatch becomes particularly relevant when one considers the replacement of local interconnects. Recent research, however, suggests that these limitations may be overcome, although to do so may require the development of new optical technologies. One such technology is the field of plasmonics, where optical signals are propagated along nanoscale metallic wires through the generation of plasmons at the metal-dielectric interface [36, 37]. The field is quickly growing and shows much potential, both as its own technology and for the potential to act as an intermediary between nanoelectronics and microphotonics. Furthermore, within the next few processing generations, the electronics industry will be fabricating devices that are truly on the nanoscale, providing the manufacturing infrastructure to enable plasmonic device fabrication in a CMOS-compatible manner.

1.2 Thesis Purpose and Approach

This thesis is concerned with developing a better understanding of the materials science aspects of luminescent Si-based materials. Such better understanding, in particular of how the structure of these materials evolves with different growth and processing parameters, can lead to methods of improving the efficiency of light emission.

In the area of Si-nanocluster embedded dielectrics a large portion of the work done has been concentrated on silicon nanocrystals formed in silicon oxides and Er-doped silicon oxides. As mentioned, however, silicon nitrides present an attractive alternative due to their broader range of tunability and lower barrier for carrier injection. The literature on nanocluster formation in silicon nitrides is less extensive. The first goal of this work was to look at the fabrication of luminescent silicon nanocluster embedded silicon nitrides followed by the characterization of their photoluminescent and structural properties as a function of film composition and processing parameters. Here, the term "structural" encompasses several aspects, including the bonding structure of the films and information on the formation and growth of the nanoclusters themselves. While the bonding structure of the dielectric host matrix can be analyzed through Fourier transform infrared (FTIR) spectroscopy, details on the Si-nanoclusters are not obtainable through this method, as Si is transparent in the IR. In order to obtain information on the nanoclusters themselves X-ray absorption spectroscopy (XAS) has been used to study changes in the X-ray absorption near edge structure of the constituent atoms, which reflect the local chemical environment of the atom, as a function of the aforementioned parameters. Additionally, for several samples transmission electron microscopy based imaging has been used to provide some direct visual information on the film structure. Xray excited optical luminescence (XEOL) experiments were also performed in order to analyze the luminescence at site-specific energies. Unfortunately, XEOL from the

nitrides showed a rapid quenching effect and did not provide as much information as had been hoped.

Second, both silicon oxide and silicon nitride thin films have defect associated energy levels, which can affect the observed photoluminescent emission. It was, therefore, reasonable to ask (i) if the relative contributions of different defects could be tuned by varying the film composition and (ii) what could the information on the film structure (from FTIR and XAS spectroscopy) tell us about the observed emission. To study this several silicon oxynitride samples were grown and analyzed.

Finally, Tb, Ce, and Eu doped SRSO and ORSO thin films had been fabricated at McMaster University. Of particular interest was the observation of very intense photoluminescence (PL) from the Tb and Ce doped ORSO samples [38]. In these samples it was not expected that nanoclusters could form due to the deficiency of oxygen. The formation of more complex film structures (such as rare-earth oxides or silicates) and the presence of alternate coupling mechanisms for the excitation of the rare earths must, therefore, be considered. Using XAS the local chemical environment of the rare earths, Si, and O atoms was studied for both SRSO and ORSO Tb-doped films. A limited number of Ce samples were also analyzed, however, several of the Ce samples had been shipped off as part of a collaborative industrial project and a comprehensive sample set was not available. XEOL was used to determine at what sites efficient rare earth luminescence was excited to gain information about the excitation mechanisms for these samples.

This thesis presents the results from the above mentioned characterization work. Correlations between film structure and luminescence have been determined. While the luminescent properties of these materials and their potential applications are the driving force for research in this area, the understanding of the materials science of these films presents many interesting challenges of its own.

1.3 Contributions to the Field

The motivation for this work is largely driven by the need for a silicon-based light source. In pursuit of this an increased understanding of the materials which may serve in such a role can prove invaluable. This thesis focuses on material science aspects of luminescent silicon-based thin films of three kinds; silicon rich silicon nitrides, silicon oxynitrides, and rare earth doped silicon oxides.

In order to pursue this research it was first necessary to calibrate the deposition system for the fabrication of silicon nitride and oxynitride thin films. This involved the analysis of the effects of using different source gases and growth rates in order to fabricate films with different compositions, minimize contamination of the films, and to obtain samples that exhibited luminescence. While the details and results of this work are primarily internal to our research group, the results represent an enabling contribution both for the further study of these materials by our group and for future applications of these materials, either in the area of device fabrication or for use in optical coatings. The

PhD Thesis – T. Roschuk McMaster University– Engineering Physics use of these films in device structures is currently being explored as part of an industrial

collaboration.

The photoluminescent behavior of the initial set of films was analyzed both as a function of composition and as a function of annealing conditions (including the use of different annealing ambients). Results from this work are published in [39] and were presented at the 211th Meeting of the Electrochemical Society (2007).

The evolution of the SRSN film structure as a function of composition and annealing conditions has been explored through XAS and FTIR. In particular, XAS measurements have illustrated the clustering of Si within these films and have shown that the cluster formation process is dependent on the amount of excess Si within the films. Correlations between Si-cluster formation and the photoluminescent behavior of the films have been analyzed. For several of the films TEM-based imaging techniques have been used to illustrate that the nanoclusters formed in these films are amorphous and not crystalline. A summary of the results is to be published in [40]. A detailed paper is being prepared for submission for publication concurrently with this thesis. In the literature there are only a few papers to date that have examined the structure of silicon nitrides as a function of deposition conditions but not reporting on the effects of annealing. For both SRSO and SRSN thin films the X-ray literature is focused on the behavior at the Si $L_{3,2}$ -edge, for which, at the time of this writing, no results have been reported in the literature.

XAS and FTIR studies of silicon oxynitride thin films show little change in the structure of the nitride phase within these films. A clear silicon oxide phase is, however, observed to form. XAS shows little evidence of Si clustering during the anneal process. The samples show a blue photoluminescence, which is attributable to defects within the film. The results are being prepared for publication.

XAS and XEOL studies of luminescent Tb and Ce-doped silicon oxide thin films have yielded detailed information on the nature of the luminescence in these films. The results show different luminescent behavior between silicon rich and oxygen rich samples, indicative of the presence of different luminescence coupling mechanisms in these materials. Furthermore, information on the incorporation of the rare earth ions within the films has been obtained by studying the $M_{5,4}$ absorption edges. The results are recent at the time of this writing and are also being concurrently prepared for publication.

In addition to the contributions discussed above, which are directly related to this thesis, several other areas of research have been explored. Through the use of an aberration corrected transmission electron microscope the detailed atomic structure of Sinanocrystals formed in SRSO thin films has been explored. The results show the formation of twinning defects within the films. The concentration of these defects shows a dependence on both film composition and annealing conditions. In these SRSO samples I have also begun exploring the electronic structure at the nanocrystal interface itself using electron energy loss spectroscopy (EELS). EELS research on these films is currently being conducted in collaboration with the University of Manchester and <u>PhD Thesis – T. Roschuk</u><u>McMaster University– Engineering Physics</u> provides data similar to that of XAS, however, the data from EELS is obtained on the scale of the individual nanocrystals themselves.

Finally, in several instances I have contributed to both the experimental work and scientific discussion for papers where I was not the lead researcher. These papers discuss the structure of SRSO thin films [41], the photoluminescent behavior of SRSO thin films annealed at low-temperatures [42], and the photoluminescent behavior of rare earth doped SRSO films [38, 43, 44].

1.4 Outline of the Thesis

The primary focus of this thesis is an experimental analysis of the luminescent properties and the electronic and bonding structures of Si-based materials, particularly silicon rich silicon nitrides, silicon oxynitrides, and Tb and Ce-doped silicon oxides. In this Chapter an overview of the potential applications for Si-based light emitters and the need for research into luminescent Si-based materials has been given. Several recent texts have addressed the topic of silicon photonics in some depth and provide an overview of the field and details of necessary components outside of a Si-based light emitter [9, 10, 17]. This section provides an outline of the remainder of this thesis, which focuses now on the background necessary to understand the experimental methods used in this research and the results obtained.

Chapter 2 discusses the electronic structure and light emission in semiconductors. The physics of the light emission process in quantum confined silicon is reviewed, first
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by outlining the reasons for poor light emission in bulk Si followed by a discussion of the effects of quantum confinement and the influence of surface and defect states on the luminescence of Si-ncs. A survey of results in the literature discussing luminescence in silicon nitrides and oxynitrides is presented. Some treatment is also given to the incorporation of rare earth elements and their effects on the observed luminescence in these material systems, with specific examples from Tb and Ce-doped samples.

A review of research results in the literature and details of the materials science aspects of luminescent Si-nanocluster embedded dielectrics is given in Chapter 3. In particular, current results related to the understanding of growth parameters and the thermal evolution of Si-rich materials with annealing are considered.

The experimental methods employed in the study of these materials are discussed in Chapter 4. Details of the physics of X-ray absorption spectroscopy and the experimental equipment at the Canadian Light Source synchrotron facility are given. Details of electronic states related to inner shell electrons and the bonding structure of the constituent atoms are discussed, providing the background to interpret the X-ray absorption behavior of these materials. Optical spectroscopy-based techniques, including photoluminescence and Fourier transform infrared spectroscopy, are presented. Finally, electron microscopy-based techniques, used to obtain information about the nanostructure of several of the samples, are outlined. Details of Si-based thin film deposition are presented in Chapter 5. An outline of the calibration of the deposition system and the compositional characterization is given along with the reasoning for focusing on a subset of these samples later in the thesis.

Results and discussions from this work are presented in Chapter 6.

Finally, conclusions from this work are summarized in Chapter 7 and proposed future research projects are discussed.

Chapter 2: Electronic Structure and Light Emission in Semiconductors

The electronic structure of semiconducting materials provides the basis for understanding their optical properties, including luminescence and absorption. Two different aspects of the electronic structure are of particular importance for the work discussed in this thesis. The luminescence of semiconductors is best understood in terms of a discussion of their conduction and valence bands, between which electron-hole recombination occurs. These bands are directly related to the interaction of valence electrons in individual isolated atoms as the atoms are brought into a bound configuration within a periodic potential [45, 46]. The energy separation between the conduction and valence bands typically ranges from 0 (below which the bands overlap and the material can be considered conducting) to several eV (above which a material can be considered to be insulating). Core electrons, however, maintain more of the characteristic nature of the isolated atoms, as they are less interacting in the bonding process. It is these core electrons which are excited in the X-ray absorption process. In XAS, absorption by these core electrons can, however, reflect information about the bonding type and coordination of an atom through an energy level shift of the absorption edge. The energy range of interest in this case can span from $\sim 10 \text{ eV}$ to 100,000 eV, depending on the types of atoms within the material one is interested in analyzing.

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In this chapter we are concerned with the former aspect of electronic structure, the behavior of semiconducting materials at the conduction and valence bands. Details of the latter aspect of electronic structure, the excitation of core-electrons and the relation of X-ray absorption energies to film structure will be considered in the discussion of XAS presented in Chapter 4.

The current chapter begins with a discussion of light emission in semiconducting materials and its relation to the electronic structure at the valence and conduction bands, illustrating why Si is a poor light emitting material. Details of electronic structure itself are the subject of several textbooks and more refined theoretical models are a continued area of research. The models used are often complex and computationally intensive, although a fairly detailed understanding may be obtained through basic solid state and quantum physics. With the exception of a brief discussion on results related to the electronic structure of Si-nanoclusters, a thorough discussion of the matter is reserved for the literature, with the focus here being on understanding the relationship between electronic structure and the luminescent properties of semiconductors.

The discussion of light emission in bulk semiconductors is followed by a discussion of the physics of quantum confinement and how this enhances the efficiency of light emission in silicon, including in rare earth doped silicon nanocluster systems, along with a survey of current theoretical and experimental results in the literature from this field.

2.1 Electronic Structure and Light Emission in Bulk Semiconductors

The band structures of GaAs, a direct bandgap semiconductor, and Si, an indirect bandgap semiconductor, are shown in Figures 2.1 and 2.2, respectively [47]. The light emission process in semiconductors results from the recombination of electrons in the conduction band with holes in the valence band. During the recombination process two quantities must be conserved, momentum and energy. Recombination in direct and indirect bandgap semiconductors are shown schematically in Figure 2.3 [12, 48].



Figure 2.1: Energy band structure of GaAs. The band structure was calculated using empirical pseudopotential method. The minimum of the conduction band and maximum of the valence band lie at the same point in momentum space. Reproduced with permission from [47] (©1976 The American Physical Society).

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Figure 2.2: Energy band structure of Si. The minimum of the conduction band is offset in momentum space from the maximum of the valence band. Results are shown for both non-local (solid) and local (dashed) pseudopotential calculations. Reproduced with permission from [47] (©1976 The American Physical Society).



Figure 2.3: A schematic representation of the radiative recombination process in (a) direct and (b) indirect semiconductors. During radiative recombination in an indirect bandgap semiconductor the interaction of a phonon (with energy E_q) is required to conserve momentum.

In direct bandgap semiconductors, such as GaAs, the minimum of the conduction band and the maximum of the valence band lie at the same point in momentum space at the Brouillon zone center (Γ point). Recombination in such a system requires only the emission of a photon for energy conservation and may occur spontaneously. No secondary interaction is required for momentum conservation as the wavevector of the electron in the conduction band, k_c , is equal to that of the hole in the valence band, k_v^9 . The minimum energy of the emitted photon, E_p , is given by the difference in energies between the conduction and valance bands:

$$E_p = E_C - E_V = E_g \tag{2.1}$$

In Si the minimum of the conduction band and the maximum of the valence band lie at different points in momentum space. The minimum of the conduction band is offset from the Brouillon zone center by \sim 85% in the <100> direction (towards the X point). Recombination in such a system is a three body process (electron, hole, and phonon), requiring the simultaneous emission of a photon for energy conservation and phonon interaction for momentum conservation. The process is described by the equations:

$$E_p = E_C - E_V \pm E_q = E_g \pm E_q \tag{2.2}$$

$$\pm k_q = k_c - k_V \tag{2.3}$$

where the subscript q refers to the phonon involved in the process. Generally, E_q is small in comparison to the energy separation of the conduction and valence bands ($E_g = 1.125$

⁹ The momentum of the emitted photon is small and is generally considered negligible.

PhD Thesis – T. RoschukMcMaster University– Engineering PhysicseV in Si), although it is not necessarily negligible. Likely phonons to assist in this processare from the transverse optical (TO), longitudinal optical (LO), and transverse acoustic(TA) bands (in that order), with energies of 58, 56, and 18 meV, respectively. The TOphonon can, therefore, result in a ~5% change in the emission energy [49].

In order to understand why the need for phonon interaction severely decreases the efficiency of light emission in silicon the rates and characteristic lifetimes involved in the recombination process must be considered. In direct bandgap semiconductors such as GaAs the radiative lifetime, τ_r , is on the order of nanoseconds. For indirect bandgap semiconductors one must account for the recombination lifetime and the rate of phonon interaction, resulting in radiative lifetimes on the order of milliseconds. For GaAs and Si the radiative lifetimes are 40 ns and ~2.5-10 msec, respectively [12, 48]. In addition to radiative recombination electrons and holes may find alternative recombination pathways that are non-radiative. The efficiency of the light emission process is then given by the ratio of the rate of radiative recombination to the sum of the rates of radiative and non-radiative recombination, or expressed in terms of the lifetimes:

$$\eta = \frac{\tau_{nr}}{\tau_{nr} + \tau_r} \tag{2.4}$$

In GaAs τ_{nr} is long in comparison with τ_r and efficiencies of 10% or greater can easily be obtained. In silicon the opposite is true, τ_r is typically much longer than τ_{nr} and the efficiencies are as low as 10^{-5} %. Common non-radiative pathways in silicon that result in such a low efficiency include recombination at defects (both bulk and surface) and Auger

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recombination. In particular, Shockley-Read-Hall (SRH) recombination, which involves the trapping of an electron (or hole) by a deep level defect followed by the subsequent capture of a hole (or electron), is a common non-radiative recombination pathway. The SRH lifetime is dependent on the doping concentration within a material. It is possible to increase the radiative recombination efficiency through the use of high-purity silicon with surface passivation. Such an approach eliminates the defect related non-radiative pathways. Another method involves the reduction of the size of silicon down to the nanoscale, localizing electrons and holes in the vicinity of silicon nanoclusters and decreasing the radiative lifetime [50-52].

2.2 Quantum Confinement in Semiconducting Nanostructures

The reduction of material dimensions down to the nanoscale leads to unique behavior as quantum effects begin to have a profound influence on how the materials behave. The ability to control the dimensions and exploit the novel properties of materials on this scale has led to the recent boom in nanotechnology research (and the subsequent overuse of the term nano both in science and popular culture). In semiconducting materials the confinement of electrons and holes within nanostructures leads to changes in the electronic behavior of the materials. This in turn leads to optical behavior distinct from the case of bulk materials. In this section the effects of quantum confinement and its applications to the development of semiconducting light sources is considered.

2.2.1 Quantum Confinement

Quantum confinement effects occur as the spatial dimensions of a material are reduced. This may occur in one (quantum wells), two (quantum wires), or three (quantum dots, including nanoclusters and nanocrystals) spatial dimensions, as is shown in Figure 2.4.



Figure 2.4: Quantum confined structures. (a) Bulk; (b) quantum well; (c) quantum wire; and (d) quantum dot.

Several different length scales are often employed in the description of electronhole behavior within materials. In the discussion of low-dimensional structures in semiconductors the two length scales typically used to indicate the onset of quantum confinement are the de Broglie wavelength, λ_B , and the Bohr exciton radius, a_B^{10} [12, 53,

¹⁰ The de Broglie wavelength and the Bohr radius are related to each other. The details of their relation are most easily shown through a consideration of the hydrogen atom.

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 54]. In both cases these scales correspond typically to dimensions of nanometers or tens

 of nanometers. The de Broglie wavelength of an electron is given by the equation:

$$\lambda_B = \frac{h}{p} \tag{2.5}$$

where h is Planck's constant and p is the electron's momentum.

In semiconducting materials an electron in the conduction band and a hole in the valence band may exist in a bound state, similar in nature to a hydrogen or positronium atom. These electron-hole pairs are called excitons. The Bohr exciton radius is given by

$$a_B = \frac{4\pi\hbar^2\epsilon_0\epsilon_r}{\mu e^2} \tag{2.6}$$

where \hbar is the Dirac constant (= $h/2\pi$), ϵ_0 is the permittivity of free space, ϵ_r is the dielectric constant of the semiconducting material, e is electronic charge, and μ is the reduced exciton mass, defined as:

$$\frac{1}{\mu} = \frac{1}{m_e^*} + \frac{1}{m_h^*}$$
(2.7)

Here, m_e^* and m_h^* are the effective masses of the electron and the hole, respectively. In Si and GaAs the Bohr radii are 4.3 and 12 nm, respectively [54]. Both the de Broglie wavelength and the Bohr radius provide a general rule of thumb for the scale at which quantum confinement effects become prominent. When an electron-hole pair is confined within dimensions less than the Bohr exciton radius (referred to as the strong confinement regime) the electron and hole may be treated as individually confined particles. When the dimensions are near to or slightly greater than the Bohr exciton radius then excitonic <u>PhD Thesis – T. Roschuk</u><u>McMaster University– Engineering Physics</u> effects must be accounted for [54]. While the details will be discussed later in this section here it is noted that the formation of a bound exciton state and quantization of both electron and hole motion are considered important for the enhanced emission observed in indirect bandgap semiconductors as this leads to an increased overlap of the electron and hole wavefunctions. For this reason in materials such as Si the Bohr exciton radius is generally taken as the key parameter for defining the onset of the quantum confinement regime.

In a bulk semiconductor the energy of an electron and its wavevector are related through the expression:

$$E = \frac{\hbar^2 k^2}{2m_e^*}$$

= $\frac{\hbar^2 (k_x^2 + k_y^2 + k_z^2)}{2m_e^*}$ (2.8)

In order to understand the behavior of quantum confined structures the effects of confinement on the electron and hole wavefunctions must now be considered. The simplest case, both in terms of understanding and fabrication, is the quantum well (QW). The QW may be treated in an analogous manner to the classic quantum mechanics example of a 'particle in a box', where a particle (such as an electron) is confined within a one dimensional potential well. The full details of this example are described in any introductory quantum physics text. Conceptually, one can see the effects of confinement by first considering the case of the infinite potential well which is often used as an approximate solution for the analysis of real (finite) quantum wells. When an electron is

PhD Thesis – T. RoschukMcMaster University– Engineering Physicsconfined to a well with width dx its wavevector components, and hence its energy levels,become quantized along the direction of confinement (the x-direction for Figure 2.4(b)).The energy levels are given by:

$$E_{n_x} = \frac{\hbar^2 k_{n_x}^2}{2m_e^*}$$
(2.9)

where k_{n_x} is the wavevector and is given by:

$$k_x = \frac{n_x \pi}{L_x}; n_x = 0, 1, 2 \dots$$
 (2.10)

Figure 2.5(a) shows a common quantum well structure with a narrow bandgap layer sandwiched between two wider bandgap layers. A real such structure may be formed from a GaAs layer contained between two wider bandgap AlGaAs barrier layers. The confined energy levels and the electron wavefunctions for the special case of infinite and impenetrable, barrier potentials are shown for the cases $n_x = 1,2$, and 3 in Figure 2.5(b).



Figure 2.5: A quantum well structure. (a) A typical quantum well structure and (b) an energy band diagram illustrating the confined energy levels and wavefunctions for an electron within an infinite potential well.

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PhD Thesis – T. RoschukMcMaster University– Engineering PhysicsFor an electron in the conduction band the potential energy barriers are defined withrespect to the conduction band edge, E_c . Along the y and z directions the dimensions maybe considered semi-infinite and there is no confinement (L_y , $L_z >> d_x$). The wavevector

components along the unconfined directions are given by:

$$k_y = \frac{n_y \pi}{L_y}; n_y = 0, 1, 2 \dots$$
 (2.11)

$$k_z = \frac{n_z \pi}{L_z}; n_z = 0, 1, 2 \dots$$
 (2.12)

Since L_y and L_z are large, the spacing between energy levels is small and may be treated as a quasi-continuous energy band of discrete states. The total energy of an electron in the conduction band is then:

$$E = E_{c} + E(k_{y}, k_{z}) + E_{n_{x}}$$

$$= E_{c} + \frac{\hbar^{2}k^{2}}{2m_{e}^{*}} + \frac{\hbar^{2}k_{n_{x}}^{2}}{2m_{e}^{*}}$$

$$= E_{c} + \frac{\hbar^{2}(k_{y}^{2} + k_{z}^{2})}{2m_{e}^{*}} + \frac{\hbar^{2}k_{n_{x}}^{2}}{2m_{e}^{*}}$$
(2.13)

where E_c is included to account for the fact that the potential energy barriers are defined with respect to the conduction band. E_{n_x} then refers to the increase in energy over the unconfined case with E_1 corresponding to the increased ground state energy of an electron within the well. Excited states within the QW correspond to cases where $n_x > 1$.

It is simple enough to conceive of how a hole in the valence band experiences a similar confinement effect to that of an electron in the conduction band. Using the effective mass of the hole the shift in its energy relative to the valence band edge may be

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 calculated. The net effect of confinement on the observed emission during electron-hole

 recombination is therefore a blue-shift of the emission energy due to a bandgap widening

 associated with the quantum confined electron and hole ground states.

For a real quantum well structure the barriers are finite. In such a case there is some probability of the electron penetrating these barriers, as illustrated in Figure 2.6, which shows the case for a Si layer contained between two SiO₂ barrier layers. In this case the energy eigenvalues representing solutions to Schrodinger's cannot be solved analytically. The actual energies lie at energies below those of the infinite potential well model. A comprehensive treatment of both the theoretical and computational aspects necessary for the accurate analysis of real, finite quantum confined structures may be found in [55] and [56].





Figure 2.6: A SiO₂/Si/SiO₂ quantum well. Energy levels for n = 1 (red lines) and n = 2 (green lines) states are shown for both the electron and hole. The hole wavefunction is shown for case n = 1 and the electron wavefunction is shown for the case n = 2.

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<u>PhD Thesis – T. Roschuk</u><u>McMaster University– Engineering Physics</u> Because the wavefunction penetrates into the surrounding barrier layer surface states become particularly important to the behavior of quantum confined materials, particularly in the case where these surface states provide a localized defect through which recombination can occur.

In direct bandgap semiconductors such as GaAs and InP quantum well and multiple quantum well devices, specifically lasers, are well established technologies and are used as the active layer in a number of applications such as vertical cavity surface emitting lasers. Modern molecular beam epitaxy fabrication techniques have enabled the growth of high-quality layers with precise dimensions in order to obtain the desired operation parameters. For indirect bandgap semiconductors quantum well structures may be formed using SiO₂/Si as mentioned above or by using Si as a barrier layer and SiGe as the quantum well. Si/SiGe based materials have been particularly successful for the development of quantum cascade light emitters¹¹.

In the case of quantum wires and dots, confinement in additional dimensions leads in turn to the quantization of energy levels in two and then all three dimensions, respectively. The additional degrees of confinement then lead to the following energies for an electron in the conduction band:

$$E = E_{c} + \frac{\hbar^{2}k_{z}^{2}}{2m_{e}^{*}} + \frac{\hbar^{2}k_{n_{x}}^{2}}{2m_{e}^{*}} + \frac{\hbar^{2}k_{n_{y}}^{2}}{2m_{e}^{*}} \qquad \text{Quantum wire} \qquad (2.14)$$

¹¹ Quantum cascade lasers operate under a different principle than e-h recombination, rather, emission from a quantum cascade laser arises due to intraband transitions in superlattice structures. Emission from these devices in is the infrared (THz) regime, outside the standard range for photonics or telecommunications.

$$E = E_{C} + \frac{\hbar^{2}k_{n_{x}}^{2}}{2m_{e}^{*}} + \frac{\hbar^{2}k_{n_{y}}^{2}}{2m_{e}^{*}} + \frac{\hbar^{2}k_{n_{z}}^{2}}{2m_{e}^{*}} \qquad \text{Quantum dot} \qquad (2.15)$$

Qualitatively the energy level behavior of electrons and holes confined within a Si-nc or quantum dot¹² embedded within SiO₂ will be the same as that shown for the Si QW in Figure 2.6. In the case of the Si-nc, the bandgap will undergo further widening due to confinement in all dimensions. Distinct behavior is observed between the various confined systems when one considers the density of states (DOS). The DOS is a measure of the number of energy states that exist within a range of energies (per unit volume). In bulk materials the DOS for both the conduction or valence bands is continuous and increases as a function of the square root of energy:

$$\rho(E) = \frac{1}{2\pi} \left(\frac{2m_e^*}{\hbar^2}\right)^{3/2} E^{1/2}$$
(2.16)

In confined structures there is no longer a continuum of states for an electron to occupy. Rather, a set of subbands arise, associated with each quantum number n_x . The density of states for each quantum number is constant and a plot of the density of states gives a staircase distribution, as the density of states at any particular energy is the sum of all subbands below that energy,

$$\rho(E) = \sum_{n_x} \frac{m_e^*}{\pi \hbar^2} \Theta(E - E_{n_x})$$
(2.17)

¹² The terms quantum dot and nanocrystals are generally used to distinguish between different growth or fabrication processes used to produce the structures. In terms of the physics there is no difference between the two and the use of separate terms is a matter of convention. Various authors use the terms interchangeably.

PhD Thesis – T. RoschukMcMaster University– Engineering Physicswhere Θ is the unit step function. For the quantum wire an energy subband is associatedwith each pair of quantum numbers n_x and n_y . For a quantum wire the density of stateshas a maximum at each subband minimum and decreases with increasing energy betweenthese maxima.

$$\rho(E) = \sum_{n_x, n_y} \frac{1}{\pi} \left(\frac{2m_e^*}{\hbar^2}\right)^{1/2} \frac{1}{\left(E - E_{n_x, n_y}\right)^{1/2}} \Theta\left(E - E_{n_x, n_y}\right)$$
(2.18)

Finally, in a quantum dot the energy levels are discrete and well separated in energy. In this case the DOS is a series of delta functions at the allowed energies for the dot. Figure 2.7 shows the density of states for the case of bulk, quantum well, quantum wire, and quantum dot materials.



Figure 2.7: Density of states. The behavior of the density of states for bulk and quantum confined structures.

The need for phonon interaction in a three-body process as a limited factor in order to obtain emission in Si was discussed above. If we now consider the case of Si nanoclusters with dimensions less than the Bohr exciton radius then electrons and holes confined within the cluster both experience quantization effects in their energy levels. Furthermore, one must consider the effects of confinement on the momenta of the electron and hole. The localization of a particle to a defined region of space with width Δx leads to uncertainty in its momentum. The two are related through Heisenberg's uncertainty principle:

$$\Delta x \Delta p_x = \frac{\hbar}{2} \tag{2.19}$$

The confinement of electrons and holes therefore leads to a spread in their wavevector components. This can then lead to a sufficient overlap of the electron and hole wavefunctions in momentum space so that the need for phonon interaction is decreased. Quantum confinement, therefore, has additional effects of relaxing the k-selection rules for recombination to occur in indirect semiconducting materials [57-59].

The enhanced overlap of the electron and hole wavefunctions is considered a key parameter in the enhancement of light emission in Si-ncs. Additionally, the formation of small nanoclusters is generally considered to reduce the effects of non-radiative recombination pathways through the removal of mid-gap states which can contribute to SRH recombination in bulk Si.

2.2.2 Quantum Confinement and Light Emission in Si-Nanostructures

The discussion of quantum confinement up to this point provides the underlying basis for understanding light emission in Si-nanostructures. In order to understand the actual observed luminescence from said samples it is now necessary to consider confinement in slightly more detail and to account for the effects of surface and defect states which can act as luminescence centers in the light emission process. The luminescence of Si-nanostructures formed in porous silicon (p-Si) and in silicon oxide thin films has been extensively studied in the literature. Although some outstanding questions remain the basic nature of luminescence in these materials is understood. After first considering the details of the luminescent behavior from said samples the nature of luminescence in the less studied case of silicon nitrides will be discussed.

Luminescence from Si-ncs is generally regarded to originate from recombination within a bound exciton state. For a spherical nanocrystal of radius r the Brus model may be used to account for the Coulombic effects due to the formation of an exciton [60]. Using the Brus model, as a result of confinement the lowest energy gap becomes:

$$E = E_g + \frac{\hbar^2 \pi^2}{2\mu r^2} - \frac{1.8e^2}{4\pi\epsilon_0\epsilon_r r}$$
(2.20)

where higher order terms have been neglected. The second and third terms in Equation 2.20 account for the widening of the bandgap with the localization of the electron and hole in the nanocluster and the effects of Coulomb shielding, respectively [60, 61]. At sizes near the Bohr radius the Coulomb term cannot be ignored, however, as the size is

On the basis of the Brus model one expects a continued increase in the emission energy of Si-ncs as the size is decreased. Not surprisingly, this is what is observed from Si-nc based materials, however, the increase in bandgap predicted by this model is found to be larger than the actual observed emission in the case of small Si-ncs. One of the key neglected features of the Brus model is the effect of surface states at the Si-nc/matrix interface. In p-Si the formation of Si=O double bonds at the interface introduces the presence of a deep level mid-gap state [26]. The effects of such a state on the luminescence of p-Si are demonstrated in Figure 2.8. As the size of clusters decreases the trap states introduced by this bond result in a red-shifted emission relative to that expected from a pure confinement model alone.

Through the formation of isolated nanocrystals via selective etching followed by an oxidation step, this behavior was studied for Si-ncs formed in SiO_2 through ion implantation. The results showed an initial blue-shift due to the size reduction of the nanocrystals, however, after the formation of 3 monolayers of oxide on the Si-nc surface a red-shift of the emission energy, consistent with the behavior predicted for oxide surface states, was observed [62].



Figure 2.8: Effects of oxygen on Si-nc luminescence. As the size of the nanoclusters is reduced mid-gap trap states are introduced through the presence of Si=O double bonds. The effects become prominent after a reduction in size to below \sim 2.5 nm. Reproduced from [26].

Through the use of X-ray excited optical luminescence (XEOL) and analysis of the photoluminescence yield (PLY) after X-ray excitation the nature of the luminescence has been studied in p-Si, silicon nanowires, and SRSO based samples [63-69]. Two methods are commonly employed for the study of Si-nc systems using XAS. The first relies on the analysis of the electronic structure of the films, which relates chemical and structural information, obtained from XAS (either through the electron or fluorescence yield) and the correlation between features in the XAS spectra and the PL behavior of the samples. In this case, XAS features relate to all structures present within the film, including, for example, non-radiative Si-ncs. The second is based on analyzing the PLY

<u>PhD Thesis – T. Roschuk</u><u>McMaster University– Engineering Physics</u> from the samples, which reflects the X-ray absorption of luminescent sites. The use of XAS for the analysis of structural and chemical details of Si-based materials is discussed

in the following chapter, while details of the XAS process are presented in Chapter 4.

The analysis of the PLY from samples provides a particularly clear picture of how luminescent states may be excited at site specific energies which can then be used to deduce information on the origin of PL. An example of this is shown in Figure 2.9 [70]. Here the total electron and photoluminescence yield spectra are shown as a function of excitation energy for a SRSO sample having 38% Si which was annealed at 1100 °C for 120 min. Near the Si-Si bonding energy (1839 eV) a large photoluminescence signal is observed. A comparison of XEOL spectra at Si-Si and Si-O related edges shows that the luminescence signal arises only after excitation of the Si-ncs and corresponds to the near IR signal observed under UV excitation. In studies of p-Si the correlation between PLY and total electron yield (TEY) peaks was used to illustrate that luminescence in the samples also arises after excitation at the Si-Si bonding edge [65]. The opposite trend has been shown in the case of chainlike Si-nanowires, where excitation at the Si-Si bonding edge demonstrated the presence of only a small portion of quantum confined luminescence in the PLY signal. A stronger PLY feature was, however, observed during excitation at the Si-O bonding edge, indicating that the origin of luminescence in these samples was primarily the existence of a silicon oxide phase and that luminescence in chain-like Si-nanowires has a different physical origin than in p-Si or Si-ncs [66, 71].



Figure 2.9: XAS and XEOL spectra for a SRSO sample. (Top) Total electron and photoluminescence yield spectra as a function of excitation energy. (Bottom) A comparison of XEOL spectra at Si-Si and Si-O bonding edges. After [70].

Although the combination of PLY- and TEY-XAS provides a powerful tool for looking at the correlation between luminescent excitation and structure it is desirable to have the corresponding XEOL spectra to complement the PLY if possible, particularly at near-edge excitation energies, as was shown in Figure 2.9. In this manner one is better able to relate specific luminescence bands to the structure and chemical environment within the films. Unfortunately, depending on the experimental setup it is sometimes overly time consuming to obtain these multiple possible data sets, particularly as the facilities for performing such experiments are not typically readily accessible¹³.

TEY-XAS spectra, in combination with FTIR and Raman spectroscopy, have been used to analyze the evolution of film structure and its relation to the PL behavior of SRSO samples [69]. The evolution of the bonding structure in these films was analyzed through XAS and FTIR and was used to illustrate the re-ordering of the host matrix. For the as-deposited and low-temperature annealed films a weak PL band was observed which could be ascribed to defects and the presence of Si-N bonding. At higher temperatures both XAS and FTIR indicated a decrease in Si-N bonding within the films and the formation of a structure close to SiO₂ with embedded Si-ncs. This evolution of the film structure correlates with the onset and growth of a NIR PL band indicative of PL originating from Si-nanocrystals in the high temperature annealed films.

¹³ CCD detectors are alleviating this problem, as they enable the simultaneous collection of the XEOL spectrum and the PLY (which is the area under the XEOL spectrum). This, however, occurs at the expense of sensitivity that older monochromator/photomultiplier tube setups had.

As XAS probes the partial density of states in the conduction band the onset of absorption is sensitive to the quantum confined energy shift of the nanoclusters. Analysis of the shift in the absorption edge has been used to study the energy gap shift and to relate the results to the presence of different nanoparticle sizes in samples of p-Si [72]. Complementary data from the valence band can be obtained through X-ray emission spectroscopy (XES). The combination of the two techniques can then be used to determine the total widening of the bandgap. Comparison of this widening with that predicted using a quantum confinement model can then provide evidence of band to band recombination in the material [73].

It is worth noting that XAS studies of Si-nc systems have focused primarily on the *K*-edge behavior. Only a few reports exist on the $L_{3,2}$ edge [63, 73, 74]. This is unfortunate, as the additional results at the $L_{3,2}$ edge can provide a more complete understanding of the electronic structure and thermal evolution of the films. Furthermore, electron energy loss spectroscopy (EELS) data obtained using an electron microscope can be difficult to attain at the Si *K*-edge. The Si $L_{3,2}$ is, however, easily accessible for EELS. The $L_{3,2}$ -edge is, therefore, well suited for a direct comparison of the electronic structure probed on the nanoscale through EELS, where details of the electronic structure at the Sinc interface could be obtained, and on the 'macro'-scale through XAS. Results from such a comparison could then be used to provide not only a better understanding of luminescence centers within the films, but also for the analysis of how the film structure evolves with deposition and annealing conditions.

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In spite of extensive research that has demonstrated that luminescence in Si-ncs formed in SRSO arises from a combination of quantum confinement and the presence of localized surface states there still remains a lack of consensus of on some of the details relating to the exact mechanisms involved in the light emission process. In particular the role of defects in the PL process has been ambiguous. In a recent study electron spin resonance was used to detect interface defect states, which can both quench or be responsible for the observed PL from Si-nc systems¹⁴ [75]. Magneto-PL measurements were then used to identify PL as originating from either defects or through a quantum confined state¹⁵. PL from an N₂ annealed sample was found to be primarily related to the presence of defect states. A H₂ passivation process (at temperatures low enough to avoid inducing the formation and growth of the nanoclusters) resulted in the transition to quantum confined PL. Finally, the samples were UV-irradiated to re-introduce the defects and again a defect related PL was observed. Results such as this demonstrate that even in the extensively studied SRSO system the nature of PL can be complex and ambiguous.

In SRSO thin films, the formation of Si-ncs within a SiO_2 matrix has the advantage of passivating the nanocrystal surface, allowing one to avoid oxidation effects which would occur in p-Si with exposure to air, altering the luminescent behavior in a manner that could be critical to device performance (although this behavior in p-Si is now

¹⁴ In this study only the presence of non-radiative defect states was detected by ESR, however, the results could not rule out the presence of radiative defect states which are consistent with the magneto-PL results reported.

¹⁵ Note that the defects may be subject to a quantum confined shift in energy as the defect energies lie close to the band-edges of the Si-ncs. The emission energies are, therefore, close in value but the authors have clearly demonstrated that two forms of PL emission are possible.

<u>PhD Thesis – T. Roschuk</u><u>McMaster University– Engineering Physics</u> being exploited for the potential development of chemical and biological sensors¹⁶, see for example [76-79]). However, this passivation naturally prevents one from achieving a broad tunability of the emission wavelength, specifically to obtain blue and near-UV emission, in SRSO as can be achieved in p-Si. It is, therefore, of interest to consider the passivation of Si-nc surfaces with a different material than an oxide, such as a silicon nitride.

The recent increased interest in the use of silicon nitride based thin films for the development of silicon-based light emitting devices is twofold. First, there is the possibility of obtaining a broader tunability in the luminescence [80]. Second, nitrides exhibit a reduced barrier for carrier injection compared to the oxides. The larger barrier to carrier injection in SiO₂ presents a significant challenge for obtaining efficient electrically pumped devices. The switch in host matrix to a nitride reduces the barrier bandgap from 8.0 eV to 4.6 eV and the field strength required for carrier injection from 6 MV/cm for electrons and 10 MV/cm for holes down to ~2-4 MV/cm for the injection of both electrons and holes. A further benefit for device applications is that in SiO₂ the carrier injection field strength required is close to the breakdown field, whereas for Si₃N₄ the required field strength is well below the breakdown field of ~9MV/cm [81]. The combination of these advantages makes silicon nitride an appealing material for the development of electrically injected luminescent devices.

¹⁶ Typically, the p-Si sample is first passivated by some form of receptor molecule in order to functionalize the surface, making the sensor selective to a desired chemical or biological species.

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Bright photoluminescence, with emission peak wavelengths from 410 to 900 nm, has been reported for crystalline Si-ncs (c-Si-nc) formed in SiN_x thin films and from 450-620 in amorphous Si-ncs (*a*-Si-ncs) [80, 82-84]. In these and other reports on the luminescence of Si-ncs, the luminescence wavelength is found to red-shift with increasing silicon concentration, as one expects from a basic quantum confinement model. Here, the discussion focuses on two particular aspects of the luminescent behavior of such films; the presence of different luminescent states, due to quantum confinement and defects, and the effects of annealing on the light emitting behavior.

As luminescence from both amorphous and crystalline Si-ncs in silicon nitrides has been observed it is worthwhile to briefly consider the differences in light emission from these two forms of silicon nanostructures. The nature of the bandgap in a-Si does not lead to a well defined energy separation between the conduction and valence bands, as for c-Si. Rather, the amorphous nature of the material leads to diffuse band-edges with band tailing states. The bandgap observed for a-Si materials is strongly dependent on a number of parameters including fabrication method, quality of the film, and the passivation through hydrogenation of defects such as dangling bonds. The bandgap observed for a-Si is typically 0.3 to 0.7 eV larger than that observed for c-Si. One can, therefore, expect to find a general blue-shift in a-Si nanostructures in comparison with crystalline Si due to the larger bandgap, but also a lower degree of confinement due to a decreased depth of the potential well. This means that as the nanocluster size decreases a smaller blue-shift of the emission will be observed for the a-Si-ncs. It is likely for these

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 combined reasons that the tunability of a-Si-ncs has been observed to be less than that for

 c-Si-ncs formed in silicon nitride.

Light emission from a-Si(:H) is typically more efficient than that for bulk silicon (provided defects are sufficiently passivated) due to symmetry breaking as a result of structural disorder [85]. Theoretical modeling of the luminescence from a-Si:H and c-Si nanoclusters has demonstrated that the blueshift of the emission is comparable for the two systems, however, breaking of the selection rules allows for greater recombination rates (up to two orders of magnitude) in a-Si:H clusters for nanoclusters with diameters of \sim 2.2 nm and larger [86, 87]. H incorporation in the model accounts for the passivation of localized mid-gap states and dangling bonds. One of the key drawbacks to amorphous clusters is the presence of non-radiative defects which may arise due to random bonding states or dangling bonds within the structure that experimentally cannot be as readily removed as in the modeling. Such defects can be even more profound for nanoclusters than for bulk a-Si as a single defect in the cluster can effectively kill its luminescence. Luminescence from a-Si-ncs formed in silicon oxides has been demonstrated and the results show an enhancement after hydrogen passivation of the films, however, the efficiency of light emission is substantially lower than in similar films within which nanocrystals have been formed [42].

Although in SRSO films efficient luminescence is typically not observed until the films have been subjected to higher anneal temperatures, sufficient to cause crystallization, it has been demonstrated using high resolution energy filtered TEM that a

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significant portion of the nanoclusters remain amorphous [88]. Several recent papers have sought to analyze the proportion of *a*-Si-ncs to c-Si-ncs and their structure in an effort to determine the role of *a*-Si-ncs in the emission process [88, 89]. In samples annealed at temperatures below 1100 °C the authors found that the Si-ncs were primarily amorphous. The observed PL was used to determine the total number of emitting nanoclusters, which was found to be in agreement with the total number of nanoclusters (amorphous + crystalline, as determined by energy filtered TEM) as a function of anneal temperature. It is clear, however, that the relative roles of amorphous and crystalline clusters warrant further study.

Using a combination of energy filtered and high resolution transmission electron microscopy it has been shown that the structure of the nanocrystals themselves is not completely crystalline, but rather, that the nanocrystals have an amorphous interface layer through which the composition gradually varies from Si to SiO_2 [90]. Through a comparison of TEY and PLY-XAS it was deduced that a stressed SiO_2 layer at the surface of the Si-nc plays an active role in the luminescence.

What emerges from the above discussion is that both amorphous and crystalline nanostructures can play a significant role in the luminescent properties of materials. In SRSO films the luminescent contribution of a-Si appears to be lower than that of Sinanocrystals but further research is required to clarify the details. At lower anneal temperatures, when these clusters form, their optical activity appears to be small, however, at higher anneal temperatures, where they remain a substantial fraction of the

<u>PhD Thesis – T. Roschuk</u> <u>McMaster University– Engineering Physics</u> total number of clusters in the film, it is possible that their optical activity increases. As mentioned above, in SRSN materials a more substantial contribution to luminescence has been found from *a*-Si-ncs and the observed luminescent properties of SRSN materials will now be considered in more detail.

Although one of the advantages of using SRSN is the absence of the wavelength range limiting Si-oxide bonds, light emission from SRSN materials is not exempt from the influence of defect and surface states. In their study of the luminescence of silicon nitrides, Deshpande et al. proposed a model for light emission from a-SiN_x:H thin films on the basis of three defect states that may affect the observed luminescence from these samples [27]. The states are related to the Si⁰ dangling bond, and the N_4^+ , and N_2^0 defect states. Schematically, the positions of these defect levels and the emissions they give rise to (at ~2.5, 3.0, and 1.8 eV) are illustrated in Figure 2.10. The work in [27], however, does not consider the possible presence of Si-ncs within the as-grown films, but the analysis rather is made on the basis of an effective optical bandgap for the silicon nitride film (which lies somewhere between that of Si and Si₃N₄). The authors used hot-filament CVD and reported that PL was 8-10 times higher than that observed for PECVD samples. It is generally acknowledged that the use of different deposition systems can have a significant impact on the luminescence observed from silicon-rich materials. It is, therefore, possible that Si cluster formation within the films contribute to the observed luminescence, which the authors did not consider. Regardless of whether quantum confined clusters have formed in the films or not the model proposed by the authors and

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 its agreement with the experimental PL from a range of samples indicates that defect

 states play a substantial role in the SRSN PL process. Furthermore, the model is easily

 adapted for the consideration of Si-ncs with the defect levels being within the confined

 energy levels of the Si-ncs.



Figure 2.10: A Model of luminescent defect states in silicon nitrides. Luminescence from silicon nitrides can show contributions from several defect states related to the host matrix. The colors shown correspond to the approximate colors of the luminescence. After [27].

It is likely owing to the presence of both amorphous and crystalline nanoclusters as well as several different luminescent defects that a diverse range of PL results for SRSN materials have been reported in the literature¹⁷.

Crystalline Si-ncs formed in silicon nitride have been reported by several authors [80, 82, 91-93] and amorphous Si-ncs have been discussed by [84, 94-98]. The formation

¹⁷ This is further compounded by the different results obtained from using different deposition systems, sources, and methods.

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 of amorphous clusters and their crystallization with annealing has been discussed by [99-101].

One group has reported c-Si-ncs to have formed in as-grown nitride [80, 82]. The formation of luminescent Si-nanocrystals in as-grown material can be particularly beneficial as it removes the need for high-temperature annealing, a process that is considered a significant barrier for back-end integration. Fitting the PL data (excited using a UV laser) to the model for a confined cluster (the Brus model discussed above, Equation 2.20) and ignoring the Coulomb potential term, the authors obtain a fit between the peak position and nanocrystal size as

$$E = 1.16 + \frac{11.8}{d^2} \tag{2.21}$$

The results illustrate a trend consistent with quantum confinement. What is particularly interesting is that the results show a broad luminescence with what appears to be only a single emission band, which is considered to be evidence for the lack of recombination through defect or surface states. In order to confirm this, however, one would expect to see information on the luminescence lifetime which could illustrate that this behavior arises from band-to-band quantum confined recombination which can be combined with suitable modeling to properly attribute the luminescence. This should not be taken as a critique of the authors' results, as the behavior demonstrated is quite favorable for the nitrides, but only as a statement that further work is necessary to determine the exact PhD Thesis – T. RoschukMcMaster University– Engineering Physicsluminescent nature of these samples and its relation to the film structure¹⁸. Similarly, theemission energy of a-Si-ncs formed is as-grown samples has been found to vary withcluster size as [84]:

$$E = 1.56 + \frac{2.40}{d^2} \tag{2.22}$$

where the effects of confinement are found to be far less substantial than in the case of c-Si-ncs, as one would expect. A comparison of the intensity between amorphous (passivated by a hydrogen anneal) and crystalline Si-ncs has shown that the peak PL intensities between samples are comparable [82].

The influence of surface states has been considered in [93, 102] for the case of a set of PECVD grown SRSN films. In this work the authors saw little shift in the emission energy of the c-Si-ncs with either increased Si concentration or with annealing, as would be expected based on QCE due to the formation of larger Si-ncs. By simulating the optical gap and radiative lifetime for different Si-nc structures (terminated with various N or H related groups) the authors attributed the observed luminescence to the presence of bridging nitrogen atoms at the surface of the Si-ncs. It is worthwhile to note, however, that the authors used the 488 nm emission of an Ar laser to conduct PL measurements. Under such conditions one would not expect to see luminescence that could be attributed to the UV-emitting defects discussed in the above model which may be present within the

¹⁸ Much of the work by this particular research group is focused on the development of devices using these materials, not on the material science aspects of the films. If these devices were to become viable solutions for integration, knowledge of the material science will, however, become critical for reproducibility.
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bandgap of smaller Si-ncs. Even more distinct is the annealing behavior observed for this set of films. In contrast to the results commonly observed in the case of SRSO the optimum luminescence from these samples was found after annealing at 700 °C. Furthermore, at this anneal temperature the authors found that the integrated PL intensity initially increased rapidly with anneal time, however, after ~10 minutes this intensity remains approximately constant. The results suggest that the growth kinetics for Si-ncs formed within SRSO and SRSN films are substantially different. From the reports, however, it is not clear what the as-grown structure of these films is and how the films evolve with annealing, information that must be considered to comprehensively discuss the kinetics.

A study using two different PL excitation sources, at 325 nm (HeCd laser) and 514.5 nm (Ar ion laser) was performed in [99]. What is notable from this work is that using a 325 nm laser source, PL attributable to the presence of several defects, consistent with the model shown in Figure 2.10, was observed, however, excitation with the 514.5 nm source led only to a near-IR emission (NIR) that showed a blueshift with decreasing silicon content. The authors attribute the NIR emission to quantum confinement in Si-ncs and the other emission to the defects. After annealing, the defect related PL was observed to increase in intensity (although the particular band that increased was dependent on the sample composition). It is odd that the authors did not specifically consider the possibility that the defect related emission may be tied to the presence of nanoclusters as well. In fact, from the perspective that a ~410 nm PL peak is directly due to N related defects, one

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would expect a large peak in a sample with compositions closest to Si_3N_4 , as the amorphous as-grown PECVD film can be expected to feature a number of defects. In this sample, however, the N-related defect peak is barely present. The rapid increase of this peak with slight increases in the Si-concentration suggest in fact that while the luminescence may be due to defects its origin likely lies in the presence of Si-ncs. Finally, XPS analysis of their least Si-rich film shows barely any signal from Si bonded to Si. Any Si-ncs in this film would then be expected to be quite small and quantum confined luminescence from the nanoclusters would be expected to shift into the visible. It is therefore, more probable that the emission observed by the authors in the NIR is related to recombination at either a defect or surface state, similar to the abridging surface N atom considered earlier.

The second notable point from this work, which is of direct relevance to the work discussed in this thesis, is that after annealing at 1100 °C the Si concentration of the films appears to influence the transition from *a*-Si to c-Si nanoclusters. Using Raman spectroscopy the clear signature of c-Si forming is observed in the more Si-rich samples. As the Si concentration decreases the Raman spectra demonstrate only the presence of *a*-Si nanoclusters. The authors have considered the results no further than this but the observed behavior again demonstrates that the host matrix plays an active role in the thermal evolution of SRSN materials.

It should be noted that not all authors consider solely a model-based on Si-ncs formed within Si₃N₄ in SRSN materials. Rather, other groups consider the presence of a

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film with complex spatial chemical fluctuations, which will include Si-ncs, but also the formation of potential wells of varying depths and a more complex band-structure [81]. Such a model would be particularly suitable for as-grown or low-temperature annealed films, where incomplete phase separation and cluster formation can have occurred. Based on ESR measurements, the authors in [81] also identify various non-radiative bonding configurations which could appear as the films become more Si-rich, quenching the luminescence. The authors suggest that SRSN materials are more stable than porous Si due to a lack of H-bonds, however, this claim seems ill-founded as their own films were grown using SiH₂Cl₂ and NH₃ and are almost certainly hydrogenated.

Finally, one of the more comprehensive treatments examining the luminescent behavior of SRSN materials has recently been given in [101] for samples prepared by reactive evaporation. In this work both *a*-Si-ncs and the transition to c-Si-ncs have been considered. A discussion of the thermal evolution of film structure in this work will be considered in the next chapter. The PL behavior reported by the authors shows a more complex nature than other papers mentioned so far. PL was observed in as-grown films. Annealing of the films was done using a 10 °C/min ramp up, followed by an immediate cool-down after reaching the anneal temperature. This slow ramp up likely allows for a complex film evolution not often considered in other annealing work. At low anneal temperatures, T < 650 °C, the PL redshifts and then decreases in intensity. No PL was reported from 650-800 °C. After annealing at 900 °C the PL reappears, albeit at shorter wavelengths than the initial PL. Further increases of the anneal temperature again lead to

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a redshift of the emission wavelength. Two models are considered to explain the luminescence; quantum confinement, and band-tail states. Band-tail states within the confined Si-rich regions of the film are suggested as the mechanism responsible for luminescence in the as-grown samples, as shown in Figure 2.11. Hydrogen passivation of non-radiative defect states within the confined region is considered crucial for obtaining luminescence. At lower, but increasing, anneal temperatures hydrogen begins to outdiffuse from the sample leading to the decrease and eventual elimination of the sample PL. The authors annealed the films at low-pressure with no gas ambient, a non-conventional method for the study of these materials. Within this model, one would expect similar behavior under an N₂ ambient, however, the use of N₂ + H₂ would maintain the passivation of non-radiative defects. Such a study could confirm that the out-diffusion of hydrogen from the sample is indeed the primary mechanism of PL quenching rather than some structural variation within the films.

Above 900 °C *a*-Si-ncs form within the matrix and PL is described better through a quantum confinement model. Between 950-1050 °C these clusters crystallize leading to a blueshift of the PL which then red-shifts as the larger c-Si-ncs form at higher anneal temperatures. It is clear that the model is not applicable to the earlier discussed samples where *a*-Si-ncs have been observed to form in the as-grown films, however, overall, the authors present a rather compelling model to describe the PL behavior of SRSN materials and its applicability to multiple growth methods merits further study.



Figure 2.11: Band-tail luminescence states in a-SiN_x:H. A scheme proposed to explain the luminescence of as-grown and low-temperature annealed SRSN samples through the presence of band-tail states within a Si-rich confined region. Here E_G is the optical (Tauc) gap of the Si-rich region (x2 < x1). After [101].

The diverse range of results discussed above illustrates that the specific nature of surface state, defect, and quantum confined luminescence remains an open question in the silicon nitrides. Unfortunately, as with SRSO thin films the particular details of luminescence from these materials is strongly dependent on the method of growth and post-deposition treatment. Even with the same post-deposition treatments samples grown using different methods can show unique behavior. In order to adequately determine the nature of luminescence it is first necessary to obtain more details on the material and structure of these films so that common and differing features may be correlated with the PL results. Even in SRSO detailed comparisons of this nature for materials fabricated using different methods are only now just being undertaken [103]. The wide discrepancies in the anneal behavior of SRSN thin films make such a study all the more

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necessary. This becomes a particularly pressing problem, as the development of a Sibased light source will eventually require some form of technology transfer and scaling up the fabrication process. Knowledge of the common and differing natures of the materials will better prepare those involved in this process for the potential difficulties that may be encountered due to differing systems (and ideally provide methods of overcoming them).

Few studies have yet employed the use of X-ray spectroscopies for the study of silicon nitrides. Behavior of SiN_x films has been studied at the Si K-edge for a set of samples grown by ECR-CVD with a range of gas flow ratios (SiH₄/N₂) [104]. HREM imaging of one of their samples shows the presence of crystalline Si-ncs in the films. The results presented at the PLY-XAS edge clearly show that as the flow ratio increases (meaning more excess Si in the film) a luminescent band arises at Si-Si excitation energies. PLY-XAS at Si-N related bond energies also suggests the presence of defect related luminescent states. Unfortunately, the corresponding XEOL spectrum is presented for only one sample, at energies well above the absorption edge (E=1890 eV). In this case one is not able to distinguish what features may be attributed to the quantum-confined luminescence of the nanoclusters or whether the luminescence they are showing is primarily arising from defects. The authors also show both PL and TEY-XAS data. The PL results in particular appear to have features indicative of multiple emission bands (although the distinguishing inflection point between bands is weak and could be a feature of the detector). It is likely that the transition from one band to another could have

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 been correlated with the increase in the Si-Si bonding signal and used to better interpret

 the PL behavior.

One significant drawback to the use of silicon nitride over silicon oxide is the lack of observed gain in the nitrides [25, 105]. It is in fact, not clear that gain can be obtained in a silicon nitride based system. In Si-nc embedded SRSO thin films a four level model, as shown in Figure 2.12, is typically used to explain the observation of gain, involving the ground and excited states of the Si-nc and two localized radiative states formed within the Si-nc bandgap. Recombination of e-h pairs occurs between the localized states either through spontaneous or stimulated emission. The nature of the localized states has been tied to the presence of O related states at the Si-nc surface, such as the Si=O bond [106].



Figure 2.12: A four-level model to qualitatively explain gain in Si-nc/SiO₂ systems. Radiative recombination occurs between oxygen related interface states within the Si-nc bandgap. Competing Auger processes are not shown for clarity. After [106].

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A recent study of silicon nitride systems showed that while fast-recombination dynamics, commonly found in oxide materials that exhibit gain, are observed in nitride passivated Si-ncs no gain was observed [107]. If this is in fact the case then, while nitrides may be ideal for the development of LEDs they still leave the ultimate goal for integrable Si-emitters, the Si-laser, to be desired. The lack of observed gain in [107] does not necessarily mean that gain is impossible, however. Let us recall that it took several years of research on SRSO materials before gain was first observed in this system. Even then, however, the presence of gain in SRSO systems depends strongly on the method of preparation and the exact nature of the gain mechanism remains unknown, save that oxygen passivation appears to be required. If one can isolate the mechanisms which give rise to net losses in the nitride structure and reduce them while finding Si-N related states to enable stimulated emission, equivalent to the Si=O bond in SRSO, then gain may yet be possible to achieve.

Up to this point one additional, yet potentially significant, detail of the observed luminescence of Si-ncs (in SRSO or SRSN) has been ignored. The concept is simple enough to comprehend, yet complex to model and difficult to analyze experimentally. In both SRSO and SRSN materials a thermal anneal leads to a distribution of nanocluster sizes. In a sample with a distribution of sizes energy transfer may occur from smaller to larger nanoclusters, but not in the opposite direction. That is to say that the higher energy emission of smaller clusters can excite larger ones, however, the energy from a larger cluster is insufficient to excite the smaller clusters. Such behavior leads to complex

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 dynamics within the system itself that extend beyond the basic considerations of cluster

 size-PL relations and should be acknowledged in a complete treatment of the luminescent

 properties [108-111]. Such a treatment is, however, outside of the scope of this work.

The observation of significantly different luminescent behavior in silicon oxide and silicon nitride based materials raises the interesting question of what occurs in silicon oxynitride thin films, where both oxide and nitride bonds may be present in sufficient quantities to introduce competing radiative recombination states. A literature review of the luminescence of silicon oxynitrides shows just such behavior with luminescence attributed to oxide [112-114] and nitride [115] bonds or defects and/or quantum confinement. Often these emissions lie within similar energy ranges and could be interpreted in several ways. Indeed, one of the earliest studies on the PL of oxynitrides admits to their complexity and the difficulty in ascribing the luminescence to any particular luminescence center, although the authors were able to conclude that the luminescence likely was not due to a N-related recombination center [116]. Furthermore, the structural evolution of such films shows a more complex behavior demonstrating the presence of separate oxide and nitride phases in some samples [117]. Such results make attributing the luminescence even more difficult.

In all cases of luminescence from silicon oxynitrides the discussion proceeds from what was presented earlier for the oxides and nitrides. The added complexity of the SiO_xN_y leads to a situation where extensive research will be required to adequately resolve which possible states are, in fact, giving rise to the luminescence. As with the

nitrides it is likely that no one model will be adequate to describe the behavior of these materials for various fabrication methods and post-growth treatments. The identification of common and differing features in the structure could lead to a determination of why a diverse range of results is observed for the luminescent behavior of the oxynitrides.

2.2.3 Rare Earth Doping in Si-Nanostructure Containing Systems

A particularly interesting aspect of Si-nanostructures is their ability to efficiently transfer energy to rare earth ions incorporated within the same host matrix [29, 118, 119]. Here only an overview of this subject is considered, highlighting the distinct behavior observed in silicon-rich and oxygen-rich samples and suitable for a discussion of the X-ray based analysis of Tb and Ce doped samples performed for this work. A more detailed discussion of these films has recently been provided [38, 120].

The use of rare earth dopants allows one to obtain specific emission energies, related to transitions between electronic levels within the rare earth ions. Specific rare earths have been of significant interest due to the wavelengths of their emissions. Ce, Tb, and Eu all have luminescence in the visible regime (blue, green, green/red, respectively). They are, therefore, of interest for applications in displays and for solid-state lighting. RE ions in phosphors have been extensively used for decades in technologies such as CRT PhD Thesis – T. RoschukMcMaster University– Engineering Physicsdisplays. Er has a prominent infrared emission at 1.54 μ m, which is within thetransparency window for optical fibres, making it suitable for telecommunications¹⁹.

Although Er is not considered in this work, it has been the most extensively studied of the rare earth dopants in Si-nc systems due to its emission at 1.54 μ m. It is, therefore, useful to first briefly consider the results related to Er, as much of the literature on other rare earths builds upon them. Figure 2.13 illustrates the energy transfer process from Si-ncs to the Er³⁺ ion, along with the associated energy levels [121].



Figure 2.13: Electronic energy levels of the Er^{3+} ion and the energy transfer process. After excitation the Si-nc may recombine non-radiatively by transferring energy to the Er^{3+} ion. After [121].

¹⁹ Er also has a visible (green) emission, however, this emission is not why Er is actively studied in SRSO based materials.

An excited Si-nc may recombine non-radiatively by transferring energy to an Er^{3+} ion in the surrounding SiO₂ host, thus acting as sensitizers to the Er ions [118]. The higher excitation cross-section of the Si-ncs in comparison with the Er ions alone allows one to obtain greater Er related emission intensity. There is an abundance of literature examining the details of possible mechanisms for energy transfer between the Si-ncs and the Er ions [122-128]. What is generally agreed upon, however, is that in Si-rich films it is the formation of Si-ncs that leads to enhanced Er emission through a Förster-Dexter related energy transfer process [122].

The possibility of alternate coupling mechanisms for the excitation of Er ions, particularly in the case of ORSO samples was previously explored by D. Blakie [129]. In this case it was expected that Si-ncs should not form in the film as there was no excess Si. The possibility of sensitization through oxygen related defects that could be excited using the 325 nm emission of a HeCd laser was considered. Schematically the presence of such a sensitization mechanism is shown in Figure 2.14. Although Blakie's work on this subject was quite extensive it proved difficult to establish a direct correlation demonstrating that the luminescence was clearly tied to oxide states and was not due to the possible presence of small Si-ncs within the film²⁰. Recently, several reports have been published examining the luminescence from Er-silicates [130-132]. The possibility of silicate formation in the Er-doped ORSO films was not considered at the time, but

²⁰ This leads to the difficult question of what, at minimum, constitutes a Si-nc. Whether a Si-nc is defined on the basis of a minimum number of Si-atoms or a specific bonding configuration (e.g. one Si atom bound in a tetrahedral structure to at least (4-N) other Si atoms) is a problem that has not yet been addressed.

PhD Thesis – T. RoschukMcMaster University– Engineering Physicsmerits future consideration in the analysis of these films, particularly as silicate formationhas been found to occur in Ce:ORSO samples [133].



Figure 2.14: Energy transfer from Si-ncs or O-related defects to Er^{3+} after excitation with a 325 nm source. The possible sensitization of the Er ion through oxygen defects within the host matrix is illustrated. After [129].

In this work the luminescence from Ce and Tb-doped ORSO has been examined through XAS and XEOL, however, the related experiments which could serve to identify the luminescence mechanism of Er in ORSO have yet to be performed²¹.

As mentioned earlier, in order to obtain a full spectrum of emissions for lighting or display applications rare earth dopants other than Er may be used. Common dopants for obtaining specific colours include Ce (blue), Tb (Green), and Eu (Green/red). Here the discussion will be limited to those two RE-dopants that have been analyzed as part of this work; Tb and Ce. The energy levels of the luminescent Tb^{3+} ion are shown in Figure 2.15.



Figure 2.15: Electronic energy levels of Tb^{3+} ions in SiO₂. Radiative recombination pathways giving rise to the multiple sharp emission peaks observed in Tb-doped samples are shown. Energies are given for the energy levels of the Tb^{3+} ion between which radiative recombination occurs.

²¹ The reason for this lies primarily in the need for the proper optics and detector for the analysis of IR emission at the CLS. Difficulties have been encountered with both SRSO and ORSO Er-doped films that are known to have good IR PL. A new IR spectrometer is planned for the facility in the near future which should help resolve the nature of Er-doped luminescence in ORSO samples one way or another.

Luminescence from the Tb ion arises due to intra-4f transitions between the ${}^{5}D_{4}$ and ${}^{7}F_{j}$ (j = 6, 5, 4, 3) energy levels. This leads to a series of emission lines at 486, 546, 588, and 620 nm. Due to Stark splitting the 546 nm emission line appears as two emission lines at 542 and 548 nm. PL spectra for Tb-doped SRSO and an ORSO samples illustrating the luminescent behavior of Tb in these films are shown in Figure 2.16.



Figure 2.16: Luminescence from Tb-doped SRSO (top) and ORSO (bottom) samples. The samples have been annealed under N_2 at the temperatures shown. The SRSO sample contains 36% Si and 0.3 % Tb while the ORSO sample contains 32% Si and 0.4% Tb. Reproduced from [120].

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In the SRSO sample luminescence attributed to Si-ncs is observed at anneal temperatures up to 1100 °C. HREM imaging of the samples has shown that small nanocrystals (d \sim 2nm) form in the film at this anneal temperature. The Si-nc emission in the sample has been attributed to recombination at oxide related surface states of the nanocrystal. Emission at 546 nm is vaguely present at this anneal temperature but dominates the PL spectrum after a 1200 °C anneal. The suppression of the Si-nc signal and increase in the Tb luminescent signal are indicative of energy transfer from the Si-ncs to the Tb ions in a similar manner as proposed for Er (through a Förster-Dexter energy transfer).

Significantly different behavior is observed for Tb-doped ORSO samples. Tb luminescence has been seen in the samples annealed at temperatures as low as 600 °C. The luminescence in these samples is typically observed to peak around 700-800 °C and to decrease in intensity as the anneal temperature is further increased, indicating a decrease in the amount of optically active Tb within the films. This may be associated with a change in the structure, from Tb coordinated with 6 oxygen atoms (Tb-O₆) to Tb coordinated with 2 oxygen atoms (Tb-O₂). Through the analysis of X-ray absorption fine structure (XAFS) of Tb ion implanted into SiO₂ the Tb-O₆ coordination has previously been associated with an enhanced luminescence [134]. In these samples the host matrix can be expected to have a bandgap near that of SiO₂, therefore, excitation across the bandgap followed by energy transfer to the Tb ions through band tail or extended states is not considered a likely scenario as has been reported for SiN_x and silicon oxynitride

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 samples [135, 136]. The exact nature of Tb sensitization in the ORSO films remains

 under investigation.

In Ce two possible broad emission bands are typically observed in the luminescence spectrum corresponding to 5d to 4f transitions. The 5d states into which an electron is excited are exposed to the surrounding ligands within the local environment of the Ce. The exact nature of luminescence from Ce is, therefore, sensitive to the surrounding environment.



Figure 2.17: Energy levels of the Ce^{3^+} ion in SiO₂. Radiative recombination occurs through 5d to 4f transitions. Because the 5d states are interacting with the surrounding environment and the host matrix has a significant effect on the Ce^{3^+} luminescence. The approximate energies are given for the energy levels between which radiative recombination occurs for the Ce^{3^+} ion in SiO₂.

Luminescent behavior from Ce incorporated in SRSO and ORSO thin films is shown in Figure 2.18. In the SRSO film only a weak Ce-related luminescence is observed. One may be inclined to attribute the weak Ce luminescence to the low Ce

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 content of the films, however, in an ORSO film with approximately the same amount of

 Ce the PL intensity was ~10X in the same wavelength range. At ~800 nm a strong

 luminescence, attributable to Si-ncs, is observed. It therefore appears that in the SRSO

 films Ce is inefficiently excited.



Figure 2.18: Luminescence from Ce-doped SRSO (top) and ORSO (bottom) samples. The samples have been annealed under N_2 at the temperatures shown. The SRSO sample contains 40% Si and 0.04 % Ce while the ORSO sample contains 32% Si and 1.0%Ce. Reproduced from [120].

In ORSO samples a substantially different behavior is observed. The PL shows two different regimes with annealing. The first is a rise in Ce luminescence up to an

PhD Thesis – T. Roschuk McMaster University-Engineering Physics anneal at 800 °C after which the PL intensity drops with annealing up to 1000 °C, which is then followed by an increase in PL with annealing up to 1200 °C. From 700-800 °C the increase in PL has been attributed to a conversion to the luminescent Ce³⁺ state from the optically inactive Ce⁴⁺ state. The decrease in intensity after annealing at 1000 °C has been attributed to clustering of the Ce within the film, leading to a quenching effect. Finally, as the anneal temperature is further increased the results have been found to be consistent with the formation of a Ce-silicate phase within the films [38]. HREM and energy dispersive X-ray spectroscopy have provided further evidence for this behavior [133]. A particularly bright luminescence was observed from this sample spurring interest in developing a further understanding of the nature of this luminescence. Furthermore, Cesilicates are appealing due to the potential to increase the amount of Ce that can be incorporated into the film. In SRSO films the solubility limit of RE atoms is a limiting factor for RE doping. In this work I have concerned myself with analyzing some of the Ce doped samples in order to examine if information on the Ce luminescence mechanism could be obtained²².

²² The discussion of Ce will be more limited than that of Tb. Many of the Ce-doped samples were grown as part of a collaborative project and were sent to the industrial partner on this project for further analysis.

Chapter 3: Materials Science of Luminescent Si-nanocluster Embedded Dielectrics

In the previous chapter the light emitting behavior of several luminescent Si-based materials was considered and some basic details concerning film structure and its relation to the observed luminescence were discussed. In this chapter materials science aspects, related the thermal evolution of Si-rich films with annealing and the formation of silicon nanoclusters, are considered.

Silicon nanocluster embedded dielectrics are commonly formed through the growth of silicon rich thin films followed by a thermal anneal. The anneal process then induces the phase separation of the excess silicon and a stoichiometric silicon dielectric (e.g. SiO_2 or Si_3N_4), as shown in Figure 3.1. To date a substantial amount of the research into the materials science aspects of luminescent Si-based dielectrics has focused on silicon rich silicon oxides (SRSO). The incorporation of nitrogen into the oxide host matrix or the switch to a nitride host matrix, however, can have a profound effect not just on the luminescent properties of these materials but also on the nanocluster formation process. In the literature photoluminescence will often be reported and the presence of Si-ncs demonstrated with little consideration as to how this thermal evolution actually proceeds,

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 yet understanding this behavior is crucial to obtaining consistent performance from these

 materials.



Figure 3.1: Formation of Si-ncs within Si-rich thin films with thermal annealing. The anneal process induces a phase separation of the metastable Si-rich film into Si-ncs embedded within a dielectric host matrix.

The exact nature of the phase separation process, and the degree of completeness to which it occurs, is not just a function of the film composition but also often depends on the method of film fabrication. Common fabrication methods for producing Si-nc embedded thin films include PECVD, sputtering, and ion implantation [89, 90, 137-140]. All three of these methods are CMOS/VLSI compatible, and hence as growth techniques they themselves present no barrier towards their use with current microelectronics infrastructure. In addition to these methods polymer pyrolosis, laser ablation, and decomposition of silane have also been used to produce Si-ncs, however, the possibility of using such techniques in current CMOS technology is remote and the discussion that follows is oriented towards the CMOS-compatible processes [51, 141]. Detailed

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comparisons of the effects of different deposition methods are only recently being explored [103]. The influence of different growth methods would represent an extensive study all on its own. Here, the discussion will focus on the general trends of thermal evolution, referring to the effects of different fabrication methods only to highlight some of the areas where diverging behavior has been reported.

In order to avoid confusion, both in this chapter and later in this thesis, I will first attempt to clarify the distinction used between silicon oxides, nitrides, and oxynitrides. Several groups have produced SRSO thin films using N₂O gas as the oxygen source. This then leads to some nitrogen contamination of the films. The films are typically still referred to as SRSO, or in some cases nitrogen rich SRSO but not as silicon oxides. This seems to be a convention adopted for cases where nitrogen has not been intentionally incorporated into the material. Likewise, the sequential deposition of silicon nitrides and oxides in our own deposition system (which uses separate N₂ and O₂ source gases) has possibly led to some partial contamination of subsequent depositions. The contamination levels are typically sufficiently small so that they provide only minor deviations from the expected behavior of the films. As no oxygen was intentionally introduced into these samples I will refer to them as silicon nitrides and not silicon oxynitrides²³. Only samples which have been intentionally grown as silicon oxynitrides will be referred to as such. As

²³ In the results and discussion I will explicitly show if and how any contamination has affected the measurement. For samples where measurements have allowed I will also clarify details of the incorporation of the contaminating species.

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 will be discussed in this and the following chapters the silicon oxynitride samples often

 show their own thermal evolution behavior, distinct from both the oxides and nitrides.

A discussion of the behavior of these films is largely based on two possible, idealized, models of their structure, the random bonding model (RBM) and the random mixture model (RMM). Details of these models are considered in the next section. As with luminescence, the thermal evolution of SRSO materials has been most extensively studied to date. It is, therefore, appropriate to start with a discussion of what is known about the thermal evolution of SRSO. This is followed by a discussion of the influence of nitrogen on SRSO and then a detailed discussion of results that have been presented in the literature for SRSN samples. Finally, the thermal evolution of the more complicated silicon oxynitrides is considered.

3.1 Bonding Structure Models

In order to describe the structural evolution of Si-rich thin films it is necessary to have an understanding of the bonding network of the materials. Although the actual picture is likely more complex than that painted by the RBM and RMM models, they provide a solid basis for discussion [142].

3.1.1 Random Bonding Model

The random bonding model considers the differing types of bonding structures that can form within a material. From this basis set of bonding units the film structure is considered from the perspective of their random distribution. Silicon forms tetrahedral

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bonding units with its neighboring atoms. In Si there are 4 neighboring Si (Si-Si₄) atoms, in silicon dioxide, 4 neighboring oxygen (Si-O₄), and in silicon nitride, 4 neighboring nitrogen atoms (Si-N₄). Note that this is seen simply from the perspective of the surrounding bonds for each Si atom, and O atoms would be shared between bonding units. In SRSO excess Si within the films will lead to some Si atoms with one or more neighboring Si atoms replacing some of the O. This results in five different possible tetrahedral bonding units denoted as Si-Si_jO_{1-j} (j = 0, 1, 2, 3, 4), as shown in Figure 3.2. An appropriate statistical distribution is then used to apply these bonding units to the system under consideration. The greater the amount of excess Si the more the distribution will be shifted towards greater values of j.



Figure 3.2: Tetrahedral bonding units for the two component Si-O system. The set of possible Si-O tetrahedral bonding units formed by the coordination of Si with surrounding O or Si atoms. In a random bonding model of SRSO the distribution of units shifts more towards (e) with increasing Si concentration.

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In silicon nitride the structure still maintains a tetrahedral nature from the perspective of the Si atom and similar bonding units to those shown in Figure 3.2 can be used to build up the structure. However, each N atom makes three bonds with neighboring Si atoms (thus the bonding units are oriented differently with respect to each other in oxides or nitrides). Furthermore, these 3 bonds render the nitrides more rigid than SiO₂. The bonding units and bonding structure of silicon nitride are shown in Figure 3.3



Figure 3.3: Bonding units and structure of silicon nitride. (a) The N-base bonding unit illustrating the three bonds formed by N-atoms. (b) The Si-base tetrahedral bonding unit. (c) A schematic representation of the bonding structure of silicon nitride.

If additional atomic species are added to the model, such as for silicon rich silicon oxynitride, the model may be adapted $Si-Si_jO_kN_{4-(j+k)}$ where j = 0 for a non-Si-rich film. In the case of a hydrogenated film, hydrogen should be incorporated into the model as well. One can see how additional atomic species make the determination and application of an appropriate distribution a complex scenario.

In an ideal, homogenously deposited material, the random bonding model would provide an accurate description of the film structure.

3.1.2 Random Mixture Model

The random mixture model assumes that the film structure is composed of a mixture of a limited number of stable phases. For SRSO films this corresponds to a Si and a SiO₂ phase (i.e. only units (a) and (e) in Figure 3.2). For silicon oxynitride the RMM bonding units are SiO₂ and Si₃N₄ phases, with a Si phase added for the Si-rich films [117].

For a completely phase separated Si-rich film, as shown after annealing in Figure 3.1, the RMM would provide an accurate description of the system. From the perspective of the RMM as much as 100% of the excess Si within the films may go into the formation of Si-ncs. That is to say that complete phase separation between the excess Si and the stoichiometric dielectric host can be attained, although in such a case one could argue that the model inappropriately treats the Si-nc interface region.

3.2 Structural Studies of Si-based Materials

Prior to surveying results related to the structural evolution of Si-rich materials let us first consider a simplistic picture of the nature of the bonding structure of as-grown films, specifically for the case of PECVD.

Generally, film structure is assumed to be neither completely RBM or RMM-like [142]. Rather, the specific conditions of the deposition can lead to a skew towards either model but elements of both are typically present. PECVD deposition is typically

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performed at low temperatures. This leads to a quenching effect at the substrate surface, resulting in the formation of an amorphous solid. Si atoms incorporated into the structure retain a tetrahedral bonding structure; however, the resulting bonds are often distorted from the ideal case. Defects such as dangling bonds have also been found to form [143]. In Si-rich films the excess Si is typically considered to be located in partially oxidized tetrahedra, leading to a RBM-like structure [142]. Using X-ray photoelectron spectroscopy (XPS) it is possible to identify the bonding states of the Si atom due to energy shifts related to the oxidation state of the Si atom. Fitting of the XPS spectra has revealed the presence of peaks that could be ascribed to the different RBM base structures, confirming this behavior [144-146].

Depending on the type of deposition system used one can expect behavior causing the as-grown materials to be act closer to the RBM or RMM. Differences of this nature have in fact been observed between sputtered and PECVD SRSO materials (having 1.6 x 10^{22} at/cm³ excess Si) [103]. A more complete phase separation appears to be seen in the sputtered samples, with up to 100% of the excess Si being incorporated in the nanoclusters. For a PECVD film only 30% of the excess Si appears to have segregated into clusters, with the rest remaining dispersed in the films. Luminescent properties of the films were found to be in agreement with this behavior²⁴.

²⁴ While the proceedings cited here do not discuss the as-grown films, during the associated conference presentation the authors stated that upwards of 90% of the excess Si was found to be in clusters for the as-grown sputtered samples.

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Although the results show clearly distinct behavior in the structural evolution of PECVD and sputtered samples, the broad distinction seen here should not necessarily be taken as evidence that PECVD and sputtered samples are always better represented by the RBM and RMM, respectively. In both PECVD and sputtering the growth of a sample is strongly dependent on the deposition parameters. Plasma density, substrate temperature, gas flow rates, deposition rate, and chamber geometry can all affect how the growth proceeds for either of these systems. Take, for example, PECVD. If the deposition rate is decreased one can expect that atoms adsorbed at the surface can migrate further before they are encapsulated by subsequently deposited material. In such a scenario the excess Si may cluster within the as-grown material (indeed, this type of behavior is observed in the nitrides, discussed later in this section).

In the above mentioned study [103] the authors suggested that Si atoms deposited using sputtering had more free energy and thus were able to migrate in such a manner to form clusters during the growth process. In order to properly assess the behavior of sputtered materials, however, one must know details of the sputtering environment. It is generally assumed that during sputtering single atoms are ejected from a target material. It is altogether possible, however, that clusters themselves could be sputtered. Calibration of the system can reduce this effect, although it would be difficult to completely avoid²⁵. This would explain why similar behavior was observed between co-sputtered and reactive

²⁵ This effect is not necessary detrimental. As part of a project setting up a sputtering system at McMaster University it was suggested to determine the appropriate conditions for the formation of luminescent Si-ncs in the as-grown samples, although this goal was not achieved under the deposition conditions used [139].

<u>PhD Thesis – T. Roschuk</u><u>McMaster University– Engineering Physics</u> sputtered samples [147]. Even in a reactive sputtering environment if clusters are sputtered the size of the Si-cluster that is finally deposited would be reduced through reactions and bonding at the cluster surface, however, one could still expect a Si-rich core. If single atoms were ejected from the sample, however, the reactive environment could be expected to inhibit this behavior. If clusters are sputtered from the target one

should, therefore, expect sputtered materials to be at least partially described by a RMM model in the as-grown case²⁶.

XPS has also been used to identify the bonding states of the Si atoms in reactively sputtered materials and the structure of these films was studied. While the bonding details could be ascribed to the formation of the different tetrahedral structures from the RBM, certain tetrahedra were found to be preferentially formed in the material, specifically, the Si-Si₄ and Si-O₄ tetrahedra that are used in the RMM [148]. The authors, however, point out that other tetrahedra are energetically unfavorable due to the intermediate valence states of the Si-atom leading to spinodal decomposition during the deposition phase and the formation of Si-clusters, adding the RMM nature to the films. The results demonstrate, however, that the films still exhibit a substantial RBM-like nature.

It is not clear exactly where ion implantation fits in the discussed scheme. As the excess Si is largely distributed at a localized depth one is tempted to consider it more as a random mixture, however, it would be necessary to first determine how the excess Si is

²⁶ This does not mean one should expect luminescence. Large cluster sizes, cluster crystallinity, and the presence of defects could all act detrimentally for the as-grown film.

dispersed within the host material. This can be done using available models and software [149, 150]. It would be expected that as the implant dose increases one would further approach the RMM situation. To the author's knowledge an extensive experimental study of ion implanted samples for comparison with PECVD and sputtered samples has not yet been undertaken.

3.2.1 Silicon Rich Silicon Oxides

As discussed in the previous section, as-grown PECVD SRSO films have a more or less homogenous structure, meaning that the excess Si is largely uniformly distributed within the film. When the film is annealed it will undergo a heat induced phase separation inducing intermediate tetrahedral bonding units to disproportionate as [142]:

$$\operatorname{Si} - \operatorname{Si}_{j}\operatorname{O}_{4-j} \longrightarrow \frac{j}{4}\operatorname{Si} - \operatorname{Si}_{4} + \left(1 - \frac{j}{4}\right)\operatorname{Si} - \operatorname{O}_{4}$$
 (3.1)

In terms of the film composition rather than bonding units this is often expressed as:

$$\operatorname{SiO}_{x} \rightarrow \left(1 - \frac{x}{2}\right)\operatorname{Si} + \frac{x}{2}\operatorname{SiO}_{2}$$
(3.2)

Ideally, the phase separation is complete and all the excess Si has coalesced into nanoclusters, however, it has already been discussed that this situation does not appear to be the case for PECVD-grown films. Let us now consider the results related to the actual thermal evolution of these films.

Two fundamental processes are possible for nanocluster formation [151]. The common interpretation is that Si-ncs form through diffusion limited cluster growth. At sufficiently high annealing temperatures nucleation sites form and clusters grow and then

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undergo a process of Ostwald ripening. At the opposite end of the spectrum one can consider at first a separation between the SiO_2 and Si phases, with the two phases forming an intermixed matrix. At high anneal temperatures the Si matrix breaks down due to what the authors of [151] have termed "spinodal decomposition", where an interconnected Si matrix forms and then breaks up leading to the formation of Si-ncs. Monte Carlo simulations of the evolution of the film structure for ion implanted samples with different implant doses have been performed. The results show that at low implant doses nucleation is preferred while at higher doses spinodal decomposition becomes more likely. At sufficiently high implant doses of Si the structure remains a spatially interconnected mix of the two phases (percolation) and nanoclusters do not form [151]. These two processes are illustrated in Figure 3.4. Again the real situation appears to be in between the two processes and elements of both can occur.



Figure 3.4: Si-nc formation through nucleation or spinodal decomposition in SRSO materials. Although the same final product is shown here, spinodal decomposition is expected in samples with higher Si concentrations, which would lead to larger Si-ncs in those films.

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Extensive experimental analysis of the evolution of PECVD-grown SRSO materials has been presented over the past several years [41, 88-90, 142, 152, 153]. In particular, the analysis of a film having 46% Si using both HREM and EFTEM, to look at both crystalline and amorphous structure, has helped paint a more comprehensive picture of the thermal evolution of these materials. Using EFTEM, where imaging is done using only electrons that have lost energy corresponding to interaction with the Si within the film (discussed in the next chapter), evidence of phase separation begins to become apparent after annealing at 900 °C [89]. Although this appears to be the lowest temperature considered in the EFTEM analysis of SRSO materials, previous work looking at the XANES spectra for these films has also examined the effects of annealing at temperatures as low as 650 °C [90]. At 650 °C little change is observed in the structure as it relates to Si-Si or Si-O bonding, however, a re-ordering of the structure associated with partial nitrogen contamination is clearly observed in the XAS spectrum. The influence of nitrogen is discussed further in the next section, while the general details related to the thermal evolution of these films will be discussed at the end of this section.

Returning to the EFTEM analysis, while phase separation is observed at 900 °C, few clear Si-ncs are observed (some small *a*-Si-ncs are present though), but rather the sample shows more of a semi-interconnected network of *a*-Si. The results show a formation process closer to spinodal decomposition, although this may be expected as the Si-excess in these films was relatively high. After annealing at 1000 °C the clear presence of *a*-Si-ncs, with defined interfaces, is observed. Furthermore, some of the clusters are

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seen to crystallize. As the anneal temperature is increased the clusters are observed to grow and become better defined and the fraction of c-Si to *a*-Si nanoclusters increases. Up to anneal temperatures of 1150 °C *a*-Si-ncs actually account for the larger portion of Si-ncs observed in the film [89].

Although clear evidence of c-Si-ncs was not obtained in the study discussed above for the sample annealed at 900 °C, XRD measurements conducted on a set of samples grown at McMaster University show the presence of Si-ncs at this temperature for a sample containing 45% Si [41]. No c-Si related peaks were observed in the asgrown samples or for a sample containing 40% Si, and the peaks were only weakly visible for a sample containing 42% Si. Increasing the annealing temperature and time was found to lead to the formation of c-Si-ncs within the films. Generally, qualitative behavioral aspects of the evolution of these materials are in agreement across various studies. The minor discrepancies between results can be taken as further evidence that the exact details of the structural evolution of these films has a strong dependence on the acct details of film preparation. Using the results from XRD it has also been demonstrated that small c-Si-ncs are under tensile stress which relaxes as the Si-ncs grow. The tensile stress emphasizes the influence of the host matrix on the Si-ncs due to the bond length mismatch between the two systems.

In addition to Si-nc formation with annealing, changes are observed within the structure of the host dielectric. The structure of the SiO_2 host is commonly analyzed through Fourier transform infrared spectroscopy. In particular the Si-O-Si stretching bond

is often taken as a measure of the film quality. A shift in the position of the absorption peak is related to the average bond angle for a Si-O-Si bonding structure. With annealing, the structure of the SiO_2 host is seen to approach that of high quality, thermally grown oxides [154].

XAS provides a powerful technique for looking at changes in the electronic structure and chemical bonding environment for both the Si-ncs and the embedding host matrix. Earlier, work related to identifying luminescence centers through XAS and XEOL was discussed (Figure 2.9). Now, the use of XAS for the analysis of the structural evolution of these materials is considered. It needs to be restated that in the literature results that will be discussed first N-contamination of the films occurs due to the use of a N_2O source. Through this and other work the authors have sought to clarify how N affects the Si-nc formation process, the specifics of which will be discussed in the following section.

XAS spectra at the Si K-edge are shown in Figure 3.5 for samples having several compositions, as-grown and annealed at 1250 °C, and for a sample containing 44% Si annealed at various temperatures [69]. The positions of the peaks associated with Si bonded to Si, N, and O are indicated.

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Figure 3.5: XAS spectra illustrating the thermal evolution of the SRSO thin film structure. With increased Si content and annealing temperatures the structure of the films changes and shows an increase in Si-Si bonding. The structure of the oxide host is also seen to change significantly with annealing as the host matrix tends towards SiO₂. Reused with permission from [69] ($\[mathbb{C}\]$ 2007 American Institute of Physics).

Except for the Si-N feature, which is ascribed only to Si-N related bonding, the peak positions indicated correspond to X-ray absorption by the extreme RBM units (Si-Si₄, Si-O₄). Caution must, however, be exercised in interpreting the spectra. As in XPS, there will be a shift in the energy for Si bound in the interim RBM units and the absorption signal will lie somewhere between the extremes. The XAS signal can then be

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a convolution of several peaks. Experimental analysis does not always address this point, as it can be complex (and somewhat arbitrary) to attempt to fit these multiple peaks, but one should recognize their presence. In the RMM, which describes the expected behavior for the annealed samples, one expects the peaks associated with the extreme bonding units to become more intense and distinct. In [69] additional analysis of the film composition and structure suggested up to 10% N in the samples. Silicon nitride references were used to obtain additional information on the Si-N peaks for the interpretation of the XAS spectra which avoided improper association of these peaks solely with Si-O RBM units.

Consider first the spectra for the sample containing 44% Si. As the anneal temperature is increased several effects are observable. At the Si-Si peak a more defined shoulder is seen to form, the signal from Si-N is seen to decrease, and the Si-O bonding peak is seen to increase in intensity and shift to slightly higher energies. The results indicate that both a phase separation and a structural reordering of the dielectric host are occurring. The decrease in the Si-N signal is attributed to the reordering of nitrogen within the film to form a more homogenous silicon oxynitride host. Due to the low concentration of nitrogen the authors expect this silicon oxynitride to act in a very similar manner to SiO₂. The decrease in the Si-Si signal after annealing at $T \ge 1200$ °C is not clearly described although the authors mention that it may be due to oxidation effects at the surface. For samples having different compositions, similar behavior is shown after annealing at 1250 °C, however, the Si-Si related peak is less prominent in samples having
<u>PhD Thesis – T. Roschuk</u><u>McMaster University– Engineering Physics</u> low excess Si but is more clearly observed for samples with high excess Si concentrations. This then raises the question of what a comparison of the Si-Si shoulder behavior would have been like for samples of different compositions annealed at 1100 °C, where this feature is more pronounced.

Evidence of Si-Si bonding is present even in the as-grown films, but the shoulder becomes more pronounced after annealing at 900 °C. Although TEM-based analysis indicates a quite homogenous structure for the as-grown films, the presence of some Si-Si₄ bonding is evidence of some Si-aggregates forming in these films. This is likely due to the presence of such bonding units within the film that are too small to be clearly distinguished through TEM.

One of the difficulties encountered in understanding the thermal evolution of SRSO films is that few reports have yet looked at the subject comprehensively. To do so is an incredibly time consuming endeavor. Often, as the interest lies primarily in the optical properties of these materials, structural characterization of an annealed film is done simply to illustrate the presence of Si-ncs and only a rudimentary description of the possible origins of that structure is given. Even in cases where a more comprehensive picture is given, one often finds that the authors have focused on only a single sample and then generalized the behavior, which of course is unsatisfactory, as shown above, because the thermal evolution can proceed along different paths (nucleation and growth or spinodal decomposition) and is influenced by a number of factors (*i.e.*, composition, anneal temperature, and anneal time). While the extensive amount of work published on

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SRSO samples has led to a firm basic understanding of the segregation behavior there are many areas where experimental results are still required to understand their behavior, such as determining the conditions where the segregation is dominated by nucleation and growth or by spinodal decomposition and correlating this behavior with the luminescent properties of the material²⁷.

3.2.2 Effects of Nitrogen on Silicon Rich Silicon Oxides

In the previous section the thermal evolution of SRSO thin films was examined. Phase separation between Si and SiO₂ has been observed through XAS. Nitrogen was generally not seen to affect the behavior of this phase separation; however, the results presented do not provide a comparison of the effects of annealing for films both with and without nitrogen. The detailed influence of nitrogen incorporation in these films has not been adequately studied through a comparison of structural characterization techniques, but rather is inferred from differences that have been observed in the PL from these samples [155]. In this study the PL behavior of samples containing nitrogen was consistent with the formation of smaller Si-ncs. The effect was attributed to the decreased diffusivity of Si in the presence of nitrogen. Through the use of N-doping a similar effect has been observed quantitatively in SRSO materials [156]. Although the XAS results

²⁷ Often, once one group has a number of publications in a specific area (e.g. EFTEM imaging of the Si-ncs for a small set of compositions) interest by other groups into performing a similar study on other compositions seems to wane. This may be due to a lack of novelty or an unwillingness to contradict the published results but should be pursued because unique results are to be expected (e.g. spinodal decomposition vs. nucleation with different compositions) and experimental verification is required.

<u>PhD Thesis – T. Roschuk</u><u>McMaster University– Engineering Physics</u> discussed earlier show that the film structure still forms a SiO₂-like host matrix after annealing, caution should be exercised in inferring information about Si-nc formation from the PL results, as the influence of this SiO₂-like oxynitride host on the luminescence process itself is not known.

Let us first consider some of the properties of Si-O and Si-N bonding. Although the Si-O bond is stronger than the Si-N bond (799.6 \pm 13.4 vs 437.1 \pm 9.9 kJ/mol, for comparison the Si-Si bond dissociation energy is 399 kJ/mol), silicon nitride forms a more strongly bound structure [157]. This is due to the rigid bonding structure of the nitrides that arises due to the need for the N atom to form 3 bonds. The influence of this structure on limiting the diffusivity of dopant and interstitial Si has been discussed in [158, 159].

Nitrogen incorporation in SRSO materials has, therefore, been observed to act as a limiting agent in the nanocluster growth process by presenting a diffusion barrier for the excess Si within the films. This behavior is consistent with the results that will be discussed in the following two sections and the results discussed for SRSN materials grown in this work. The effects of nitrogen on the Si-nc crystallization process are debatable. In [155] the crystallization threshold is typically associated with a strong increase in luminescence intensity. This effect occurs at a higher temperature in the samples containing nitrogen, yet, as will be discussed in the following two sections, nanocrystals have been observed in SRSN materials already after annealing at significantly lower temperatures.

3.2.3 Silicon Rich Silicon Nitrides

Having considered details related nanocluster formation within silicon oxides, the more extensively studied material in the literature; let us now turn to the materials science aspects of silicon nitride based thin films, which are central to a large portion of this thesis. A key distinguishing feature between silicon oxide and silicon nitride films is that (luminescent) nanocluster formation can occur in as-grown silicon nitrides. Two separate growth regimes for PECVD silicon nitrides have been identified, resulting in the formation of crystalline nanoclusters at lower growth rates and amorphous nanoclusters a slightly faster (but still relatively low) growth rates as indicated in Figure 3.6 [28, 80, 84, 160].





Crystalline Si-ncs were observed under low growth rate conditions using a NH_3 source, however, *a*-Si-ncs were formed when a N_2 source was used. It is clear then, that

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there are two effects that play a role. One is the growth rate; the other is the influence of hydrogen on the crystallization process. Hydrogen induced crystallization is already a well known effect and has been previously demonstrated at low growth rates [161, 162]. The formation of the *a*-Si-ncs is associated with the N₂ source gas causing the dissociation of Si-H bonds (from the silane source) and the formation of N-H bonds. This leads to dangling bonds at the Si atoms which can act as nucleation sites for the growth of the *a*-Si-ncs. The authors predict that a joint region with both amorphous and crystalline Si-ncs should exist [28]. The possibility of this is questionable though as two different N source gases to collect the Si-nc formation data presented. It may be that without the additional H provided by an NH₃ source c-Si-ncs cannot form, even at the lowest growth rates, however, with the use of a NH₃ source hydrogen induced crystallization may result in *a*-Si-ncs not forming.

It is worth commenting on the method used to image *a*-Si-ncs. In these and other studies authors demonstrate the presence of *a*-Si-ncs in a silicon nitride matrix through TEM or HREM, assigning the darker regions to the Si-ncs on the basis of their greater density (or atomic density) [84, 163]. Without further details of their methods and the reasons for this assignment this appears counter-intuitive. This assignment works well enough for SRSO materials, particularly images presented for superlattice structures, as the density of Si is indeed greater than that of SiO₂ [164, 165]. The density of Si₃N₄ is,

however, greater than that of Si^{28} . For high quality Si_3N_4 and c-Si the densities are 3.44 and 2.33 g/cm³, thus the density of nitride is almost 50% greater than that of c-Si. Even accounting for a decreased density for the nitride, due to the deposition method and hydrogenation, and assuming an increased density of the Si, due to a closer packed amorphous phase over the diamond lattice structure, the assumption of a switch in the material with greater density is questionable without some references to this effect or some justification. As a critical example, a a-Si/Si₃N₄ superlattice structure is shown in Figure 3.7 [94]. It is apparent in their labeling that the *a*-Si layers appear lighter than the SRSN layers, and yet for the annealed sample darker spots in the SRSN layer are labeled as a-Si-ncs. Note that contrast from the substrate is due to its crystallinity (Bragg contrast), causing it to diffract the electron beam and appear dark in the bright field image. The substrate cannot be taken as a reference for contrast between two amorphous phases. In some cases the authors appear to be referring to the atomic density of Si in Si, Si₃N₄ or SiO₂. If such is the case then the Si atomic density of Si is indeed greater than that of Si_3N_4 , however, it is not clear how the influence of the N (or O) in the film can be disregarded for the discussion of contrast, nor does it explain the behavior discussed for the superlattice shown in Figure 3.7.

²⁸ This is true for atomic density as well. The atomic density of Si₃N₄ is typically given in molecules/cm³, Once we account for the number of the constituent atoms in silicon nitride and compare with the total atomic density of Si one finds that silicon nitride is the greater of the two. A quantitative measure of the atomic density in silicon nitrides is given in [166]. The total atomic density (Si + N) is ~6-7 x 10^{22} atoms/cm³. For comparison the atomic density of Si is ~5 x 10^{22} atoms/cm³. The same is true even if we weight the atomic density by the atomic mass or Z of Si and N.

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 It has already been discussed that in SRSO films EFTEM provides an excellent

 method of imaging Si-ncs (amorphous and crystalline) unambiguously. The use of

 EFTEM would be preferable to demonstrate that the darker spots assigned to *a*-Si-ncs do

 indeed correspond to Si. Even in such a case, however, the argument concerning density

 or mass-thickness contrast requires clarification. Several other contrast mechanisms can

 occur in TEM, although their interpretation can be more complex and they will not be

 discussed here, that should be considered to explain the observations in these images.



Figure 3.7: (a) Bright field TEM and (b) HREM images of an a-Si/Si₃N₄ superlattice structure. Dark spots in (b), indicated in some instances by white arrows, have been labeled as a-Si-ncs. Reproduced from [94].

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The thermal evolution of SRSN films is not yet well studied. The general trend is simply to verify the presence of Si-ncs (typically through HREM or Raman spectroscopy) and then to move on to a discussion of the optical properties. Details of the structure are sometimes inferred from the luminescent behavior (often by way of comparison with similar known trends from SRSO materials) but not experimentally verified. FTIR is commonly employed to look at changes in the structure of the nitride host and Si-H bonding, however, these experiments yield no direct information on the structure and formation of Si-ncs.

As in the discussion of the luminescence of these materials, the most complete work in this area to date has been provided by Molinari *et al.* for a set of samples prepared under reactive evaporation [101, 167, 168]. The composition of the SiN_x films in these studies varies from x = 0.1 to 0.63. Some of the films are, therefore, quite Si-rich. The as-grown films were found to be amorphous, however, the presence of Si-rich regions is evidenced through an *a*-Si signal in the Raman spectra. During annealing from 500-900 °C the nitride host is seen to reorder, showing an increase in Si-N bonding. Annealing at temperatures of 950 °C or greater leads to the formation of c-Si-ncs, confirmed through Raman spectroscopy, XRD, and TEM analysis of the films. XPS spectra for the as-grown and 950 °C annealed samples show behavior more consistent with an RBM model, with interim bonding structures shifting the spectra towards the Si-Si₄ unit as more Si is incorporated into the films. After annealing the sample with x =0.63 at 950 °C a clear phase separation is observed in the film with the XPS spectra being dominated by two peaks associated with Si-Si₄ and Si-N₄ bonding units. The result is consistent with the more RMM-like nature expected for a phase separated film. Similar behavior was observed for all samples, however, the onset of such behavior was seen at anneal temperatures as low as 800 °C for the more Si-rich samples. The Si-ncs are observed to grow with increased annealing temperatures, however, this growth was found to be slower in samples containing more nitrogen. Similar behavior has been reported for a set of PECVD grown samples [96]. The PECVD grown samples show two distinct effects though; (i) a more homogenous as-grown structure and (ii) no crystallization of the Si-ncs, even after annealing at 1100 °C, although the authors report substantial growth of the Si-ncs, in contrast to the growth limited behavior reported by others due to the nitride host. It is difficult to ascertain how unexpected this behavior is though, as the authors report only the growth conditions for the films but nothing that allows for an assessment of how Si-rich the film is (either composition or refractive index).

This behavior contrasts slightly with that reported in [93], where evidence of cluster formation was observed in samples annealed at only 700 °C. In [93], however, details are not discussed of the structure of the as-grown film making a comparison of different thermal evolution processes impossible at the present time. Crystallization at lower anneal temperatures has also been observed in [98], where c-Si-ncs were found in the films after annealing at 900 °C.

The XANES has been studied at the Si *L*-edge for a set of SiN_x samples formed by ion bombardment of Si with N_2^+ . A crucial feature from this study is that the position of

the Si L-edge shifts to higher energies with increased nitrogen content which is associated with the change from Si-Si₄ bonding units towards Si-N₄, reflecting the change in chemical potential for the atoms as they are surrounded by more nitrogen [169]. The result is valuable for the interpretation of *L*-edge behavior, but it is difficult to ascertain how uniform the implantation is and whether Si-ncs may remain, or if most Si atoms have bound with at least some N atoms, leading to the shift in the absorption edge.

3.3 Silicon Oxynitrides

Of the different luminescent Si-based materials discussed in this work silicon oxynitrides present the largest set of conflicting results within the literature. The complex bonding nature of these films presents several potential defects which may play a crucial role in the observed luminescence. Furthermore, the structure of the deposited film and how phase separation progresses during annealing depend strongly on the fabrication method employed for film growth.

Many authors term their oxynitride films as Si-rich, and while in some cases this is obviously justified (for example, $SiO_{0.17}N_{0.07}$ [113]), it is not always clear what defines a Si-rich oxynitride (SRSON) and I have seen no reports that explicitly state such a definition. As such I aim here to outline such a definition. The stable phases of silicon oxynitride are SiO₂, Si₂N₂O, and Si₃N₄. The bonding units for SiO₂ and Si₃N₄ have already been discussed, for Si₂N₂O the bonding units are slightly distorted Si-N₃O tetrahedra [158]. The non-equilibrium deposition conditions used in PECVD growth, however, allow for a full range of SiO_xN_y films to be grown and stoichiometric films can be formed by considering the requirement for 2, 3, and 4 bonds for the O, N, and Si atoms, respectively, as [170]:

$$2x + 3y = 4$$
 (3.3)

This implies that there is a stoichiometric line that the films may follow, with interim bonding units for the oxynitrides. This is not to imply that Si-clusters will not form in the film as a result of the bonding conditions, which may happen as a result of the deposition conditions. What this does imply, however, is that under such a situation it is possible for the film to phase separate after annealing without the need for Si to form clusters.

Silicon rich films would then be defined by the situation where Equation 3.3 becomes an inequality and

$$2x + 3y < 4 \tag{3.4}$$

This leads to the situation where there are insufficient N or O atoms to satisfy the bonding requirements for the Si atoms within the film. In such a case $Si-Si_4$ clusters could be expected to form. The alternate inequality would indicate that there are either O or N rich regions in the film.

A study of the structure of silicon oxynitrides (including Si-rich specimens) has recently been presented [117, 171, 172]. In this work the authors have used XAS to look at the XANES for the films. In the least Si-rich sample little change in the bonding structure of the film is observed for annealing up to 750 °C and the sample shows behavior consistent with a more homogenously deposited film (RBM-like). After

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annealing at 850 °C it is readily apparent that Si-clustering has occurred in the film through the appearance of an Si-Si related peak. Little change is observed though for the bonding structure of the host matrix, meaning that the Si has phase separated from the film, but a homogenous silicon oxynitride host still remains. The authors state that the annealed sample may be better described through the RMM, however, the lack of change in the Si-O,N bonding structure suggests that the film would be better described by a RMM of Si within a random bonded oxynitride host. In samples with more excess Si, however, Si and SiO₂-like phases are seen to appear after annealing at 1000 °C. Evidence of a silicon nitride or oxynitride phase is still present, which may indicate either incomplete phase separation, or the phase separation of the film into Si-Si, Si-N, and Si-O components, as the interim absorption peak shows a feature near that found for Si₃N₄. It is difficult to adequately compare the behavior of the more-Si-rich samples with that of the least Si-rich, as the anneal temperature in the latter case is lower. While the structure is RBM like, the authors point out that the spectra are consistent with the formation of Si- O_3N and Si-ON₃ tetrahedra, but that the Si- O_2N_2 tetrahedron is unstable.

An earlier report on SiO_xN_y , also using XANES to look at the bonding structure, suggests that N incorporated into the films acts substitutionally to O atoms, and that the film retains an SiO_2 -like nature [173]. Furthermore, the material is found to be homogenous and no indications of phase separation of Si or Si_3N_4 were seen. The set of samples considered did, however, have compositions closer to silicon oxide, where one may expect nitrogen atoms to be forced to act substitutionally. Such behavior can be <u>PhD Thesis – T. Roschuk</u><u>McMaster University– Engineering Physics</u> confirmed by looking at the N *K*-edge, which shows a resonant line (RL) associated with N-dangling bonds which occurs because N is unable to form a third bond when incorporated substitutionally for O [169] as is confirmed by the authors in [171].

Chapter 4: Characterization Techniques

The characterization techniques used in this work may be classified under several general headings relating the excitation mechanism and the detected signal; (a) photon in - photon out, (b) photon in - electron (or ion) out, (c) electron in - photon out, and (d) electron in - electron out. Figure 4.1 illustrates several of the signals generated and the experimental techniques that make use of them. Techniques used in this work are underlined and shown in orange.



Figure 4.1: Possible characterization techniques with photon or electron excitation. Signals generated for various characterization techniques involving incident photons or high energy electrons. *XAS is shown as a transmission based technique, however, it is common to measure the electron and fluorescence yields from the sample surface, which are proportional to absorption.

In many cases the principles behind these techniques are quite similar. For example, EELS and XAS both rely on the absorption of energy by core electrons within the sample and qualitatively they provide similar information concerning the electronic and chemical structure of materials. The two methods are distinguished by the size scales at which they operate and the size of features they can resolve, making them complementary techniques.

The key experimental techniques used in this work are photoluminescence (photon in, photon out) and X-ray absorption spectroscopy (XAS). The XAS signal was measured in two ways. The total electron yield from a sample measures the number of electrons ejected from the sample during the XAS process (Photon in, electron out). The fluorescence yield arises from the recombination of electrons and holes formed in the core states through the XAS process (photon in, photon out).

X-ray excited optical luminescence (XEOL) was used for site specific excitation of luminescence from the samples considered in this work. Several difficulties with this technique were encountered for the analysis of SRSN samples, however, the technique has proven quite valuable for the analysis of rare earth doped thin films.

In addition to these primary characterization techniques, Fourier transform infrared spectroscopy (FTIR) has been used to analyze changes in the bonding structure within the films as a function of composition and annealing. TEM-based methods, such as high resolution electron microscopy (HREM), energy filtered transmission electron microscopy (EFTEM), electron energy loss spectroscopy (EELS) have also been used in
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 order to observe the presence of nanoclusters in the samples considered in this work and

 to look at details of the electronic structure on the scale of the nanoclusters themselves.

In this chapter the experimental details of XAS, XEOL, PL, FTIR, and several TEM based characterization techniques are outlined. In many cases the details of each of these techniques are the subjects of entire texts themselves. Various studies that have employed these techniques for the analysis of Si-ncs have been cited in the previous two chapters. For the reader interested in the full theoretical details of these and related techniques the following texts, from which key parts of this chapter are drawn, are recommended.

An introduction to X-ray spectroscopy based techniques may be found in the texts by Agarwal [174], Koningsberger and Prins [175], and Stöhr [176]. For a text examining the specific applications of synchrotron spectroscopies, including XAS, Sham provides a good collection of techniques and relatively recent survey of applications and results [177]. Additionally, David Attwood's lectures at Berkeley University on Synchrotron Radiation for Materials Science Applications are archived online (complete with audio and video) and provide an excellent introductory resource on the subject [178].

Williams and Carter [179] provide an excellent and widely used reference on the basics of TEM and many TEM based methods. Another good introductory text that examines a broad range of TEM based techniques is that of Fultz and Howe [180]. Details of analytical electron microscopy have been drawn from the chapter by Botton in

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 the text by Hawkes and Spence [181] and a detailed treatment of EELS may be found in

 Egerton [182].

As mentioned, EELS and XAS provide qualitatively similar information. As such a text on either technique serves as a suitable reference for understanding the details of core electron excitation and its relation to chemical binding, atomic coordination, and electronic structure. For both techniques the X-ray data booklet is an invaluable reference for the physical properties of the elements and for the interpretation of XAS and EELS spectra [183].

An easily accessible introduction to optical characterization techniques for semiconductors, including PL and FTIR may be found in Perkowitz [184]. FTIR absorption peaks have been drawn from this text and from many of the papers discussed in the previous two chapters, as the technique is widely employed for the study of Si oxide, nitride, and oxynitride materials.

4.1 X-ray Absorption Spectroscopy

In this section the details of XAS are considered. Rather than being a measure of the intensity of transmitted X-rays, XAS is commonly performed using the measurement of two types of surface emission, the total electron yield (TEY) and the fluorescence yield (FLY).

4.1.1 Principles of XAS

XAS is in fact a broad term encompassing several different characterization techniques involving X-ray absorption. While some of the principles of these techniques are related, they provide different and complementary information regarding the materials. The work considered here focuses primarily on X-ray absorption near edge structure (XANES), also known as near edge X-ray absorption fine structure ²⁹ (NEXAFS). For this reason XANES will be most heavily treated in this section. XANES typically refers to the region from the absorption edge, which occurs at the binding energy for the atomic site of interest, up to 30 eV above this edge. The exact boundary is system specific and depends on the absorption features for a given element related to details of its local chemical environment. XANES will be discussed in more detail in the following section.

The region from $\sim 50 \text{ eV}$ above the absorption edge and extending to $\sim 1000 \text{ eV}$ further is known as the extended X-ray absorption fine structure (EXAFS) region. EXAFS arises when a photoelectron is excited through XAS and undergoes a single scattering process from atoms surrounding the absorbing atom. The technique provides structural information about the local environment of the excited atom.

The XANES and EXAFS regions are illustrated in Figure 4.2 for a c-Si wafer, such as the ones used as substrates in this work.

 $^{^{29}}$ Some authors consider XANES and NEXAFS to refer to slightly different regions, with XANES focused on the region up to ~30 eV above the absorption edge and NEXAFS from ~10-70 eV above the edge. There is no strict divide between the two techniques.



Figure 4.2: A typical XAS spectrum for a bare Si wafer. The regions used for various XAS related techniques are indicated.

The XAS process is illustrated in Figure 4.3. In XAS an incoming photon with energy equal to or greater than the binding energy of a core electron will excite an electron into the conduction band of the material of interest creating a core hole³⁰. An XAS spectrum is obtained as the energy of the incoming X-rays is scanned over a range of interest related to the material under study.

³⁰ This is true for semiconductors. In the case of metals the excitation will be to unoccupied states above the Fermi energy.



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(c) Core-hole decay via X-(b) Core-hole decay via ray emission **Auger recombination**

Figure 4.3: The XAS process. (a) An incident X-ray excites a core electron into the unoccupied conduction band. X-ray absorption is proportional to the PDOS of the conduction band. The core-hole may then decay through either (b) the Auger process or (c) X-ray emission. A measure of the intensity of the emitted X-rays as a function of energy is the basis of XES which provides the PDOS of the valence band.

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As XAS excites a core electron into the conduction band (or above the Fermi level in the case of metals) the spectra recorded by XAS reflect the density of states in the conduction band (CB). This is illustrated in Figure 4.3(a). Quantum mechanical selection rules apply, specifically the dipole selection rule. This means that there must be a change in the orbital angular momentum (or azimuthal) quantum number:

$$\Delta \ell = \pm 1 \tag{4.1}$$

where ℓ is the orbital angular momentum quantum number and $\ell = 0,1,2$, and 3 refer to the s, p, d, and f orbitals, respectively. As such, one actually probes only the partial density of states (PDOS) of the conduction band. Further to this the following selection rules apply:

$$\Delta n \neq 0 \tag{4.2}$$

$$\Delta \mathbf{j} = \mathbf{0}, \pm \mathbf{1} \tag{4.3}$$

where n is the principal quantum number and j is the total angular momentum quantum number.

For the reader unfamiliar with the notation associated with the absorption edges let me here briefly outline the nomenclature used. Transitions are designated using spectroscopic notation which relates to the principal quantum number. *K*, *L*, *M*, *N*, and *O* edges refer to the n = 1, 2, 3, 4, and 5 core levels. The *K*-edge has n = 1 and $\ell = 0$ (*s* character). Transitions involving the *K*-edge then have a final state $\ell = 1$ (*p* character). At the *L*-edge the core levels are 2*s* or 2*p*. Transitions probed from the 2*s* sublevel again involve final states with *p*-character, giving rise to the *L*₁-edge. Spin-orbit coupling

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related to the j-quantum number gives rise to two 2p sublevels, $2p_{1/2}$ and $2p_{3/2}$. The final states probed by excitations from these sublevels then have *s* and *d* character and give rise to the L_2 and L_3 edges, respectively. The $L_{3,2}$ edge then refers to both sublevels of the 2p core level. The number of sublevels associated with each quantum number is 2n + 1 and one can see how the nomenclature proceeds.

The fluorescence yield in XAS is strongly related to the technique of X-ray emission spectroscopy (XES). In XES a sample is excited using fixed x-ray energy to generate core-holes. When valence electrons decay to fill the core holes, a measure of the intensity of the emitted X-rays as a function of their energy will reflect the PDOS of the valence band, as is shown in Figure 4.3(c).

Two possible decay processes may then occur when an electron from the valence band fills the hole created by the absorption process; the process can create an Auger electron, where the energy from the recombination process is transferred to an electron in a higher lying energy level, or the recombination process may result in the re-emission of an X-ray, as shown in Figure 4.3(b) and (c), respectively. The Auger electron may escape from the sample or undergo inelastic collisions, setting off a cascade and generating secondary electrons, as illustrated in Figure 4.4. The ability of the electrons to escape from the sample depends on their energy and their depth from the sample surface. The measurement of the signal from all electrons (Photo-, Auger, and secondary) escaping from the sample is referred to as the total electron yield, whereas the measurement of the X-rays emitted during the recombination process is referred to as the fluorescence yield. PhD Thesis – T. Roschuk

Note that the Auger and fluorescence processes are competitive and core-hole decay for an atom can only occur through one or the other. For lighter elements the TEY is typically greater than the FLY providing a better signal to noise ratio, however, X-rays have a greater escape depth than electrons within a material and thus the FLY allows one to probe more of the bulk than the TEY. Typically it is possible to measure both signals simultaneously. One could, in principle, make the TEY even more sensitive by appropriately biasing a detector such that only those Auger electrons with the highest energies (escaping from near the surface) are detected, although this technique is not of interest for this work. As mentioned earlier both the TEY and FLY are proportional to the amount of X-ray absorption by the sample and the two yields are common XAS measurement techniques.



Figure 4.4: Electron yield processes. An Auger electron generated by core-hole decay after X-ray absorption may escape from the sample or may undergo inelastic collisions, generating secondary electrons. The total electron yield is the sum of Auger, secondary, and photoelectrons (not shown) generated in the XAS process.

The sampling depths for TEY and FLY have previously been determined experimentally for SiO₂ [185]. For the TEY the sampling depths are ~5 and ~70 nm at the L and K-edge, respectively, although some authors list sampling depths at the K-edge as large as 100 nm [69]. For the FLY the sampling depths were found to be ~60 nm for the L-edge and several hundred nanometers at the K-edge. The density of hydrogenated, PECVD grown silicon nitride is slightly greater than that of Si or SiO₂, however, the sampling depths are considered to be within a comparable range.

Finally, a third method of detection exists, the photoluminescence yield (PLY). The PLY can also be measured simultaneously with the TEY and FLY, provided the detection chamber can accommodate the necessary optics. As the PLY is strongly related to XEOL, a discussion of the basic principles behind the PLY will be reserved for later in this chapter.

4.1.2 Interpretation of XAS spectra: Bonding Configurations, Electronic States, and X-ray Absorption

The interpretation of XAS spectra has already been alluded to in the previous chapters. As XANES probes the unoccupied PDOS of the conduction band it reflects the electronic structure of the material under consideration. The technique is element specific as the binding energies of core electrons for the different atomic species are unique.

Features in the XANES spectrum are sensitive to changes in chemical states, coordination, and hybridization as well as to charge transfer effects (as with XPS). That is

<u>PhD Thesis – T. Roschuk</u><u>McMaster University– Engineering Physics</u> to say, XANES is specifically sensitive to the orbitals surrounding the atom whose core level we are exciting from. The local bonding environments of the excited atoms, whose structure can be represented by the different RBM bonding units, lead to shifts in the absorption energy that can be associated with the particular bonding units.

An analysis of the shape and position of peaks within the XAS spectra, therefore, allows for a determination of the bonding structure of the films and the analysis of how this structure changes with post-deposition processing of the materials. Reference spectra, particularly for Si, SiO₂, and Si₃N₄, then assist greatly in simplifying the identification and analysis of XANES spectral features. Several papers, discussed in the previous Chapters provide reference data, particularly for SiO_x or SiO_xN_y samples, at the Si *K*edge [64-66, 69, 72, 117, 171-173]. XANES behavior at the Si *L*-edges for a set of ion implanted silicon (with varying doses of N or O) has been studied in [169]. Furthermore, reference samples, specifically, a bare Si wafer and an ICP-CVD grown Si₃N₄ sample, were measured for this work.

X-ray absorption at the $M_{5,4}$ edges of the RE elements has been studied in [186]. Information at the RE $M_{5,4}$ edges allows for the determination of details regarding the ionicity of the RE atom, as the spectral signature differs for different ionic states. This is shown for Ce and Tb in Figures 4.5 and 4.6, respectively. It is, therefore, particularly compelling to examine these edges as only certain ionicities correspond to luminescent states for the RE ions³¹.



Figure 4.5: XAS Spectra for Ce ions at the $M_{5,4}$ edge. The top three spectra correspond to the theoretically calculated dipole excitation spectra from the Hund's rule ground level configuration f^n to the $d^9 f^{n+1}$. The total spectrum is a weighted function for all f^{n+1} levels and gives the DOS in number of atomic levels per eV. The Ce XAS signal shown at the bottom is the measured signal from a pure Ce sample. Reproduced from [180].

³¹ The L_3 -edge has also been used for the analysis of Tb-doped materials in the literature [134]. The energy for this edge (~7.5 keV) is well outside of the capabilities of the beamlines used in this work but could be accessed using the Hard X-ray MicroAnalysis (HXMA) beamline at the CLS.

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Figure 4.6: XAS Spectra for Tb ions at the $M_{5,4}$ edge. The TbAl₂ XAS signal shown at the bottom is the measured signal from a sample containing Tb (a pure Tb sample was unavailable at the time of study). The spectra designations are as for Figure 4.5. Reproduced from [180].

4.1.3 X-ray Absorption Spectroscopy: Experimental Details

XAS experiments for this work were performed at the Canadian Light Source (CLS) Synchrotron Facility. In this section details of the two beamlines used in this work will be presented. The CLS is a third generation synchrotron source providing high brilliance (flux per unit area, per unit solid angle, per unit energy bandwidth). The setup allows for high spectral resolution, suitable for conducting experiments such as XAS. While only soft x-rays have been used in this work the CLS beamlines make use of

PhD Thesis – T. RoschukMcMaster University– Engineering Physicselectromagnetic radiation spanning the range from the Far-IR to hard X-rays (1 meV outto 40 keV). One of the current beamlines under construction will extend this range to 100keV for biomedical imaging and therapy applications. XAS studies therefore, compriseonly a small, though often-used, set of the possible experimental techniques that can beperformed with a synchrotron source.

4.1.3.1. XAS Beamlines at the Canadian Light Source Synchrotron Facility

Two complementary beamlines have been employed to conduct these experiments at the Canadian Light Source (CLS) Synchrotron Facility; the 11ID1 high resolution spherical grating monochromator (SGM), and the 11ID2 variable line spacing planar grating monochromator (VLS-PGM) [187]. Schematics of the SGM and VLS-PGM beamlines are shown in Figures 4.7 and 4.8, respectively.



Figure 4.7: A schematic of the SGM Beamline at the CLS. The SGM beamline operates from 240-2000 eV. Reproduced from [188].



Figure 4.8: Schematic of the VLS-PGM Beamline at the CLS. The VLS-PGM beamline operates from 5.5-250 eV. Reprinted with permission from [189]. ©2007, American Institute of Physics.

The key distinguishing features between the two beamlines are the energy ranges, and thus the absorption edges they can access, over which they operate. The VLS-PGM operates from 5.5-250 eV while the SGM beamline operates from 240-2000 eV. Using both beamlines complementary data from different absorption edges can be obtained.

The spot size on the sample during the measurement process is adjusted by varying the size of the entrance and exit slit widths. Typically the entrance slit width is fixed at 50 μ m and the exit slit width is adjusted. An increase in the slit width results in a greater photon flux on the sample, increasing the measured signal, however, this occurs at the expense of resolution.

Each beamline has three separate energy gratings (low, medium and high – LEG, MEG, HEG) operating over different energy ranges, as shown in Figures 4.9 and 4.10 for the SGM and PGM beamlines, respectively. In regions where there is overlap the higher

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energy grating is preferred for increased resolution and again the decision between flux and resolution must be made.



Figure 4.9: Photon flux at the SGM beamline. The data was obtained by adjusting the exit slit widths such that a beam current of 100 mA was maintained during the measurement. (Plot courtesy of T. Regier, CLS).

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Figure 4.10: Photon flux at the VLS-PGM beamline. The data was obtained using 50 μ m x 50 μ m slits and has been normalized to a beam current of 100 mA. (Plot courtesy of L. Zuin, CLS).

Full details of the SGM and PGM beamlines are discussed in [187, 189-191].

Table 4.1 outlines the relevant electron binding energies for the constituent atomic species of silicon nitride and oxynitride materials and highlights which of these absorption edges are accessible by the SGM and VLS-PGM. Absorption edges accessible by these beamlines and related to Ce- and Tb-doped samples are provided in Table 4.2.

Table 4.1: Electron binding energies at the N, O, and Si absorption edges. The energies accessible using the SGM beamline at the CLS are indicated in red, while those accessible using the PGM beamline are shown in blue. Data from [183].

	Absorption Edge Energies [eV]							
Element	K 1s	$L_1 2s$	$L_2 2p_{1/2}$	$L_3 2p_{3/2}$				
N	409.9	37.3						
0	543.1	41.6						
Si	1839	149.7	99.82	99.42				

Table 4.2: Electron binding energies at select Ce and Tb absorption edges. The energies accessible using the SGM beamline at the CLS are indicated in red, while those accessible using the PGM beamline are shown in blue. Data from [183].

	Absorption Edge Energies [eV]								
Elements	$M_4 \mathrm{3d}_{3/2}$	M5 3d5/2	$N_1 4s$	N ₂ 4p _{1/2}	N3 4p3/2	N4 4d3/2	N5 4d5/2		
Ce	902.4	883.8	291	223.2	206.5	109			
Tb	1276.9	1241.1	396	322.4	284.1	150.5	150.5		

At the SGM beamline the LEG, MEG, and HEG were all used to access (i) the O and N K-edges, (ii) the Ce $M_{5,4}$ edges, and (iii) the Tb $M_{5,4}$ edges and the Si K-edge, respectively. Only the HEG was used at the VLS-PGM beamline to access the Si L-edges and the Ce and Tb $N_{5,4}$ edges.

Measurement of the TEY is done by grounding the sample and measuring the sample current using a Keithley Model 6485 Picoammeter. The FLY is measured using two Burle microchannel plates mounted in a chevron configuration. A high negative voltage is placed across the plates and the signal is collected by an anode and measured using another Keithley 6485.

4.1.3.2. Experimental Parameters

A 50-100 μ m exit slit width was used during the measurement of the Si *K*-edge. For measurements at the N and O *K*-edges the exit slit width was decreased to 20 μ m. For the Tb and Ce *M*-edges 50 μ m slits were used. Energy step sizes, ΔE , were varied from 0.1 to 1 eV in order to optimize the scan time and resolution. The greater step size was used in the pre-edge region and at energies well beyond the near-edge structure, while the smaller step size was used to better resolve features in the near-edge region. A 1s integration time was used.

At the VLS-PGM beamline an exit slit width of 50 μ m was used. Again, a 1 s integration time was used for most measurements. As with the SGM beamline some scans were conducted with increased exit slit width and integration times. ΔE was varied from 0.1 to 0.5 eV over the scan range. Some measurements were performed with a 0.05 eV step size in the region near the $L_{3,2}$ edges, however, no additional spectral features were observed.

4.1.3.3 Data Processing

A transparent gold mesh, inserted along the XAS beamline, monitors beam current to the experimental endstation through the use of a picoammeter. Both the TEY and FLY signals are normalized by dividing the measured signal by the beam current. This process accounts for several factors. First it removes any effects due to fluctuations of the beam current. Second, the flux on the samples is a function of energy, as the <u>PhD Thesis – T. Roschuk</u><u>McMaster University– Engineering Physics</u> gratings used to tune the excitation energy have a spectral dependence (i.e. they are more efficient at some energies than others, see Figures 4.9 and 4.10). This dependence is removed by the normalization process. Finally, any additional effects due to the beamline

optics that could create artifacts in the final spectrum, such as absorption by one of the beamline components, are also removed.

In order to account for shifts in the absorption edge position a bare Si wafer was used as a reference sample as the position of the Si-Si₄ peak is well established. The energy spectrum was then corrected by determining the energy offset for the reference sample and linearly adjusting the energy axis of the spectra for all samples.

4.1.4 Limits of XAS

It is important to consider what XAS based spectroscopies can tell us about the structure of materials, particularly for embedded nanostructures. XAS can tell us how much of an element is incorporated into a film in a specific atomic coordination or bonding state and how the structure of the film evolves through the analysis of changes in this structure. It cannot provide details about the specifics of nanostructure (*i.e.*, size of the nanoclusters). For example, in the case of Si-nanoclusters formed in the materials that are the subject of this work, the intensity of the Si-Si₄ signal will be proportional to the amount of Si-Si bonding within the film/clusters. This tells us little about whether the

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 signal arises from a few large clusters or from many small clusters amounting to the same

 amount of silicon contained within the same sampling volume³².

In order to precisely obtain information regarding the nanostructure complementary techniques must be employed, such as transmission electron microscopy based methods (including HREM, EFTEM, and EELS). One drawback of a technique such as TEM is that the sample preparation and measurement processes are more tedious than those for XAS. This means that a greater number of samples can typically be analyzed more quickly with XAS, allowing one to assemble a more complete picture of the materials under study, which is particularly important when a large parameter space presents itself. This is not to undervalue TEM-based studies of these materials, which provide a wealth of information. Ideally, one would be able to do both in order to provide a comprehensive comparison and analysis of the structural evolution on the nanoscale (through TEM) and the structural evolution of the film as a whole (through XAS). Electron microscopy based techniques are discussed briefly later in this chapter and have been used for the study of several of the samples. A comprehensive comparison of results from the two techniques is a suitable area for future work.

³² This is not exactly correct. The total surface area of the system having many smaller nanoclusters will be larger than that of a single nanoclusters having the same amount of silicon, therefore, the two systems will not produce exactly the same absorption spectra.

4.2 X-ray Excited Optical Luminescence

X-ray excited optical luminescence (XEOL) is a powerful technique for looking at the origin of luminescence in materials. As discussed above XAS provides a site selective method of probing materials. As the X-ray absorption process is sensitive to atomic species and their chemical environment, by analyzing the luminescence of materials as they relax after excitation one is able to determine specifically, and ideally unambiguously (although not always, for reasons that will be discussed below), which bonding sites and electronic states lead to which optical emissions.

Figure 4.11 shows a schematic of the XEOL process [67]. An incident X-ray is absorbed. The core hole it creates is filled with electrons from shallower energy levels through one of the decay processes discussed earlier. The hole created in these shallower energy levels is then filled by yet shallower or valence electrons. More electrons and holes can be created through inelastic scattering with the Auger electrons or through re-absorption of the fluorescent X-rays. The electrons and holes then thermalize to the bottom and top of the CB and VB, respectively, where they can recombine radiatively, as discussed in Chapter 2. This recombination may occur through a direct transition or through radiative defects.


Figure 4.11: The XEOL process. An incident x-ray is absorbed, generating a core hole. Successive filling of the core holes by electrons from shallower energy levels results in the formation of electrons and holes in the CB and VB, respectively, which can then recombine radiatively. Reproduced from [67].

As the recombination may occur through radiative defects, in some cases XEOL allows one to associate the excitation with a specific site, however, this does not guarantee that the observed emission is related to the direct recombination from the CB to the VB (or to QC-states associated with nanostructures). Note that this still allows for a determination of the sites from which luminescence originates. A further difficulty is presented by the de-excitation radius, which is the space range over which interactions that produce the electrons and holes in the CB and VB, respectively, during the decay processes can occur. This radius is dependent on the excitation energy and details of the sample itself, with lower energies leading to a smaller interaction range. Additionally, nanostructures can exhibit more site-selective properties as they create boundaries for
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 interactions to occur. These boundaries are obviously a greater enhancing factor in the

 case of free-standing nanostructures than for embedded ones.

The processes described above occur within certain time-scales. By monitoring the time dependence of the XEOL decay processes the lifetimes of excited states may be determined. It is then possible to window the emission from XEOL over specific time ranges and observe the occurrence and contributions of long and short lived states. This process is known as time-resolved XEOL (TRXEOL) and can yield valuable information regarding the physics of the luminescence process. The tunability of a synchrotron source for site-selective excitation makes this a unique and powerful technique. Currently at the CLS, TRXEOL capabilities are limited, although work is underway to develop the instrumentation to perform such experiments.

Finally, it was mentioned earlier that the PLY is strongly related to XEOL. The PLY is the yield of all luminescence in the optical emission range of interest and, therefore, is simply the integrated XEOL intensity. For both the SGM and VLS-PGM beamlines at the CLS an Ocean Optics QE65000 spectrometer was used to measure both the XEOL spectra and PLY. With the appropriate chamber geometry and equipment XEOL (or TRXEOL), TEY, and FLY are often simultaneously measured.

4.3 Optical Spectroscopies

4.3.1 Photoluminescence Spectroscopy

Photoluminescence (PL) is a valuable, often-used, characterization tool in the analysis of semiconductors. PL is similar in nature to XEOL, which was discussed in the previous section. Indeed, PL is the more straight forward of the two techniques and is only discussed after XEOL because X-ray based techniques are the focus of this work. What distinguishes PL from XEOL is that in the case of PL the incident photon typically has energies within the visible or ultraviolet range. The incident photon, with energy greater than the bandgap of the material of interest, is absorbed by the sample, creating an electron-hole pair. Unlike XEOL only a single electron-hole pair will be generated per incoming photon. Recombination of the electron-hole pair then leads to light emission at energies characteristic of the material under consideration, either from band-to-band recombination or other luminescence centers, such as radiative defects.

Photoluminescence experiments were conducted using a HeCd UV-laser emitting at 325 nm. Figure 4.12 shows the photoluminescence setup at McMaster University. An Ocean Optics spectrometer is used for measurement of the emission spectrum. Spectral calibration of the detector was performed using the emission spectrum of a Hg(Ar) lamp. Intensity calibration was performed using an Ocean Optics standard irradiance calibration lamp. Full details on the setup and correction for the system optics are discussed in [192]. PhD Thesis – T. Roschuk



Figure 4.12: A schematic of the photoluminescence setup at McMaster University. A HeCd laser emitting at 325 nm is used as the excitation source. The emission spectrum is measured using a CCD spectrometer.

4.3.2 Fourier Transform Infrared Spectroscopy

While photoluminescence and XAS are dependent on the electronic structure of materials, infrared spectroscopy involves the resonant absorption of light at energies less than the bandgap of semiconductors. The energies at which IR absorption occurs correspond to the vibrational and rotational modes of chemical bonds within the films. The energy, or wavenumber, at which this resonant absorption occurs is characteristic of the bonding atoms and bond type.

FTIR spectrometers operate on the same basic principles as a Michelson interferometer. A schematic of an FTIR spectrometer is shown in Figure 4.13. A

PhD Thesis – T. RoschukMcMaster University– Engineering Physicsbroadband IR source provides a beam which is split down two paths by a beamsplitter;light reflected from the beamsplitter is directed towards a moving mirror and lighttransmitted through the beam splitter is directed towards a fixed mirror. Upon reflectionfrom these two mirrors the beams recombine at the beamsplitter forming aninterferogram, the intensity of which is dependent upon the optical path length difference, Δ , of the beams after reflection from the mirrors.



Figure 4.13: A schematic of a FTIR spectrometer. The spectrometer operates on similar principles to a Michelson interferometer. Reproduced from [193].

For a source spectrum with intensity S(f), where f is the optical frequency (in wavenumbers) the intensity of the recombined beam is then:

$$I(\Delta) = \int_{-L}^{+L} S(f) [1 + \cos(2\pi f \Delta)] df$$

= $\frac{1}{2} I(0) + \int_{-L}^{+L} S(f) \cos(2\pi f \Delta) df$ (4.4)

where I(0) is the intensity at $\Delta = 0$ and the limits of the integral, $\pm L$, are the limits of motion for the moving mirror. Ideally, these limits would be $\pm \infty$. The limited range of motion for the mirror imposes a limit on the resolution obtainable from the system. The resultant interferogram is then simply the Fourier transform of the source spectrum. Taking the inverse Fourier transform, typically by employing a fast Fourier transform through a computer, one then recovers the original source spectrum:

$$S(f) = \int_{-L}^{+L} \left[I(\Delta) - \frac{1}{2} I(0) \right] \cos(2\pi f \Delta) d\Delta$$
(4.5)

In the absence of a sample one simply recovers the source spectrum or a background spectrum which can be used to account for environmental absorption effects. When a sample is mounted the fast Fourier transform recovers a signal that is the product of the film transmission coefficient, T(f), and the source spectrum. The ratio of the two spectra then allows one to recover the transmission spectrum of the sample alone. The absorbance spectrum of the sample is then obtained through the relation:

$$A(f) = \log \frac{1}{T(f)} \tag{4.6}$$

Analysis of FTIR spectra is typically performed through comparison with known reference spectra which are readily available for silicon oxides, nitrides, and oxynitrides. Table 4.3 summarizes the key FTIR absorption peaks for silicon oxynitrides (including oxides and nitrides). The exact peak position is heavily dependent on the bonding angle between the constituent atoms and can be used to obtain more detailed information about the film structure.

Peak	Peak Position (cm ⁻¹)			
Si-O Stretching	1050-1080			
Si-O Bending	800-815			
Si-O Rocking	450-465			
Si-OH	3640			
Si-N asymmetric stretch	890			
Si-N symmetric stretch	490			
Si-H Stretching	2140-2260			
Si-H Wagging	640			
Si-H Bending	880			
N-H Stretching	3340			
N-H Bending	1180			
N-H ₂ Stretching	3450			
N-H ₂ Bending	1550			
H ₂ O	3400			

Table 4.3: FTIR absorption peak positions for silicon oxynitrides

FTIR spectroscopy was conducted using a ABBomen WorkIR 100 operating from 400-4000cm⁻¹ with a scan resolution of 4 cm⁻¹. In order to improve the signal to noise ratio an average of 128 scans was taken for the samples. The spectrometer was purged

through the use of a dry nitrogen line. Prior to each set of scans a background reference sample was obtained. The design of this particular spectrometer, however, does not include an isolated sample area and as such, over the course of the set of scans for each sample the measured signal is susceptible to fluctuations in atmospheric conditions. This effect is reduced, but not completely removed through the use of the nitrogen purge line. Fortunately, these fluctuations do not overlap with the key spectral features of interest for the films under study.

Samples were deposited onto undoped, high-resistivity, double side polished <100> Si wafers. A reference wafer was used to measure the substrate background in order to subtract its effects from the measured spectrum.

4.4 Electron Microscopy Based Techniques

Although electron microscopy based techniques have proven important for some studies related to the analysis of the samples discussed in this work, the focus of this thesis is not specifically on the area of the electron microscopy related characterization. As such only a brief overview of the electron microscopes used in this work and the basic principles behind several characterization techniques will be discussed.

4.4.1 Transmission Electron Microscopes

In this work four different transmission electron microscopes have been employed for the analysis of Si-nc embedded materials. A 200 keV JEOL 2010F and an aberration corrected 300 keV FEI Titan were used to perform HREM imaging of the samples. The JEOL 2010F has been fitted with a Gatan imaging filter (GIF) and was also used for some EFTEM and EELS measurements. STEM imaging and EELS measurements were performed using a VG-STEM HB601 UHV and the SuperSTEM facility at the Daresbury Research Park (UK). Both microscopes have been fitted with fitted with Gatan Enfina energy loss spectrometers. With the exception of the SuperSTEM all the microscopes used in this work are located in the Canadian Centre for Electron Microscopy at McMaster University.

The high resolution obtainable with TEM arise from the small wavelength of an electron accelerated at high voltages. Accounting for relativistic effects the wavelength, λ , of an electron with energy E = eV (where V is the accelerating voltage) is given by the expression:

$$\lambda = \frac{h}{\sqrt{2m_e E \left(1 + \frac{E}{2m_e c^2}\right)}} \tag{4.7}$$

where h is Planck's constant, m_e is the electron mass, and c is the speed of light. At accelerating voltages of 100, 200, and 300 keV the electron wavelength is then 3.7, 2.5, and 1.9 x 10⁻² Å. In fact, as opposed to optical microscopy where the limit of resolution is bounded due to the wavelength of light, in the electron microscope it is limited rather by aberrations due to the electron optics³³.

³³ Although not to the same scale as electron microscopy, theoretically one could obtain high resolution through x-ray microscopy. Indeed, scanning transmission x-ray microscopy (STXM) does just this. One of the major limiting factors of STXM, however, is the lack of suitable x-ray optical components (zone plates)

With the improved resolution due to wavelength in mind, electron microscopy may be considered in an analogous manner to optical microscopy. The ray diagrams for

image and diffraction pattern formation are shown in Figure 4.14(a) and (b), respectively.



(a) Image formation in TEM

(b)Diffraction pattern formation

Figure 4.14: Ray Diagrams illustrating (a) image and (b) diffraction pattern formation using an electron microscope. Colors are used only to assist with ray tracing.

In conventional TEM there are two methods of image formation, bright field (BF-TEM) and dark-field (DF-TEM), as illustrated in Figure 4.15. BF images are formed by inserting an objective aperture after the specimen in the back focal plane of the objective lens and allowing only the transmitted, undiffracted, electron beam to pass through. PhD Thesis – T. RoschukMcMaster University– Engineering PhysicsContrast then arises primarily due to diffraction. Crystalline regions that diffract the
incoming electron beam appear dark in the BFTEM image. In DFTEM the objective
aperture is used to select one of the diffracted beams for imaging and only those regions
that diffract appear bright. Examples of BFTEM and DFTEM images are shown in Figure4.16 for Si-nanocrystals embedded in SRSO films. Note that DFTEM is sensitive to the
orientation of a crystal, and only crystals oriented such that they meet the Bragg condition
for a given diffraction spot will be seen.



(a) Bright field imaging

(b)Dark field imaging

Figure 4.15: Conventional TEM imaging. (a) BFTEM is performed by selecting the direct beam and (b) DFTEM by selecting one of the diffracted beams³⁴.

³⁴ The method shown here is actually referred to as the 'dirty' dark field due to effects related to the nonideality of the lenses. It is better to tilt the incoming beam such that the diffracted rays chosen for DFTEM pass through a centrally located aperture (Axial dark field).

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immense progress in the past few years due to the development of aberration correctors



Figure 4.16: BFTEM and DFTEM of c-Si-ncs embedded in a SRSO film. (a) a BFTEM image and (b) a DFTEM image. This particular set of images was obtained using a 120 keV Philips CM12 TEM.

High-resolution imaging is attained by recognizing that the diffraction pattern is related to the Fourier transform of the real-space atomic arrangement. With BF or DF-TEM images high resolution detail cannot be obtained as choosing only one diffraction spot yields essentially only truncated components of the Fourier transform in reciprocal

space. For HREM at least two beams are necessary (the transmitted beam and one diffracted beam). The transmitted beam then acts as a phase reference for the electron wavefront. Interference between the transmitted and diffracted beam leads to a series of lattice fringes representative of the real space atomic arrangement. Resolution is improved by sampling a larger portion of reciprocal space. This technique has seen

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PhD Thesis – T. RoschukMcMaster University– Engineering Physicsimmense progress in the past few years due to the development of aberration correctorswhich allow for a greater sampling of reciprocal space. Sub-Angstrom resolution can nowbe obtained using aberration corrected TEMs such as the FEI Titan. A HREM image of aSi-nanocrystal embedded in an SRSO thin film is shown in Figure 4.17. In fact, in theimage several nanocrystals are visible, however, only one is in focus and on zone axis inthis image.



Figure 4.17: A HREM image of a c-Si-nc embedded SRSO thin film. Several other c-Si-ncs are visible but are out of the focal plane or off zone axis for the image. Note the presence of twinning defects in the Si-nc itself.

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In both conventional TEM and HREM it is also possible to have contrast due to mass-thickness effects. This contrast increases as a function of Z or Z^2 due to elastic scattering as a result of Coulomb interactions as electrons pass near the atoms [180]. It is likely owing to this effect that various authors ascribe dark regions to *a*-Si-ncs in their TEM images, however, as discussed in the previous chapter the justifications for doing so in SRSN (or SRSO) systems require deeper consideration.

STEM is distinguished from conventional TEM through the use of a small probe. Rather than a broad beam illuminating the sample, the electron beam is focused down to a small size and then scanned across the sample and data is collected for each point defined for the scan. In such a case individual atoms act as scatterers of the electron beam. In comparison with HRTEM, where the image is formed through phase differences and interference as the diffracted beams are re-combined, STEM imaging can allow for a more direct interpretation. In STEM a common method to image the samples is through the use of a high angle annular dark field (HA-ADF) detector. The details will not be discussed here, however, Z-contrast (also called HAADF contrast) is the primary contrast mechanism. By combining STEM and electron energy loss spectroscopy (discussed momentarily) one can obtain in-depth information on the electronic structure of materials with high spatial resolution. A schematic illustrating the electron optics and the detector locations for a STEM is shown in Figure 4.18.



Figure 4.18: A schematic illustrating the optics for STEM operation. The location of the ADF detector is shown. In the image OL refers to the objective lens system and Cm refers to the condenser 'minilens'. Reproduced from [181].

4.4.2 Electron Energy Loss Spectroscopy

As has been mentioned, qualitatively, the data obtained through EELS is similar in nature to that of XAS. In EELS the energy loss of high energy electrons as they pass through a sample is measured. The energy loss experienced by an electron is related to core-electron excitations giving rise to a similar core-edge structure as seen in XAS. The EELS equivalent to XANES is called electron energy loss near edge structure (ELNES). The EELS spectrum is measured using a spectrometer mounted after the projector lens in the TEM. The electrons then pass through a magnetic sector which disperses them as a function of energy.

In addition to core-electron excitations there are other methods of energy loss. The region from 0 to 50-100 eV is referred to as the low-loss region. In this region one of the primary methods of energy loss is through the generation of plasmon excitations within the material under study. Plasmons refer to the collective oscillations of outer shell electrons within a solid that occur in the form a longitudinal travelling wave. The plasmon energy, E_p , is dependent on the material under study and is given by the expression

$$E_p = \hbar \omega_p \tag{4.8}$$

where ω_p is the plasmon oscillation frequency:

$$\omega_p = \sqrt{\frac{ne^2}{m_e \varepsilon_0}} \tag{4.9}$$

Here n is the density of free electrons, m_e is the effective mass of the electron, and ε_0 is the permittivity of free space. The plasmon energy is material specific and the low-loss spectrum then provides further details for materials analysis. Depending on the thickness of the sample multiple plasmons may be excited by an electron as it passes through the sample. The excitation of multiple plasmons is reflected in the EELS spectrum by peaks at integer multiples of E_p . Two sample EELS spectra are shown in Figure 4.19, illustrating (a) the low loss region where plasmon excitation dominates and (b) the 'high' loss region where coreedges are seen. The most intense peak at 0 eV in the low-loss spectrum is the zero-loss peak, corresponding to electrons that have passed through the sample without interaction and hence, no energy loss.



Figure 4.19: Sample EELS spectra. (a) A low-loss spectrum for Si showing the Si plasmon. (b) A core-loss spectrum over an extended range for a LiFePO₄ sample showing the presence of several core-loss peaks. The feature at 300 eV is due to a scale change. (LiFePO₄ spectrum courtesy of C. Maunders).

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The absorption edge energies for EELS are the same as in the case of XAS, listed in Table 4.1, as they relate to the same core-edge excitation mechanism. In the low-loss region the relevant plasmon energies for this work are 17, 24, and 23 eV, corresponding to Si, Si₃N₄, and SiO₂ plasmon energies, respectively [89, 194]. One should exercise some caution in the interpretation of the low-loss spectrum, however, as the presence of regions that do not have complete phase separation between the excess Si and the dielectric host (i.e. silicon monoxide, SiO), may have their own characteristic plasmon energies. That is to say that the exact position of the plasmon peak can shift with composition. In fact, from the earlier discussion and a consideration of the RBM one expects a plasmon shift with changes in the composition for a homogenous film.

4.4.3 Energy Filtered Transmission Electron Microscopy

The basis of EFTEM imaging can be understood by considering the EELS spectrum. The amount of energy lost by an electron as it passes through a sample is characteristic of the atomic species, and the chemical environment of these species, with which the electron interacts. In EFTEM one then filters the electrons such that only those electrons with energies within a certain window are used to produce an image. The resulting image is then selective to the areas with specific chemical environments. EFTEM can, therefore, be used for elemental mapping of the sample.

In principle any feature corresponding to electron energy loss due to the chemical environment of interest could be used (plasmon peak or absorption edges). In practice it is often convenient to use the lowest energy features accessible as the signal strength is <u>PhD Thesis – T. Roschuk</u><u>McMaster University– Engineering Physics</u> significantly higher. This is due to a decrease in the interaction cross-section with increasing energy. Provided the plasmon peaks can be distinguished they can provide an excellent basis for EFTEM imaging.

EFTEM is extremely advantageous in looking at the structure of Si-rich materials as it is sensitive to the chemical environment of the constituent atoms, not their crystallinity. Thus, one is able to obtain information on both amorphous and crystalline structures.

In this work two methods have been employed in order to obtain EFTEM images of the samples. The first involves operation of the electron microscope in the TEM mode, while the second was performed in STEM mode and I will refer to the techniques as such.

Operation in the TEM mode is simpler to employ and is favorable if the effort is to demonstrate the presence of amorphous nanoclusters within the film and to obtain a rough estimate of their sizes. Measurements were performed by taking successive images using an energy slit to form the image using only a selected energy range. The process is analogous in nature to TEM imaging, where only a specific diffraction spot was used to form an image and an aperture was used to filter out the other diffraction spots. The energy window was then scanned across a range of energies, providing images at different energy slices. The drawback of this method is that the energy window used for filtering the image is typically quite large (at least for the JEOL 2010F used here). This means that one will be imaging a portion of the sample outside of the exact energies that correspond specifically to the Si-ncs. In particular, if there is a Si-rich region surrounding

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the Si-nc where there is an incomplete phase separation the electron energy loss in this area will be intermediate between that of Si and the dielectric, but a portion of this will be sampled within the large energy window. Thus nanocluster sizes will be overestimated.

EFTEM imaging in the STEM mode is performed by obtaining an EELS spectrum at each point in a STEM scan. One can then define an energy window and extract the signal at that energy for each point of the scan. Operation in the STEM mode offers a very fine energy window, allowing for spectral features to be more clearly resolved and for precise energy filtering of the image. Furthermore, excellent spatial resolution is obtained. However, in this instance it is not possible to image as great an area of the sample as in the former case. Furthermore, the focusing of a high energy electron beam to a very small probe size increases the probability of inducing damage to the sample. Both modes of obtaining EFTEM images are sensitive to sample drift and in order to obtain useful information it is necessary to have a stable stage upon which the sample is mounted.

To summarize the two modes of operation and distinguish them; operation in the TEM mode is done by collecting images filtered to allow only electrons with a certain range of energies to pass through. In the STEM mode one is collecting the EELS spectra at a series of points along the sample. The signal from the EELS spectra within a particular energy range are then used to extract an image from the data.

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 To conclude this section, Figure 4.20 illustrates an example of EFTEM imaging.

 Two images are shown for an SRSO film, one extracted at the Si plasmon energy and one

 extracted at the SiO₂ plasmon energy.



Figure 4.20: EFTEM images of Si-ncs in an SRSO thin film. (a) Image extracted at the Si plasmon energy and (b) at the SiO₂ plasmon energy for a broad area of the film. Note the complementary nature of the images, with Si-regions appearing as light spots in (a) and dark spots in (b), while the opposite trend is observed for the SiO₂ host matrix. (c) A STEM image of a Si-nanocrystal illustrating the area where EELS data was acquired. Contrast in the lower ~1/4 of the image is an artifact of the detector. (d) The EFTEM image of the Si-nc extracted from the EELS data for (c).

Chapter 5: Fabrication of Si-nanocluster embedded dielectrics

Silicon nitride-based materials, which are the primary focus of this thesis, have been fabricated using the inductively coupled plasma chemical vapour deposition (ICP-CVD) system at McMaster University. A second deposition system, the electron cyclotron resonance plasma enhanced chemical vapour deposition (ECR-PECVD) system, capable of *in-situ* doping of the films with rare earth elements during the growth process, was used to fabricate silicon oxide based thin films doped with Ce and Tb.

In this chapter the details of the SiN_x and SiO_xN_y films grown for this work, both to calibrate the ICP-CVD system and for further characterization, will be discussed. Characterization results for several of the calibration samples will be presented to illustrate why certain samples were chosen for further study. Additionally, several SRSN films were deposited with the ECR-PECVD system and with a conventional PECVD system. Details of the fabrication of these films will also be given here and a comparison of their behavior presented in the following chapter. A more complete comparison between these systems is the subject of current research.

In order to optimize the different characterization methods used in this work several different substrates have been used. Primarily, the films were deposited onto Czochralski-

PhD Thesis – T. Roschuk McMaster University– Engineering Physics grown single side polished (SSP) <100> Si wafers. These samples were used for XAS, PL, TEM, and RBS analysis. Several samples were also grown on glassy carbon substrates in order to facilitate RBS measurements by removing the background associated with an Si-substrate. Undoped, high-resistivity double side polished (DSP) <100> Si wafers were used for FTIR measurements. A bare wafer was retained from the order of wafers for background subtraction.

This chapter is not intended to provide an introduction to the details of thin film growth/deposition. Details of the deposition chemistry involved and the principles behind film growth in our systems have been described in depth in several theses and papers [38, 120, 129, 170, 195, 196]. While the chemical species and details of the growth environment are recognized as important to the properties of the as-grown films, they have not been directly analyzed as part of this work. As part of the comparison between films fabricated using the three aforementioned PECVD-based deposition systems a study examining specific details of the growth environment could yield some information on how the structural differences between as-grown films arise, particularly when different precursor gases are used.

5.1 Inductively Coupled Plasma Chemical Vapour Deposition

A schematic of the ICP-CVD system is shown in Figure 5.1. The full details of the system have been recently described as part of H. Zhang's M. A. Sc thesis [196].



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Figure 5.1: The ICP-CVD System at McMaster University. The system has been used for the growth of silicon oxide, silicon nitride, and silicon oxynitride thin films.

Silane, SiH₄, (30% SiH₄ diluted in Ar) was used as the Si source. The system is fitted with both pure N_2 and 10% N_2 diluted in Ar gases which may be used as the nitrogen source. Similarly, pure O_2 and 10% O_2 diluted in Ar gases are available for the oxygen source. A pure Ar source was used to maintain chamber pressure and/or the quality of the plasma during the deposition process.

Films were typically grown by maintaining a constant SiH₄ flow and varying the nitrogen and/or oxygen flow in order to change the film composition and obtain Si-rich films. During the calibration process this was done for several fixed SiH₄ flows. The background chamber pressure was on the order of 10^{-7} - 10^{-8} Torr. The substrate stage was heated to a temperature of 300 °C, resulting in a substrate surface temperature of 120 °C. An RF power of 300 W was used for all depositions.

During the deposition process the growth was monitored *in-situ* using a J. A. Woollam spectroscopic ellipsometer, operating from 600-1100 nm. Ellipsometric modeling provides virtually real time information regarding the film thickness and optical constants. The refractive index, n, is listed for the samples at 632.8 nm. Post-deposition, the refractive indices and thicknesses of the samples were also measured using a Philips 2000 single wavelength ellipsometer operating at 632.8 nm. The results were found to agree to within 5%, with the exception of the most Si-rich samples (n > 2.35). In such a case, however, one must account for an increase in the extinction coefficient of the films, due to Si-clustering, as Si is not transparent at this wavelength.

5.1.1 Calibration of the ICP-CVD system for the fabrication of luminescent silicon nitride and oxynitride thin films

The initial run of samples were grown using Ar diluted N₂ (listed as N₂/Ar). The list of samples and their deposition conditions are given in Table 5.1. Instabilities during the deposition process were observed for samples SRSN-4, 6, and 11, and thus details of their characterization are not reported here. Of this run of samples luminescence was only observed for those grown using a low silane flow (5 sccm). It is interesting to note that the growth rate for this set of samples falls near the range identified in Figure 3.6 as leading to the formation of *a*-Si-ncs within as-grown SRSN thin films. Recall that in the proposed model the size of the Si-ncs decreases with increasing growth rate and it is PhD Thesis – T. Roschuk McMaster University– Engineering Physics

the deposition system [28]. Furthermore, it is not clear from the work discussed in [28] how far the authors have explored the limits of their model. Differences in the kinetics involved in the growth processes between different deposition systems may influence the exact range over which this behavior occurs. I will return to a discussion of the as-grown behavior of the films and a discussion of clustering in the following chapter when results from the structural analysis of these materials are presented.

Table 5.1: SiN_x calibration samples. The initial set of calibration samples used to determine the growth parameters for obtaining luminescent SRSN films.

Sample #	SiH4 [sccm] ¹	N ₂ /Ar [sccm] ¹	Ratio of N ₂ /SiH4	Ar [sccm] ¹	n @ 632.8nm ± 5%	Thickness [Å] ± 5%	Deposition Time [min] ²	Growth Rate [Å/min]	Deposition Pressure [mTorr] ³
SRSN-1	15	28	1.87	0	2.60	1030	9.1	113 ±9	3.0
SRSN-2	15	40	2.67	0	2.33	1010	10.5	96.8 ± 7.1	3.7
SRSN-3	15	50	3.33	0	2.43	1000	10.7	93.5 ± 6.9	4.8
SRSN-5	10	50	5	0	2.09	1000	13.8	73.0 ± 5.0	4.0
SRSN-7	10	40	4	0	2.17	1000	13.7	73.1 ± 5.0	3.7
SRSN-8	5	40	8	0	1.75	1000	21.8	45.9 ± 2.8	3.0
SRSN-9	5	30	6	8	1.82	998	23.0	43.5 ± 2.6	3.0
SRSN-10*	5	20	4	17	2.00	902	23.0	39.2 ± 2.4	3.0
SRSN-12	5	10	2	27	2.29	998	26.8	37.2 ± 2.2	3.0
SRSN-13	5	5	1	32	2.48	990	28.1	35.2 ± 2.1	3.0
SRSN-14	5	15	3	22	2.13	998	26.2	38.1 ± 2.3	3.0
SRSN-15	5	35	7	4	1.80	994	22.4	44.4 ± 2.7	3.0
SRSN-16	5	25	5	13	1.92	998	23.9	41.8 ± 2.5	3.0
SRSN-17	5	45	9	0	1.72	990	20.3	48.7 ± 3.0	3.4

* Thickness and refractive index were only measured post-deposition w/ a Philips 2000 ellipsometer

¹ The error in the flow rates is ± 1 sccm.

² An error of 20 seconds (.3 min) has been associated with the deposition time.

 3 The error in the deposition pressure is 0.15% of the reading.

The luminescent behavior of the samples is shown in Figure 5.2 and a comparison between the PL from a SRSO and a SRSN film is shown in Figure 5.3. The initial results appeared quite promising. A more blue-shifted PL was observed for the SRSN films with respect to what had been observed in the SRSO films. Even in the as-deposited samples a shift in the PL emission characteristic was seen relative to what one would expect in a QC system.



Figure 5.2: Luminescence from a set of as-grown SRSN films used for calibration of the ICP-CVD system. The films show a redshift of the emission peak with increased Si-concentrations, characteristic of the behavior expected in a QC system.

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Figure 5.3: A comparison between the PL from a SRSO and SRSN thin film. The films have both been annealed at 1100 °C under an Ar ambient for 60 min. The PL spectra have been normalized to their peak intensities to better illustrate changes in the spectral shape.

After annealing a notable difference was observed between the SRSN and SRSO PL. Whereas the PL from SRSO samples is typically observed to be a smooth distribution around a central peak, typically associated with a Gaussian distribution of Si-nc sizes, the presence of multiple emission peaks was readily observed in the SRSN films. As seen in Figure 5.3, a central peak is located at ~650 nm, while a high energy shoulder is seen at ~450 nm.

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In spite of promising results for the luminescence of these samples, a compositional analysis through Rutherford backscattering (RBS)³⁵, performed at the University of Western Ontario, revealed the presence of up to ~20% oxygen in the samples. As this was a non-negligible amount of oxygen that was unintentionally introduced into the samples it posed a significant dilemma, as one could not simply consider these lightly oxygen contaminated silicon nitrides with such a high oxygen content, nor could a controlled method of reproducing the compositions be proposed. Furthermore, concurrent with this work, measurement of the sample thicknesses revealed some non-uniformity over the area of the entire wafer. While not an issue for the luminescence characterization, this non-uniformity poses a problem if one were interested in device fabrication or required precise layer thicknesses for the fabrication of superlattice structures. A nipple extension was added at the ICP source region within the chamber, changing the distance between plasma gas introduction into the chamber and the substrate stage. This extension resulted in better uniformity, however, it also slightly modified the properties of the as-grown films. These issues led to the need for the growth of a new set of films. Nevertheless, this initial set of films was used to identify a growth range over which luminescent SRSN films could be fabricated.

The source of the oxygen contamination could not readily be identified. It is possible that as the source gases share a common line into the chamber that residual

³⁵ I have not discussed RBS in the experimental section as it has been extensively described in recent theses looking at the correlation between growth parameters and film composition and in this work the focus is on the structural evolution of luminescent films with annealing. Analysis of RBS spectra was performed using the QUARK software package [197].

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oxygen within the line that has not been completely purged from previous depositions led to the contamination. Similarly, it is possible that residual oxygen remains within the deposition chamber. Several efforts were made in order to determine the source and to remove the oxygen contamination. These involved a complete bake-out of the chamber immediately prior to deposition, variation of the substrate temperature during growth, an increase in the RF power, and the use of a pure N₂ source gas instead of the N₂/Ar mixture. Although there were varying degrees of success from these efforts, only the use of a pure N₂ source resulted in the formation of SRSN films having little oxygen contamination³⁶.

With the use of a pure N_2 source appearing to be promising, a set of several compositions of SRSN films were grown. The details of the growth parameters for these films are given in Table 5.2. In order to analyze the influence of oxygen incorporation, silicon oxynitrides (SiON) were grown by taking the least Si-rich SRSN showing good luminescence, which could be expected to show the most influence of N-related luminescent states, and adding an oxygen flow to the deposition process. Ideally, with an increase in oxygen within the film one would hope to see contributions from both nitrogen and oxygen related defects.

As mentioned in the previous chapter the FLY at the Si K-edge can originate from depths of several hundred nanometers. In order to obtain a suitable signal from the

³⁶ Oxygen is very difficult to completely remove. The formation of a native oxide on the substrate surface and oxidation of the sample after deposition will both lead to the presence of some oxygen in the material.

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samples, particularly from the Si-ncs, and to obtain both a useable TEY and FLY from the measurement process a set of thicker samples ($\sim 2 \mu m$) were grown for XAS characterization. XAS experiments at the *K*-edge have primarily been conducted with these thicker samples. Unfortunately, the use of thicker samples led to large amounts of self-absorption in the FLY signal [198]. While this can be corrected, the TEY signal alone proved to be sufficient for the analysis in this work. As it is possible that the $\sim 10X$ increase in thickness for the samples grown for XAS experiments (in comparison with an initial set of thinner samples whose PL and FTIR spectra were studied) could have an effect on the observed results a comparison of the effects of thickness was conducted.

Table 5.2: SRSN and SiON thin films grown for structural characterization. SRSN films are shown in orange. SiON films in green, and the Si_3N_4 reference sample in blue.

			-					-	
Sample #	SiH ₄ [sccm] ¹	N ₂ [sccm] ¹	O ₂ /Ar [sccm] ¹	Ar [sccm] ¹	n @ 632.8nm ± 5%	Deposition Time [min] ²	Thickness [Å] ±5%	Growth Rate [Å/min]	Substrate
T013	5	5		2	1.88	95.1	2530	26.6 ± 1.4	DSP
T016	5	5		3	1.88	113.7	3000	26.4 ± 1.4	SSP
T017	5	5	2	3	1.69	120.0	3640	30.3 ± 1.6	DSP/SSP
T018	5	3		3	2.17	113.2	2490	22.0 ± 1.1	DSP/SSP
T022	5	4		2	1.90	103.4	2500	24.2 ± 1.3	DSP/SSP
T025	5	5		3	1.88	749.3	20000	26.7 ± 1.3	SSP
T026	5	3		3	2.03	879.7	20000	22.7 ± 1.1	SSP
T027	5	4		3	1.93	794.0	20000	25.2 ± 1.3	SSP
T028	5	5	2.4	3	1.67	650.0	20000	30.8 ± 1.6	SSP
T030	5	3.5		3	1.94	815.0	20000	24.5 ± 1.2	SSP
T031	5	20			1.81	701.0	20000	28.5 ± 1.4	SSP

¹ The error in the flow rates is ± 1.0 sccm.

 2 An error of 20 seconds (.3 min) has been associated with the deposition time.

5.1.2 Annealing Treatments

The samples were annealed in a quartz tube furnace under a flowing gas ambient at temperatures ranging from 460 °C to 1200 °C for times up to 120 minutes. Several anneal ambients were used in the study of these samples; N₂, N₂ + 5%H₂, Ar, and Ar + 5%H₂. The addition of hydrogen to the annealing gas ambient was found to increase the PL observed from these samples by up to ~6X, an effect attributed to the passivation of dangling bonds in the Si-ncs. A comparison of the PL after N₂ and N₂ + 5%H₂ annealing is shown in Figure 5.4. Similar behavior has been reported for sample SRSN8 after a 1000 °C anneal under Ar and Ar + 5%H₂ ambients [39]. The exact degree to which hydrogen passivation affects the PL depends on several factors, such as anneal temperature and sample composition.



Figure 5.4: The effects of hydrogen in the anneal ambient on the luminescence of SRSN thin films. The results are shown for sample T018 [Table 5.2] after annealing at 700 °C for 60 min. The PL was found to increase by up to ~6X with the use of hydrogen during the anneal process.

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A N_2 (or $N_2 + 5\%H_2$) ambient was found to be preferable to Ar due to some degradation effects observed in the film after annealing under an Ar ambient at high temperatures (T \geq 1100 °C). The degree of this degradation was seen to be more severe in films that were more Si-rich. Similar behavior has been seen in SRSO samples. The reasons for this have not been explored in this work. The results considered in this work focus primarily on samples annealed in $N_2 + 5\%H_2$. Note that in the thicker samples the effects of incorporating hydrogen into the anneal ambient were observed to be less profound and the PL signals were on comparable scales. This can be understood through a consideration of diffusion processes. During the anneal process hydrogen incorporated during the deposition will diffuse within the sample. Any hydrogen that reaches the sample surface and out-diffuses from the sample will escape into the flowing anneal gas and will not re-incorporate into the films. If hydrogen is present in the anneal gas, however, some of the hydrogen will diffuse into the sample³⁷. In a thin sample nearly all of the incorporated hydrogen can out-diffuse, however, the use of hydrogen in the gas ambient ensures that a amount sufficient to passivate defects is able to re-incorporate into the film³⁸. In a thick sample, however, only hydrogen within a certain depth from the surface will out-diffuse. Hydrogen from deeper within the sample will diffuse such that the concentration throughout the sample will be roughly uniform. The addition of

³⁷ It is not necessary that more hydrogen be incorporated than is lost to get a significant improvement in behavior. Rather, it is only necessary that enough hydrogen reincorporate to passivate any dangling bonds within the film.

³⁸ The out-diffusion of hydrogen SRSO thin films annealed under Ar has been previously studied. Annealing leads to only trace amounts of hydrogen remaining in the sample [193].

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 hydrogen to the anneal gas will only lead to hydrogen incorporation up to some limited

 average depth, but this hydrogen will not have as substantial a role in the passivation

 process as sufficient hydrogen may have been present in the film to begin with.

5.1.3 Non-ICP-CVD grown SRSN samples

For comparison several SRSN samples were deposited using the ECR-PECVD and a conventional PECVD system. A schematic of the ECR-PECVD system is shown later in this chapter. A total of five samples were grown, the details of which are given in Table 5.3. During the deposition the substrate stage was heated to a temperature of 300 °C.

Sample #	SiH ₄ [sccm] ¹	N ₂ /Ar [sccm] ¹	n @632.8nm ± 5%	Thickness [Å] ± 5%	Deposition Time [min] ²	Growth Rate [Å/min]	Deposition Pressure [mTorr] ³
ECR- SRSN-1	3	30	1.88	820	15.0	54.6 ± 3.6	2.30
ECR- SRSN-2	3	15	1.93	920	20.0	46.0 ± 2.9	1.39
ECR- SRSN-3	3	9	1.94	890	25.0	35.6 ± 2.1	0.97
ECR- SRSN-4	5	5	2.32	1200	20.0	60.0 ± 3.8	0.81
ECR- SRSN-5	5	10	1.98	790	15.0	52.6 ± 3.5	1.18

Table 5.3: ECR-PECVD grown SRSN thin films.

¹ The error in the flow rates is ± 1 sccm.

 2 An error of 20 seconds (.3 min) has been associated with the deposition time.

 3 The error in the deposition pressure is 0.15% of the reading.

For the as-grown samples a strong PL signal was only observed in samples ECR-SRSN-4 and ECR-SRSN-5, although a weak PL was seen for sample ECR-SRSN-3. Samples ECR-SRSN-4 and ECR-SRSN-5 were selected for further structural

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 characterization and comparison with the results from samples grown using the ICP-CVD

 system.

Finally, a related project involves the deposition of SRSN thin films using NH_3 instead of N_2 as the nitrogen source gas. Currently, an NH_3 source is not available on either the ECR-PECVD or ICP-CVD systems and the samples were fabricated using a conventional PECVD system. The samples were grown using an RF power of 50 W. Deposition parameters for these samples are listed in Table 5.4. Results from these samples will be briefly presented to further illustrate the differing nature of structural aspects of these films arising from the use of different deposition systems and growth gases.

 Table 5.4: PECVD SRSN thin films grown using an NH₃ source. (Data courtesy of P. Wilson).

Sample #	SiH4 [sccm]	NH3 [sccm]	n @632.8nm ± 5%	Thickness [Å] ± 5%	Deposition Time [min]	Growth Rate [Å/min]	Deposition Pressure [mTorr]
TFNH3-11	100	1.2	2.14	2320	20	116	500
TFNH3-12	100	1.4	2.09	2222	20	111	500
TFNH3-13	100	1.6	2.05	2325	20	116	500
TFNH3-14	100	2	1.98	2573	20	129	500

5.1.4 Additional Considerations – SRSN Thin Films

The reasons for choosing a certain subset of the samples were provided in the previous section, some based on experimental results (to focus on a luminescent set of In this section I aim to identify several additional observations concerning these materials that have been made throughout the course of this work, some of which present areas suitable for future work.

The first relates to stress effects in the films. For ICP-CVD grown SRSN films the samples were stable both as-grown and with annealing for thicknesses up to 1 μ m. The samples grown to thicknesses of 2 μ m were found to exhibit cracking after annealing. ECR-grown samples were far less stable. An initial calibration set of samples (Table 5.3) with thicknesses of 100 nm were found to have no significant stress problems, however, attempting to grow slightly thicker films (even 150 nm) under the same conditions produced samples that cracked either during the cool down process or almost immediately after being removed from the deposition chamber (which may still be related to cool down). This indicates that significant stress is present in the SRSN samples, particularly those grown with the ECR-PECVD system, that has not been analyzed or quantified in this work.

Second, the optical constants reported from the set of SRSN samples discussed here is lower than those typically reported for PECVD grown nitrides. Several effects must be considered in this regard, the first of which is hydrogenation. Hydrogen is incorporated into the as-grown films either through its residual presence in the chamber or the incomplete dissociation of the silane molecule. Second, film densities can greatly vary depending on deposition conditions (including gas flow, growth rate, substrate
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temperature). A less dense film is expected to have a lower refractive index. Finally, one cannot ignore the nature of the method used for measuring the refractive index. Ellipsometry provides very accurate values of the ellipsometric parameters, delta and phi, however, information concerning the refractive index, extinction coefficient, and film thickness are all extracted from the measured ellipsometry constants via appropriate modeling. The modeling process is not simple, particularly with Si-rich films, as an appropriate model needs to treat the Si-rich layer as an effective medium. This is similar to deciding to treat the structure of the material through a RBM or RMM, as discussed in the previous chapter. Furthermore, silicon is not transparent in the visible. This means that the effect of silicon clusters being present in the film will be a non-zero extinction coefficient, as has been observed in SRSO films, particularly after annealing [154, 193]. In this work a refinement of ellipsometric models for these materials has not been undertaken, however, the results presented in the next chapter could be used to do exactly this, as they provide structural information which could be used to suitably incorporate structural phase information into the model³⁹. Ellipsometric modeling of the properties of silicon oxynitride thin films on the basis of the RBM has previously been presented in [200].

Finally, the main interest in this work was to fabricate luminescent SRSN samples and to analyze their structural evolution with annealing. The preliminary analysis of these

³⁹ This is not to say that the models used while monitoring the growth process are not good. In fact, they have been developed over the past several years by considering exactly the type of details just mentioned [199]. The discussion here is only meant to imply that with the availability of structural data, particularly considering the formation of Si-ncs, it may be possible to further refine these models.

<u>PhD Thesis – T. Roschuk</u> <u>McMaster University– Engineering Physics</u> samples allowed for the identification of a set of samples that showed good PL, as-grown and with annealing, however, there were several samples where no luminescence was observed in the as-grown case and even after annealing some of these samples showed poor PL characteristics. These poor-emitting samples have not been explored in this work.

5.2 Rare Earth Doped Silicon Oxide Thin Films fabricated by ECR-PECVD

A schematic of the ECR-PECVD system is shown in Figure 5.5. As mentioned earlier, details of the deposition system have been discussed in several recent theses and papers. In this section the deposition parameters used to fabricate the Ce and Tb doped samples analyzed in this work will be presented. Details of the composition and luminescent properties of these films have previously been discussed in [38] and a detailed discussion of their fabrication and characterization has been presented [120].



Figure 5.5: The ECR-PECVD System at McMaster University. The system has been used for the growth of silicon nitride and rare earth doped silicon oxide thin films.

As with the ICP-CVD system, silane is used as the Si precursor while the oxygen precursor was $10\%O_2$ diluted in Ar. During the deposition process the sample stage was heated to a temperature of 350 °C, resulting in a substrate surface temperature of 120 °C. A Jobin-Yvon single wavelength (HeNe) ellipsometer is used to monitor the growth process. Rare earth doping of the films is accomplished through the use of a volatile metal-organic precursor, *Tris(2,2,6,6-teramethyl-3,5- heptanedionato)-RE(III)* (RE(tmhd)₃), RE = Tb, Ce. The RE was introduced to the sample chamber through the use of an Ar carrier gas. A list of the deposition parameters for those rare earth samples analyzed in this work is provided in Table 5.5 while their compositions, thicknesses, and refractive indices are provided in Table 5.6. It has already been briefly mentioned that the set of Ce-doped samples available for this work was limited. As such only a single sample is being considered for this work⁴⁰. Fortunately, this is the ORSO sample that had displayed a very bright luminescence, which makes it the Ce-doped sample of greatest interest.

	0.10 00	<u>eta samp</u>	Test 1 Idap					
Sample	Forwarded	Reflected	SiH ₄ Flow	O ₂ Flow	RE Cell	Ar Flow	Deposition	
	Power [W]	Power [W]	Rate	Rate	Temp [°C]	Rate	time [min]	
Ce031	509	7	2	30	200	10	15:00	
ТЬ012	500	5	20	56	153	25	9:30	
ТЬ015	420	10	7	24	160	30	30:00	
Ть016	420	10	7	24	160	20	30:00	

 Table 5.5: List of Re-doped samples. Adapted from [120].

⁴⁰ Several other samples have been made available by our industrial collaborator, however, insufficient data is available regarding the composition of these samples, save the type of RE-dopant used and the anneal temperature.

Sample	Absolute Atomic Areal Density ¹ $[x10^7 \text{ atoms/ cm}^2]$				Si [at.%]	RE [at.%]	Thickness [Å] ± 5%	Index of Refraction, n
	Si	0	RE	Ar			1	± 5%
Ce031	1.42	3.00	0.0408	0.055	32.04	0.90	684	1.51
Tb012	2.09	3.76	0.00163	0.004	35.71	0.28	938	1.66
Tb015	2.13	4.59	0.0517	0.083	31.75	0.75	1059	1.50
Tb016	1.88	4.17	0.0256	0.072	31.25	0.42	920	1.49

 Table 5.6: Composition, thickness, and refractive index of the Re-doped samples. Orich samples are shown in blue and Si-rich samples in red. Adapted from [120].

¹ The error for the areal atomic densities is $\sim 2-3\%$.

Chapter 6: Results and Discussion

Three types of materials have been considered in this work, silicon rich silicon nitrides, silicon oxynitrides, and rare earth doped silicon oxides. In this chapter results from the characterization of these three material systems are considered beginning with the nitrides, which have been the subject of the bulk of the research performed for this thesis, followed by the oxynitrides. Finally, the RE-doped silicon oxide samples are considered, illustrating what information can be obtained with XAS in order to provide the basis for further work on these materials.

6.1 Silicon Rich Silicon Nitrides

In this section the evolution of SRSN film structure with thermal annealing and the correlation of the structural changes with the luminescent behavior of the samples are considered. The section begins by first examining details of the nanocluster crystallinity in the SRSN samples. The photoluminescent properties of the as-grown SRSN films are considered. Results from XAS experiments are then presented, looking at the Si and N *K*-edges and the Si $L_{3,2}$ -edge and correlated with the PL properties of the films. The evolution of film structure with annealing is then examined through the use of XAS along with FTIR spectroscopy and correlated with the luminescent behavior of the annealed samples. The effects of sample thickness are considered by comparing results from PL and XAS experiments for both thick and thin films. As discussed in Chapters 2 and 4,

PhD Thesis – T. RoschukMcMaster University– Engineering PhysicsXEOL is an excellent technique for identifying luminescence centers; however,difficulties were encountered when attempting to perform XEOL studies of the SRSNthin films. An explanation for this behavior is presented. The influence of the depositionsystem is then considered through the comparison results for samples grown using ICP-CVD, ECR-PECVD, and PECVD. Finally, the use of STEM, EFTEM, and EELS for theanalysis of Si-ncs in SRSN thin films is briefly discussed.

6.1.1 Si-ncs in SRSN – Structural Considerations

Let us first consider some of the HREM-based results obtained from the SRSN films, particularly as it pertains to the structure (crystalline or amorphous) of the Si-ncs. An HREM image of silicon nanocrystals formed in a SRSO thin film was shown in Figure 4.17. HREM images of both high (T026) and low (T016) excess Si concentration SRSN thin films are shown in Figure 6.1. While in a SRSO sample the lattice fringes indicating the presence of a crystalline structure were readily apparent and a number of nanocrystals could be seen, no such structure is observed for the SRSN samples grown in this work⁴¹. Some isolated nanocrystalline structure was occasionally observed, as shown in Figure 6.1(d). One should not be misled by the image into thinking that this implies that the Si-ncs are primarily crystalline. Only a few isolated nanocrystals were found in

⁴¹ Several samples of varying composition and subjected to a range of annealing conditions were examined extensively using HREM and STEM. No clear evidence of nanocrystals was observed in any of these samples. X-ray diffraction patterns, obtained for some of these samples, also showed a lack of peaks associated with crystalline Si.

PhD Thesis – T. Roschuk McMaster University– Engineering Physics the films and the image shown in Figure 6.1(d) is for the most Si-rich sample considered in this work. The bulk of the material analyzed showed no crystalline structure.

Si-nc formation in SRSN films contrasts with that observed for SRSO films, where c-Si-ncs are readily observed. The nitride matrix appears to act as a barrier to the crystallization of the nanoclusters. Results in the literature indicate, however, that this strongly depends on the method of film growth. As discussed earlier in this thesis, c-Si-ncs have been observed by other groups in SRSN systems for films grown using different methods (source gases or deposition techniques) [80, 101].

It is sufficient for the current discussion to note that HREM imaging of the samples demonstrates that there is little evidence of nanocrystal formation in these films. This indicates any Si-nc formation in the SRSN films grown for this work using ICP-CVD must be primarily in the form of amorphous nanoclusters. I will return to the discussion of some of the EELS and EFTEM work related to these films later in this chapter. For the SRSN samples grown using the ECR-PECVD and PECVD systems, the structure has not yet been analyzed using TEM-based techniques.



Figure 6.1: HREM images of SRSN thin films. (a) T016 annealed at 700 °C (b)-(d) sample T026 annealed at 1100 °C. Both samples were annealed under an $N_2 + 5\%H_2$ for 60 minutes. Images (a) and (b) were obtained using the JEOL 2010F while images (c)

and (d) were obtained using the FEI Titan.

6.1.2 PL and XAS Studies of the As-grown SRSN Thin Films

PL for both the thick and thin as-grown samples is shown in Figure 6.2. The agreement between thick and thin films is quite good, even for samples T018 and T026 (shown in the inset), where the largest discrepancy was seen between the samples in

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terms of their refractive indices. One can see that with an increase in Si-concentration (refractive index) the peak shifts to longer wavelengths. As such, one would have expected the peak from sample T018 to be further red-shifted than that of T026, which, however, is not the case. All of the thick films have an oscillatory nature to the PL. This is a result of their large thicknesses, which leads to interference effects in the luminescence.



Figure 6.2: Photoluminescence of the as-grown SRSN samples. Spectra are shown for (a) thick and (b) thin samples^{42,43}. The oscillatory nature of the PL in (a) is a result of interference effects due to the large sample thicknesses. The inset in (b) shows a comparison between the PL of samples T018 (red) and T026 (black).For both sets of samples the emission peak redshifts with an increase in Si-concentration.

 $^{^{42}}$ In order of least to most Si-rich the sample numbers are T031 (the Si₃N₄ reference sample), T025, T027, T030, and T026 for the thick samples and T016, T022, and T018 for the thin samples.

⁴³ Sample T022 in Figure 6.18(b) was measured after someone had 'realigned' the optics on the PL system and is on a different scale than T016 and T018. Re-measurement of a reference sample and sample T016 show PL reduced by a factor of 3.5-4. Adjusting the PL puts the peak intensity of T022 at the same height as the low energy shoulder of sample T016, which is consistent with the trends observed for the thick samples.

Two general trends can be seen in the PL data as the Si concentration is increased; the PL peak shifts to longer wavelengths and the intensity of the PL emission decreases. The results are consistent with what one would expect from quantum confinement of Sincs. Confinement is strongest in the least Si-rich samples, yielding the greatest efficiency. As the Si concentration is increased the degree of confinement decreases and the efficiency drops off, leading to the weaker emission observed for the more Si-rich samples.

Although the results are consistent with QC, there are two possible views of the film structure which could give rise to the observed PL from these SRSN samples. As the Si-concentration is increased there may be some localized Si-rich regions in the film, consistent with the model depicted in Figure 2.11 on pg. 60. Confinement of electrons and holes within these regions then leads to an increase in the efficiency of radiative recombination. The second possible mechanism for excitation of the PL is to assume that the samples have a homogenous structure. The bandgap is narrowed relative to Si₃N₄ due to Si-Si bonding but there are no localized Si-rich regions (except the extremely localized individual bonding units). Electrons are then excited across this bandgap. In both cases luminescent recombination can occur through defects or surface states, as illustrated in Figure 2.10 on pg. 53.

For sample T016 there are two distinct emission bands, one with a dominant peak at 457 nm (2.7 eV), and the other from 560-590 nm (2.2-2.1eV). The same high energy emission band is seen in sample T022, although it is greatly reduced in intensity and is no

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longer the dominant peak in the spectrum. Furthermore, the main peak emission from T022 appears within the same energy window as the 560-590 nm emission observed from sample T016. Finally, for sample T018 neither of these emission bands is readily observed, only a weak, low energy emission at 690 nm (1.8 eV). The observation of common emission energies between samples T016 and T022 suggest the presence of defects through which the recombination occurs. The thick samples confirm this behavior with samples T027 and T030 showing largely the same peak structure. Sample T030 was grown with a lower nitrogen flow and is expected to be the more Si-rich of the two, although their refractive indices are comparable. However, the lack of a shift in the emission energy illustrates that recombination for the two samples likely proceeds through a common defect or surface state. An increase in Si content for T030 leads a lower degree of confinement and the luminescence efficiency in this sample is decreased.

The observed shift of the peaks to shorter wavelengths arises from a widening of the bandgap with the formation of less Si-Si₄ type bonds as the Si-content of the films is reduced. Only in a sample having little excess Si is the bandgap sufficiently wide to excite the higher energy emission and the 457 nm emission is only efficiently excited in the least Si-rich samples. A weak luminescence is observed for the as-grown Si₃N₄ reference (T031), likely arising from recombination through similar defects as in the least Si-rich films. The sudden drop in intensity for this sample reveals some further information concerning the luminescence. There is no reason for significantly less optically active defects to be present in the Si₃N₄ film than in sample T025. Furthermore,

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the optical bandgaps of the two samples can be expected to be similar. As such efficiently excitation of the high energy luminescence should be possible in both films but this is not the case for the Si_3N_4 reference. This demonstrates that another component comes into play for sample T025 enhancing the efficiency of the luminescent process. Through the formation of small Si-rich regions in the film, electrons and holes generated during the PL process are confined, leading to an increase in the emission efficiency. The PL properties of the films are, therefore, more consistent with the formation of Si-rich regions within the films than with the formation of a homogenous film structure. Details of the film structure will be further considered when results from XAS experiments are presented and discussed.

The lack of a shift in the emission energy between samples T018 and T026, which, on the basis of their refractive indices (Table 5.2 on pg. 158), have slightly differing Si-concentrations, suggests that the 690 nm emission is also associated with recombination through defects or surface states. The energy of this emission, 1.8 eV, is consistent with the energy associated with recombination between N-related defects, as was shown in Figure 2.10, on pg. 53.

Some efforts have been made to fit the peak structure; however, the quality of the fit relies on a number of assumptions regarding the emission peaks and the results are not yet conclusive. They do suggest, however, that in addition to the dominant peaks that may be associated with defects or surface states discussed here, there is a third, weaker component that shifts with concentration. This third peak may be associated with a non-

<u>PhD Thesis – T. Roschuk</u><u>McMaster University– Engineering Physics</u> defect related quantum confined recombination in these samples. The presence of this peak does not affect the main arguments of this thesis, as the peak follows similar trends as the PL in general (red-shifting with increased Si content and decreasing in efficiency).

Let us now consider details of the local chemical environment of the as-grown films, as determined by XAS, specifically looking at the XANES and its correlation with the PL properties of the films. The TEY-XANES spectra at the Si K-edge for the thick as-grown samples are shown in Figure 6.3 along with the reference Si and Si₃N₄ samples. In the near-edge region three key peak features are of note. At 1839-1841 eV the peak associated with Si-Si₄ bonding is seen for the Si-reference sample, however, a distinguished peak is not seen at this position in the SRSN samples. The Si_3N_4 reference sample shows a peak at 1844-1845 eV, which is associated with the Si-N₄ bonding tetrahedra. Although crystalline Si₃N₄ reference samples were not used for this work, other authors have shown the peak to occur at 1843.5 eV for such samples, which is in agreement with the reference peak for the amorphous Si₃N₄ sample analyzed here [69]. Finally, near 1847 eV a small shoulder is present in the spectra. Absorption at 1847 eV is characteristic of Si bound in silica (Si-O₄ tetrahedral bonding). As an additional note, the crystalline form of silicon oxynitride, Si₂N₂O, shows a peak in between the nitride and oxide characteristic peaks at 1844.6 eV [69].



Figure 6.3: SRSN K-edge TEY-XANES Spectra for as-grown SRSN samples along with Si_3N_4 and Si references. The characteristic peak positions for Si, Si_3N_4 , and SiO_2 (Si-Si₄, Si-N₄, and Si-O₄ bonding, respectively) are indicated by dashed vertical lines. An increase in Si-Si related bonding is observed as the Si-concentration of the films is increased.

One can see in the spectra that as the Si content of the films is increased the onset of the absorption edge occurs at lower energies. In general, the Si-in-silicon-nitride peak is observed to broaden with increasing Si content, with the peak becoming less defined. The smooth single peak behavior of the samples is indicative of a RBM-type structure, with the distribution of tetrahedra skewing slightly towards that of Si-Si₄ when more Si is incorporated into the films. This illustrates an increase in the amount of Si-Si₄ bonding in the film as the Si concentration in the films is increased. The fact that a smooth

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distribution is not seen extending to the Si-O related shoulder indicates that the oxygen incorporation is not consistent with a distribution of RBM oxynitride bonding units, but rather that there is a distinct oxide or oxynitride related phase in the films. EELS data, which will be considered later in this Chapter, indicate the presence of little oxygen within the film itself. This means that either (a) the oxygen concentration is small and its presence is only apparent after sampling a large area of the sample (as in the XAS measurement) or (b) oxygen lies near the surface of the films and was likely incorporated through oxidation. Neither situation is ideal; however, neither situation poses any significant problems in the interpretation of the results in terms of treating the films as SRSN.

XANES spectra at the Si *K*-edge comparing the thick and thin as-grown samples are shown in Figure $6.4^{44,45}$. In general there is good agreement in the spectral shape and position, indicating that the as-grown samples have comparable structure. The exception to this are samples T018 and T026, however, the likely reason for this is the need for a recalibration of the energy axis due to a mechanical issue later in the run where T018 was measured⁴⁶. The main differences appear to relate to the partial oxidation of the samples.

⁴⁴ Only a handful of the thinner samples have been analyzed at the K-edge, particularly the as-grown samples, so the comparison is not comprehensive at this edge. A more detailed comparison in made later in this section at the Si $L_{3,2}$ edge.

⁴⁵ One can see that the spectra for samples T016 and T018 are noisier than the other spectra. This type of behavior was due to some instabilities during the XAS run where these samples were measured. The nature of the instability is not known.

⁴⁶ The offset in the absorption edge between T018 and T026 is due to a mechanical issue part way during the run. The Si-reference used for calibration was measured prior to this and the recalibration of the energy scale is off for several samples from late in the run.

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In samples where a slightly higher Si-O related peak is seen the Si-N related peak is reduced in intensity. There is no direct correlation with the degree of surface oxidation and Si content for the thin films, as both T016 and T018 show greater Si-O related absorption than T022, which has a Si concentration intermediate between the two. Finally, absorption in the Si-Si₄ region is moderately higher for the thin films, indicative of a slight increase in Si-Si bonding. This increase in the Si-Si related signal can be attributed to some inhomogeneity across the thicker films.



Figure 6.4: Si K-edge XANES for a set of as-grown thick (2 μ m, red lines) and thin (250 nm, black lines) samples. (a) Samples T025 and T016, (b) samples T027 and T022 and (c) samples T026 and T018.

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Recall, that the XANES spectra reflect not only the chemical environment of the Si atoms but also the density of states in the conduction band. The extension of the absorption edge to lower energies represents a narrowing of the conduction band as the Si concentration of the films is increased and more Si-Si bonds form. A comparison XANES and PL (Figure 6.2 on pg. 173) from these samples reveals details of the correlation between film structure and luminescence. In the least Si-rich samples only small Si-ncs form and a wider bandgap is observed for the samples. Only in these samples are the high energy (shorter wavelength) emissions observed. As the bandgap of the materials decreases with an increase in Si, shorter wavelength emissions are no longer efficiently excited as the defects or surface states that give rise to these emissions lie outside of the bandgap. The XANES spectra then provide direct evidence that the observed wavelengths of the PL emission peaks are correlated with the amount of Si-Si bonding that occurs within the films.

Information regarding the bonding environment of the nitrogen atoms is determined through analysis of the N *K*-edge. XANES spectra at this edge are shown in Figure 6.5. In comparison with the Si *K*-edge, the N *K*-edge is relatively featureless, presenting only a broad absorption peak that onsets at 400 eV. This peak is related to N-Si trigonal bonding (N-Si₃). There is, however, a small shoulder that can be distinguished on the low energy side of the peak at ~401 eV. This shoulder is either the resonant line (RL) associated with the presence of N-dangling bonds within the film or due to N-H bonding. FTIR spectra, to be discussed in the following section, do indicate the presence

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of N-H bonds within the as-grown films and, as such, it is likely the latter, however, on the basis of these measurements it is not possible to definitively distinguish this matter [169, 201]. Not unexpectedly, this peak is also distinguished for the Si_3N_4 reference sample; Even though the film has stoichiometric composition it is an amorphous structure and the nature of PECVD growth makes the formation of either N-H or dangling bonds possible. The RL has been seen to be more prevalent for SiON films where the nitrogen atoms are incorporated substitutionally for O atoms, making the formation of dangling bonds more probable [172].



Figure 6.5: N *K*-edge XANES Spectra for the as-grown SRSN samples. The peak structure is primarily characteristic of trigonal N-Si bonding but shows a shoulder feature at ~401 eV associated with either N-dangling bonds or N-H bonding.

For samples T025, T026, and T031 an increase in intensity with decreasing silicon content is observed. Such a decrease in intensity is expected as the number of N-atoms in the films is decreasing relative to the number of Si-atoms as the Si concentration

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is increased, however, the decreased intensity for the Si-rich films is more substantial than one would expect as the samples have compositions that are not far off Si_3N_4 . Little shift is observed in the peak position indicating that N is primarily trigonally bound to Si in these films. For samples T027 and T030 the absorption edge peaks at slightly lower energies. The peak positions observed for samples T027 and T030 are closer in energy to the RL which may act as an electronic defect to produce charging effects. Charging of the samples was found to be quite prevalent at the N K-edge, as will be more clearly shown later for a set of annealed samples. The XANES at the N K-edge is then the product of several effects; changes in the concentration of N-Si bonds, which decrease as the Si concentration of the films in increased and result in a decrease in the intensity of the absorption signal; charging of the samples, which results in a decrease in the absorption intensity as less electrons escape the sample; and due to the structural disorder of the asgrown films, which results in the formation of dangling bonds. This can then lead to an increase in charging from the samples and a shift of the XAS peak as well as a decrease in the absorption intensity.

Finally, let us now consider the XANES of these samples at Si $L_{3,2}$ edge. The Si $L_{3,2}$ edge spectra for the as-grown reference samples are shown in Figure 6.6. Recall that at the Si $L_{3,2}$ -edge the TEY is surface- and near-surface sensitive, with a sampling depth on the order of nanometers. For the FLY, the sampling depth is on the order of 10-100 nm and provides information regarding the bulk of the films. The FLY is then of more interest for the analysis of these materials at the $L_{3,2}$ edge as the sampling is characteristic

PhD Thesis – T. RoschukMcMaster University– Engineering Physicsof the general film structure, including the formation of Si-ncs within the bulk. At ~99.5eV the Si-Si4 related absorption edge is clearly visible as a step in the Si-referencespectrum. In the Si3N4 spectra several features are visible. The peak associated with Si-N4bonding is seen at ~104.5 eV in the FLY spectrum. Note that it is barely seen in the TEYspectrum, appearing only as a small shoulder. A set of double peaks at 105.6 and106.1eV, characteristic of silicon oxides, is seen in both the TEY and FLY spectra,reflecting the oxidation that has occurred at the surface of these samples. This produces aSiOxNy layer and results in the observed shift in peak positions between the FLY andTEY due to the change in bonding structure within the first few nm below the samplesurface.



Figure 6.6: XANES spectra at the Si $L_{3,2}$ -edge for the reference Si and Si₃N₄ samples. At the Si $L_{3,2}$ -edge the TEY samples only the first several nanometers of the film while the FLY, which samples from 10-100 nm, provides a better indication of the film bulk structure.

In the FLY spectrum the effects of oxidation are still partially apparent; however, the nitride structure of the bulk of the film is clearly seen. Here the discussion will focus on details of the XANES at the Si-Si and Si-N related edges. Two additional features of the spectra that will not be considered in detail are seen at 108.5 eV and 115.9 eV. It is difficult to definitively ascribe these peaks as it is clear that the oxide surface influences the FLY spectrum and they may relate to either Si-O or Si-N bonding, as peaks characteristic of both types of bonding structure can be present in this area [169].

In analysis of the SRSN peaks at the $L_{3,2}$ edge the assumption has been made that absorption immediately prior to the Si edge at 95.0 eV can be taken as a baseline and be used to remove any offset in the absorption spectra. Choosing a precise energy at which the absorption offset is removed is, however, difficult due to the presence of a slowly increasing low-energy tail. A change in the energy at which the offset is removed would result in a shift of the curves relative to one another but will not affect the discussion of peak shape and position.

The FLY-XANES spectra for the as-grown SRSN samples are shown in Figure 6.7(a). As the Si-concentration of the films is increased the Si-N peak is observed to shift to lower energies. This shift is accompanied by a broadening of the peak, particularly on the lower energy side, indicative of the increase in Si-Si bonding within the films. As discussed for the Si *K*-edge this behavior is characteristic of a RBM type structure with a distribution of bonding units. In general the height of the Si-N bonding peak decreases

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 with increasing Si content, however, one can see that it is difficult to assign a definitive

 trend here, particularly with the abnormally high signal observed for sample T030.



Figure 6.7: XANES spectra at the Si $L_{3,2}$ -edge for as-grown SRSN samples. (a) Unnormalized and (b) normalized at 120 eV. Sample T027 has been omitted from (b) due to a substantial amount of noise observed in the spectrum.

Although XAS spectra are often normalized at a post-edge energy, where it can be assumed that the PDOS between samples shows little variation, in order to better analyze variations in the peak intensities, this is difficult to do with the current SRSN samples. The main problem is that the evolving film structure in these samples leads to changes in the absorption spectra over the entire XANES range explored in this work. One can see that the normalization condition is not suitable for the as-grown samples in Figure 6.7(b), <u>PhD Thesis – T. Roschuk</u> <u>McMaster University– Engineering Physics</u> as the relative peak intensities show no correlation with composition and artificially high peaks are observed for some samples. Different post-edge absorption is seen between samples, which leads to this behavior and, as such, the spectra will be left unnormalized (with the exception of normalization to the incident photon flux).

6.1.3 Annealing Studies of ICP-CVD-grown SRSN Thin Films

TEY-XANES spectra for the annealed sample T025 are shown in Figure 6.8. The image is quite convoluted with the number of spectra shown; however, it is suitable here to illustrate several key points for the analysis of SRSN films. At 1839-1840 eV one can see that a shoulder arises after annealing the films. The shoulder is only faintly seen at 800 °C but is clearly discernable after annealing at 900 °C and above. The silicon nitride peak position shifts to higher energies with annealing, towards that of the Si₃N₄ reference sample. Finally, after a 1000 °C anneal the Si-O related peak increases in intensity, an effect that is not readily apparent in any of the other spectra. A similar trend was observed for all samples annealed at 1000 °C during this particular anneal run, indicating that either oxygen was present in the furnace or that the samples may not have sufficiently cooled prior to their removal from the furnace, resulting in their oxidation. The Si-N related peak is also seen to shift to a higher energy after the 1000 °C anneal

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 than for the silicon nitride reference sample, further confirming the oxidation of the sample and a shift towards silicon oxynitride related bonding structures⁴⁷.



Figure 6.8: Si *K*-edge XANES Spectra for the sample T025. The sample has been annealed at the temperatures shown under $N_2 + 5\%H_2$ for 60 minutes. The inset shows an expanded view of the Si-Si₄ related peak region illustrating the increase in Si-Si bonding with annealing.

Si K-edge spectra for samples T027 and T026 are shown in Figures 6.9 and 6.10, respectively. Similar trends are observed in both systems as for the sample T025,

⁴⁷ Some oxidation is seen for almost all samples annealed at higher temperatures, however, not to the extent seen at 1000 °C for this set of samples.

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however, as the Si concentration is increased, an increase in the signal at ~1839 eV is observed to onset at lower anneal temperatures. For sample T027 it is apparent from the shifting Si-N related peak that a structural reordering has onset at 600 °C. A distinct shoulder, associated with Si-Si₄ bonding, is observed after annealing at 800 °C. For sample T026 the edge onset occurs at lower energies after annealing as low as 600 °C, indicating an increase in the amount of Si-Si₄ bonding, with a defined shoulder been observed after a 800 °C anneal.







Figure 6.10: Si *K*-edge XANES Spectra for the sample T026. The sample has been annealed at the temperatures shown under $N_2 + 5\%H_2$ for 60 minutes. The inset shows an expanded view of the Si-Si₄ related peak region.

The *K*-edge behavior of the samples provides clear evidence for the formation of Si-clusters within the film. The shift of the Si-N bonding peak and the onset of a shoulder at the Si in Si bonding energy of 1839 eV are indicative of a phase separation occurring within the samples. The ICP-CVD grown films are in a metastable state. The interim bonding units (Si-Si_xN_{4-x}; 0 < x < 4) are not thermodynamically favorable; however, at low temperatures there is insufficient energy to drive the phase separation process at any

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appreciable rate. Once the films are annealed at higher temperatures, Si within the film tends towards the two more energetically favorable Si-Si₄ and Si-N₄ tetrahedral structures as the film phase separates to form Si-ncs embedded within a Si₃N₄ host. This is not to say that Si-Si bonding or Si-ncs are not observed in the as-grown films. In fact, as discussed in the previous section, analysis of the as-grown XAS spectra shows that in the more Si-rich films the absorption edge is observed to onset at lower energies, indicating that there is an increase in Si-Si bonding within with an increase in Si concentration. However, the as-grown films have a more homogenous mixture of bonding structures, with the interim structures decomposing with annealing.

The intensity of the Si-edge at 1839 eV is shown for the various samples in Figure 6.11 as a function of anneal temperature. As the Si-concentration of the films is increased, the appearance of a distinct Si-phase occurs at lower temperatures. In sample T026 a large increase in the absorption signal is seen at anneal temperatures as low as 600 °C, while for samples with lower Si content this increase is more prominent from 800-900 °C. The results indicate that the activation energy for Si-nc formation decreases in the more Si-rich samples. Similar behavior has been observed for SRSO samples [41]. In SRSO samples the size of the nanoclusters increases with higher anneal temperatures, leading to an increase in the observed signal at 1839 eV, for anneal temperatures up to 1100 °C (as was shown in Figure 3.5 on pg. 90). At higher temperatures the XAS signal could be seen to decrease. In the SRSN samples, the XAS signal peaks at lower temperatures (~900 °C, recall that the oxidation of the samples annealed at 1000 °C

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 means that the data at that temperature cannot be considered reliable). The results

 indicate that the host matrix plays an active role in cluster formation, affecting the

 energetics of the process.



Figure 6.11: Intensity of the XAS signal at 1839 eV as a function of anneal temperature. An error of approximately $\pm 10^{\circ}$ C is associated with the anneal temperature. Error associated with the intensity of the x-ray absorption signal is contained within the size of the data point. For reference the XAS signal of the as-grown Si₃N₄ sample is shown. Only the as-grown point is shown for sample T030. Lines are drawn as a guide to the eye only.

At higher anneal temperatures little change is seen in the structure of the Si-Si₄ bonding peak, however, the peak related to Si-N₄ bonding both shifts in position and varies in intensity (Figures 6.8-6.10), indicating that changes in the structure of the film at these higher anneal temperatures relate primarily to the structural reordering of the silicon nitride host. As discussed, annealing results in a phase separation within the films,

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causing a change in the structure from more RBM-like to more RMM-like and decreasing the number of interim bonding units to form Si-ncs embedded within Si_3N_4 . This process leads to the observed shift in the Si-N related peak towards that of the Si_3N_4 reference sample. The increase in intensity of the Si-N related peak after annealing at 1100 °C indicates an increase in the number of Si-N₄ bonds, demonstrating that the structural reordering of the Si_3N_4 continues at high temperatures.

The behavior of the N K-edge with annealing is shown in Figure 6.12 for samples T025, T026, and T027. A slight shift to higher energies is seen with annealing, as well as a narrowing of the peak. The noisiness of the spectrum is due to charging effects for the sample. The shift in peak position is most prominently seen for samples T025 and T027. A sharper, low-energy peak observed for these samples is close in energy to the RL associated with dangling bonds. This peak is observed only in the as-grown films or samples annealed at low temperatures. At higher anneal temperatures the results indicate that N is primarily trigonally bonded (N-Si₃) and that there is little change in the bonding structure for the N atoms within the film. The narrowing of the peak demonstrates there is some local structural reordering, likely related to changes in the bond angle and length. Such reordering is to be expected with annealing as the bonding structure of the amorphous solid is typically distorted, particularly for the as-grown films. In the most Sirich sample, T026, no evidence of the RL is seen in the XANES. N-atoms in this sample are then primarily trigonally bonded to 3 Si atoms and few dangling bonds exist in the film.



Figure 6.12: N *K*-edge XANES Spectra for the annealed SRSN samples. (a) T025, (b) T026, and (c) T027. The spectra are noisy due to charging of the sample during the measurement process.

Let us now consider the XANES at the Si $L_{3,2}$ edge as a function of annealing for SRSN samples. XANES spectra for the thick films annealed up to 900 °C are shown in Figure 6.13. After annealing at low temperatures all samples show an increase in the absorption edge related to Si-N₄ bonding at 104 eV relative to the as-grown films. It is not clear how much of this can be associated purely with changes in the Si-N bonding structure as it remains to be determined how the post-edge background, associated with Si-O bonding at the film surface, relates to these changes with annealing. Although the sampling depth for the FLY at the Si $L_{3,2}$ -edge is comparable to that of the TEY at the Si *K*-edge, one can readily see that there is an increase in the intensity of the Si-O related double peak, indicative that surface contributions have a greater effect on the measurement at the Si $L_{3,2}$ edge. The Si-N peak shifts slightly to higher energies with increased annealing temperature, as expected from the formation of a more stoichiometric silicon nitride host which occurs as the film undergoes a phase separation.





Figure 6.13: FLY-XANES spectra at the Si $L_{3,2}$ for the SRSN samples annealed at the temperatures shown. (a) T025, (b) T026, and (c) T027. At low anneal temperatures an increase in Si-N bonding is observed relative to the as-grown films.

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Changes at the Si-Si₄ related absorption edge may be more clearly seen in Figure 6.14. A linear fit has been made to the pre-Si edge region and a baseline subtraction performed in order to more clearly illustrate changes in the edge structure. In samples T025 and T027 no clear structure is observed at the Si-Si₄ edge. A small edge can be seen for sample T027 annealed at 460 and 600 °C, however, there is no apparent structure at higher anneal temperatures. In the more Si-rich sample T026 one can see that after annealing at 600 °C the absorption edge extends to the Si-Si₄ edge region. At 800 °C a peak in this region becomes more defined. For sample T026 this is consistent with what was observed at the Si K-edge. It is not clear why no signal is observed in the less Si-rich samples T025 and T027. T027 shows some indication of the peak broadening to indicate the formation of Si-clusters. At higher anneal temperatures the Si-N₄ peak shifts to higher energy and narrows, indicative of the change in bonding structure of the silicon nitride host matrix, however, no Si-Si₄ related peak is observed to form. At the PGM beamline a narrower exit slit was used than at the SGM beamline, as such the discrepancy may come from sampling a smaller area of the sample. Measuring over a smaller area may not allow for enough of the smaller Si-ncs to be sampled to generate a significant signal. Furthermore, in a small Si-nc system one expects the absorption edge to be pushed to higher energies, thus the weak signal may be 'masked' at the *L*-edge by the significantly more intense Si-N₄ peak.



Figure 6.14: XANES spectra zoomed in near the Si absorption edge for the SRSN samples annealed at the temperatures shown. (a) T025, (b) T026, and (c) T027. A straight line has been fit to the pre-Si edge and subtracted from the spectra in order to clarify the behavior in this region. The vertical line indicates the position of the Si-Si₄ absorption edge.

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The previous figures have discussed the structure of the thick films annealed at temperatures less than 1000 °C. At higher temperatures some anomalous behavior is seen for these samples at the Si $L_{3,2}$ edge as is shown in Figure 6.15.



Figure 6.15: Si $L_{3,2}$ -edge XANES for the thick SRSN samples annealed at high temperatures. (a) T025, (b) T026, and (c) T027. The left hand column shows the full spectrum while the right hand column shows the reduced range for comparisons with the thicker samples. The spectra for T = 900 °C are shown for comparison with the previous spectra.
Partial oxidation of the samples was observed at an anneal temperature of 1000 °C, as discussed for the results at the Si K-edge. The XANES at the Si $L_{3,2}$ edge does not show a substantial increase in Si-O related bonding, however, in comparison with the structure at 900 °C a decrease in the Si-N related peak is observed. No structure at the Si-Si₄ peak energy is observed. After annealing at 1100 °C one can see that samples T025 and T026 show a drastically different edge structure, consistent with crystalline Si. What is particularly odd is that this behavior is seen in sample T025 and not T027, which is the more Si-rich of the two but appears "normal" at this anneal temperature. Furthermore, no evidence of a Si-N related peak is seen in samples T025 and T026 after the 1100 °C anneal. Sample T026 has been analyzed with TEM and was discussed earlier in this chapter. Although some nanocrystals have been observed in the film, such observations were rare. At 1200 °C evidence of any Si-Si and Si-N bonding is lost from samples T025 and T027, but not from sample T026. Sample T026 displays a large degree of selfabsorption at the Si-Si₄ edge energy leading to the abnormal peak structure of the spectrum.

The total electron yield for sample T026 at high anneal temperatures is shown in Figure 6.16. Similar XANES as what was seen in the FLY is observed after annealing at 1100 and 1200 °C. The results suggest the formation of a silicon or oxidized silicon overlayer structure at 1100 °C. Some evidence of such a structure should be observed through TEM; however, using TEM-based methods the structure of T026 has been analyzed primarily within the bulk of the film, not at the surface and no evidence of such

PhD Thesis – T. RoschukMcMaster University– Engineering Physicsa structure has been seen. It is then likely that the abnormal edge structure at the Si $L_{3,2}$ isindeed a surface effect.



Figure 6.16: Si $L_{3,2}$ -edge TEY-XANES for sample T026 annealed at high temperatures. The surface sensitive TEY-XANES suggest the formation of a silicon or oxidized silicon overlayer after high temperature annealing.

As mentioned previously, it is known from the *K*-edge spectra that some oxidation of these samples occurred at 1000 °C. If the source of this contamination was not completely removed then it should not be surprising that additional oxidation effects occurred at higher anneal temperatures. Oxidation does not seem to completely describe the observed effects, however, as it does not explain the lack of a Si-N absorption structure. Furthermore, the effects of oxidation were clearly seen in the *K*-edge spectra at 1000 °C. No clear increase in the Si-O bonding signal was observed at higher temperatures. It has been shown for silicon nitride films that one of the byproducts during PhD Thesis – T. Roschuk McMaster University– Engineering Physics annealing can be the production of NH₃ molecules [202]. This was, however, for the case of samples formed using an ammonia precursor in which more N-H bonding could be expected. It is possible that annealing under a hydrogen containing ambient results in the formation of such chemical species, depleting the surface of nitrogen. It is, therefore, likely that the result is a product of several factors related to the annealing process. Such results have not been observed after high temperature annealing for the thin SRSN samples, which will now be considered.

The $L_{3,2}$ -edge XANES spectra for the thin samples T016 and T018 are shown in Figure 6.17. Unlike the thicker sample T025, sample T016 shows the presence of a faint peak in the absorption spectrum just above the Si-Si₄ absorption edge. The peak is slightly more prominent after annealing at 800 °C and above, which is consistent with what was seen at the *K*-edge for the thicker samples. Similarly, Si-Si related absorption is more clearly seen for sample T018 than for T026, presenting a sharply defined peak. The spectrum for T018 annealed at 1100 °C illustrates behavior characteristic of self absorption showing an inversion in the absorption behavior from 99.9-102.0 eV. It is also worth noting that no clear Si-N related peak is seen in the as-grown sample T018. As was seen for sample T026, the Si-N related peak for the most Si-rich sample is broad and weak in intensity, however, the absence of any clear peak is somewhat puzzling but will be considered momentarily. After annealing a clear peak associated with the silicon nitride host is seen at 104 eV. The Si-Si peak follows a trend similar to that observed at the *K*-edge for the thicker sample, being clearly present after annealing at 700 °C but <u>PhD Thesis – T. Roschuk</u> <u>McMaster University– Engineering Physics</u> showing little growth with further annealing. The thinner set of samples were not annealed at temperatures lower than 700 °C, as such, it is not possible to say at what temperature the phase separation onset occurs.



Figure 6.17: Si $L_{3,2}$ -edge XANES for a set of 250 nm SRSN samples. (a) T016 and (b) T018. The left hand column shows the full spectrum while the right hand column shows the reduced range for comparisons with the thicker samples. A peak associated with Si-Si bonding is observed after annealing.

We see from the deposition conditions (Table 5.2 on pg. 158) that sample T018 has a slightly higher refractive index than sample T026. This has been assumed to be due to the inclusion of absorption in the determination of the refractive index for T026,

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however, it may be that the thinner sample does contain slightly more Si. In fact, the XAS data at the L-edge supports such a suggestion. One can see that in the as-grown samples the Si-N related peak spreads and decreases substantially in intensity with increased Sicontent. If the sample is more Si-rich it is possible that the Si-N related peak could be more difficult to distinguish. After annealing, however, the phase separation of the samples and the structural re-ordering of the host matrix lead to an increase in Si-N₄ type bonding as the matrix tends towards a stable structure. An increased amount of Si in the sample would then lead one to expect both a poorly defined Si-N peak in the as-grown film and a more intense Si-N₄ related peak after annealing, as is indeed seen for this sample. It is then clear that the Si L-edge provides an excellent absorption edge for the study of the structural changes of the host matrix (Si-N₄ bonding), as changes in the XANES are far more pronounced here than at the K-edge, however, the K-edge has typically been seen to have a more pronounced Si-Si₄ bonding edge, as was evidenced for the thicker samples, making it more suitable to the study of Si-nc formation. It is clear that using a combination of the two allows for the detection of details that may be missed or not clearly resolved in one technique or the other 48 .

It then remains to determine what leads to the quantitative differences at the Si $L_{3,2}$ edge between thick and thin samples grown under the same conditions. Behavior at the $L_{3,2}$ edge in the thinner samples is in good general agreement with the data from the Si

⁴⁸ There is also an element of experience to all of this. As more XAS experiments have been performed we were better able to determine and refine the experimental conditions and optimize them for the study of these materials.

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K-edge for the thicker samples. It is possible to attribute the differences to a change in the kinetics of film growth as the sample grows thicker, resulting in an inhomogeneity through the thicker films. Although measurements at the Si $L_{3,2}$ edge are more surface sensitive, in the thin samples a significant portion of the bulk is still sampled. Furthermore, inhomogeneity over the thickness of the thin films is minimal. In the thicker films this inhomogeneity is more profound, leading to the abnormal XANES seen after high temperature annealing. At the Si $L_{3,2}$ edge the XANES reflects primarily a surface region where the effects of this inhomogeneity are more pronounced. Finally one cannot rule out the influence of memory effects in the deposition chamber which can affect the film composition and structure.

In the discussion of the as-grown samples, sample T022 was in good agreement with the thick sample T027 at the Si *K*-edge. XANES spectra at the Si $L_{3,2}$ edge for sample T022 are shown in Figure 6.18. One can see that even in the as-grown sample Si-N bonding features more prominently than for samples T016 and T018. Furthermore, the Si-N peak is sharper than that observed for the other films. A clear Si-Si₄ related edge, undetected at the *K*-edge, shows evidence of Si-ncs within the as-grown film, a feature not readily observed for any of the other films discussed in this work. The sharp Si-N related peak, which shows little shift with annealing, is a feature of a more stoichiometric Si₃N₄ host matrix in the as-grown film. The results illustrate that sample T022 does not have RBM like structure, but rather that it is RMM like. The distinguishing features during the growth process for this particular film are a lower Ar flow and a slightly lower PhD Thesis – T. RoschukMcMaster University– Engineering Physicsgrowth rate. It is possible that for the ICP-CVD system these conditions are suitable tolead to the *in-situ* formation of Si-ncs within a Si₃N₄ host⁴⁹. Such behavior has beenreported by other groups in the literature and was discussed in Chapter 3 [80, 160]. Notethat there are three variables at play here, growth rate, Ar concentration in the chamber,and chamber pressure during the deposition. Resolving what has led to this behavior isout of the scope of this work; however, with the results presented here it is possible toshow the structural aspects that will be associated with the luminescent behavior of thesefilms. It is then a matter of performing a more comprehensive analysis of the effects ofgrowth parameters in order to reproduce such structures.



Figure 6.18: Si $L_{3,2}$ -edge XANES for sample T022. The inset in the right hand panel shows the Si-Si bonding region. The sample shows a Si-Si related edge, even in the asgrown case.

⁴⁹ This is actually quite an interesting result as it would define a threshold where the growth kinetics change. Unfortunately, sample T022 was measured with XAS near the end of this work and the results were unexpected as the growth rate was only marginally slower than that of T027, and the possible influence of Ar (and chamber pressure) on the growth has not been considered.

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Further details regarding the evolution of the silicon nitride host matrix are obtained by considering the FTIR spectra for these samples. FTIR spectra, shown in Figure 6.19, were obtained for the thinner samples T013, T018, and T022 which were deposited under the same conditions as samples T025, T026, and T027, respectively. The most prominent peak in the spectra, seen at ~890 cm⁻¹ is due to the Si-N asymmetric stretching mode. The peak at the edge of the plots, at ~485 cm⁻¹, corresponds primarily to the Si-N symmetric stretching mode, however, absorption related to the Si-O rocking mode at 460 cm⁻¹ makes it difficult to distinguish changes in this peak related solely to Si-N bonding.

In a sample with low excess Si content (T013) little change is observed in the FTIR absorption spectra with annealing⁵⁰. The largest change appears to be due to oxidation, resulting in the formation of a clear peak 1080 cm⁻¹ (Si-O stretching). Only a slight change in Si-N bonding is observed at 890 cm⁻¹, corresponding to the Si-N asymmetric stretching mode. In sample T022 the re-ordering of the Si-N phase is more apparent. At all of the considered anneal temperatures, the FTIR difference spectra show an increase in absorption related to Si-N bonding.

The effects of annealing are more profoundly seen in the FTIR spectra for the most Si-rich sample considered in this work. At the lower anneal temperatures (700-800

 $^{^{50}}$ Sample T013 was only annealed at higher temperatures. This was done on the basis of some of the initial results from the oxidized SRSN films grown using a N₂/Ar mixture which suggested better PL properties after high temperature annealing. Subsequent work with the SRSN films illustrated better PL at lower anneal temperatures.

PhD Thesis – T. RoschukMcMaster University– Engineering Physics°C) a small change in Si-N absorption is observed. The increase in Si-N bondingbecomes more prominent after annealing at 900 °C, however, only little change in theabsorption intensity is seen at successively higher anneal temperatures.



Figure 6.19: FTIR Spectra for the SRSN samples. (a) T013, (b) T022, and (c) T018. The left panels show the FTIR spectra and the right panels show the difference spectra between the annealed films and the as-grown film in order to better highlight changes in the absorption peaks. The spectra have been intentionally offset for clarity. The noisy region from ~1300-1750 cm⁻¹ is due to atmospheric absorption as a result of the setup of the FTIR system, as is the dip at ~600 cm⁻¹ in (c).

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Although some oxidation of the samples is observed, the FTIR spectra demonstrate that the amount of oxygen within these samples is, in fact, quite low and Si-N bonding is predominant in the films. Furthermore, oxygen is detected primarily after annealing, not in the as-grown films, indicating that oxygen contamination in this set of samples does not occur during the deposition process.

Unlike SRSO films, which can show a notable shift in the peak position with annealing, due to a re-ordering of the films and a change in the bond angle between the Si and O atoms, little shift is observed in the SRSN films [193]. This is a result of the rigid nature of the silicon nitride structure. The formation of 3 bonds by the nitrogen atoms provides less freedom for a reorientation of the atoms within the film.

In all of the samples it can be seen that the signal from Si-H and N-H bonding is decreasing as the films are annealed, indicated by the local minima in the difference spectra at 2150 and 3140 cm⁻¹, respectively. Thus, even under a hydrogen anneal the majority of hydrogen is out-diffusing from the sample. Such a result is not unexpected, as similar behavior has been observed in SRSO thin films [137], where it was demonstrated that the introduction of hydrogen into the anneal gas results a small amount of hydrogen within the films (much less than the as-grown films) whereas the samples annealed without hydrogen in the anneal gas showed no indication of Si-H bonding. Experiments in [137] were conducted at the Si-H bending mode at 880 cm⁻¹, which is not easily analyzed in the nitrides due to its proximity to the Si-N asymmetric stretching mode, and

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 at the Si-H stretching mode. As such, here the discussion of hydrogen incorporation will

 be limited to the Si-H and N-H stretching modes.

The Si-H (2140-2260 cm⁻¹) and N-H (3340 cm⁻¹) stretching modes for the asgrown films are shown in Figure 6.20. In the absence of a reference Si_3N_4 sample grown on DSP Si sample T023 has been used, which was grown at a higher nitrogen flow than the SRSN films analyzed in this work, however, not as high as that determined to produce a near stoichiometric film during calibration of the system. As the Si-concentration of the films is increased one can see the number of Si-H bonds within the films is increasing, while the number of N-H bonds is decreasing.



Figure 6.20: FTIR Analysis of H-bonding in the as-grown SRSN thin films. The amount of Si-H bonding within the films increases with increased Si-concentration while the amount of N-H bonding decreases.

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The effect of annealing on H-bonding within the films is illustrated in Figure 6.21 through sample T022. As the sample is annealed hydrogen bonding within the films decreases. Si-H bonding decreases gradually, yet is still partially present even after annealing at 1100 °C. N-H bonding decreases to a greater extent at lower anneal temperatures, being barely detectable at 800 °C and essentially non-existent at greater anneal temperatures.



Figure 6.21: FTIR Analysis of H-bonding for sample T022 annealed at the temperatures shown. Both Si-H and N-H bonding within the film decrease with annealing.

By combining the results from XAS experiments with the FTIR data it is possible to paint a comprehensive picture of the structural evolution of the SRSN samples. The asPhD Thesis – T. Roschuk McMaster University– Engineering Physics

grown films display a homogenous bonding structure, as would be predicted from a RBM assuming an appropriate distribution of bonding units to account for the Si-richness of the films. At low anneal temperatures a phase separation onsets leading to Si-ncs embedded within Si_3N_4 , as discussed in the analysis of the XAS results. The phase separation of the excess Si within the films shows a dependence on the film composition, with the onset of clustering occurring at lower anneal temperatures for more Si-rich films. The clustering of the Si within the films is essentially complete by 1000 °C, with no increases in X-ray absorption at the Si-edge being seen as the anneal temperature is further increased.

Further changes in the film structure relate to a re-ordering of the Si-N bonds within the film, evidenced through both XAS and FTIR. In samples having less excess Si, only a small re-ordering of the bonding structure is observed. As the silicon concentration is further increased this re-ordering becomes more substantial. XAS spectra indicate that the structural reordering of the films affects primarily the Si bonding, with N-atoms within the film showing only X-ray absorption attributable to trigonal N-Si₃. Some N-Si_xH_{3-x} bonding must, however, also be present in the films, as evidenced through the N-H stretching peak in the FTIR spectra. These N-H bonds likely give rise to the XANES near in energy to the RL associated with N dangling bonds (Figure 6.12 on pg. 194).

Hydrogen is incorporated into the films during the deposition process. In a sample that has little excess Si the hydrogen is incorporated in the form of N-H bonds. As the excess-Si content is increased the number of N-H bonds decreases and more Si-H bonds form. Annealing results in the breaking of all of the N-H bonds and no evidence of N-H

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bonding is observed at anneal temperatures greater than 1000 °C. While the number of Si-H bonds decreases with increasing anneal temperature, under a $N_2 + 5\%H_2$ annealing ambient some Si-H bonding is still observed in the film, even after annealing at 1100 °C, a similar result to what has been observed in SRSO films, where the absence of hydrogen during the anneal process was found to result in an absence of Si-H bonding [137].

Let us now consider the PL properties of the SRSN films after subjecting them to thermal annealing under a $N_2 + 5\%H_2$ ambient for 60 minutes. PL spectra for the most Sirich films, T026 and T018, are shown in Figure 6.22. With annealing sample T026 shows an initial increase in the PL intensity at 460 °C followed by a substantial drop with annealing up to 700 °C, a slight increase at 800 °C, and then a decrease in the PL back to a similar intensity as the as-grown case. Finally a small increase in the PL intensity is seen after annealing at 1200 °C. The increase at 800 °C is relatively insubstantial. No clear detectable change is seen in the peak emission wavelength except after annealing at 1200 °C. At this temperature the emission shifts to shorter wavelength and a high energy shoulder, similar to that discussed for the least Si-rich as-grown samples (Figure 6.2 on pg. 173), may even be present.

The initial increase can be attributed to the onset of a phase separation and the passivation of defects that existed in the as-grown film. In the more Si-rich film clustering was seen to onset a lower energies, indicating that there is less of a barrier to Si-nc formation in these films. At 460 °C a sharpening of the Si-N related peak at the *L*-edge could be seen, indicating that the nitride host is reorganizing which would result in a

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 decrease in the number of non-radiative defects such as dangling bonds. This behavior is

 common to all the SRSN films; particularly the thick ones which have been treated at

 lower anneal temperatures.



Figure 6.22: Photoluminescence spectra for samples T026 and T018. Spectra are shown for samples T026 annealed at (a) low and (b) high anneal temperatures and for (c) T018. The y-scale in (b) has been magnified 4X that of (a) in order to better illustrate the spectra. The as-grown PL has been plotted in (a) and (b) as a reference.

At anneal temperatures as low as 600 °C a peak associated with Si-Si bonding was seen to form at the *K* and *L*-edge indicating a large increase in the amount of Si-Si bonding in the film. There is sufficient Si-Si bonding and cluster formation that the efficiency of the luminescent emission intensity drops again at low anneal temperatures due to the formation of large Si-ncs. At the higher anneal temperatures the increases in intensity are not substantial enough to attribute them to any specific change in structure. The sharp, defined crystalline Si-type peak observed at the *L*-edge after annealing at 1100 °C gives no detectable change in the PL of this sample. At 1200 °C the peak is notable in that it extends to higher energies after this anneal. The peak is still quite weak, however. Details of the peak structure are difficult to discern due to interference effects in the spectra. The peak structure is better resolved for the thinner sample, T018, which shows a similar change in the PL after a 1200 °C anneal.

For sample T018 the PL intensity for the as-grown sample was comparable with that of the thicker sample. The PL peak intensity increases after annealing at 700 °C and then decreases with annealing up to 1100 °C. The sample has not been annealed at lower temperatures, and based on the results from T026 it is likely that the optimum anneal temperature for the film is lower than 700 °C. With higher annealing temperatures the decrease in PL intensity follows a similar trend to that seen for the thicker sample. Similar behavior was observed at the Si $L_{3,2}$ edge for sample T018 as what was observed at the Si K-edge for sample T026. In both cases it the decrease in PL can be attributed to growth of the clusters beyond the QC regime, resulting in a decrease in PL efficiency.

With annealing up to 1100 °C no shift is seen in the PL position in either sample T018 or T026, indicative that the PL proceeds through surface or defect states. As-discussed for the as-grown films the energy of the emission is consistent with recombination through N-related defect states. XAS and FTIR results showed that as the anneal temperature is increased structural reordering of the silicon nitride host occurs. This structural reordering may then result in a decrease in the number of N-related defects, further contributing to the reduction in the PL intensity.

For sample T018 a clear shift in the emission peak to higher energies is seen after annealing at 1200 °C. The shift in the PL peak position suggests the formation of smaller Si-ncs which may result from a breakdown of the film structure at high temperatures and the growth of the Si-ncs beyond what is energetically favorable for the silicon nitride matrix to accommodate. Higher energy emissions can then be excited by these smaller Sincs. The PL spectrum shows the presence of a prominent emission near 610 nm, as well as a low energy shoulder near ~400 nm. The peak structure is similar to that of the asgrown sample T022 (Figure 6.2 on pg. 173) suggesting the PL process still proceeds through defect states.

Next, consider the PL from the least Si-rich samples, T025 and T016, shown in Figure 6.23. For the thick film there is an increase in the PL intensity up to 600 °C. From 700 to 900 °C there is a decrease in the total PL signal. Over the same range, however, one can see that the low-energy portion of the spectrum has become more intense, indicating a greater prominence for the high energy emission. This shift in the emission

PhD Thesis – T. Roschuk McMaster University– Engineering Physics energy occurs at the same anneal temperatures over which a defined Si-related phase was seen to form at the Si K-edge (Figure 6.8 on 188).



Figure 6.23: Photoluminescence spectra for samples T025 and T016. Spectra are shown for samples T025 annealed at (a) low and (b) high anneal temperatures and for (c) T016. The y-scale is the same for (a) and (b). The as-grown PL has been plotted in (a) and (b) as a reference.

Consider Figure 6.24, which illustrates the conduction band for a structure with Si-rich areas. As the film is annealed Si will diffuse and coalesce to form Si-ncs. This produces two effects. The first is a reduction in the area over which the Si-rich region/cluster extends. The second is to increase the barrier height of the surrounding nitride by depleting it of excess Si. The net effect is then an increase in the ground state energy level resulting in a blue-shift of the emission. The nitride host acts as a barrier for Si diffusion and Si-nc growth. As such only Si within a limited range will coalesce to form the Si-ncs in a sample having a low excess Si concentration.



Figure 6.24: Changes in the conduction band structure with annealing. The reduction in size and increase in barrier height result in an increased energy for the ground state energy level within the Si-nc.

In a sample containing more Si the barrier to diffusion is decreased and larger nanocrystals can readily grow at higher anneal temperatures. A blue shift of the emission, such as that seen for samples T025 and T016, can be attributed to the formation of Si-ncs in a low Si-concentration sample.

Returning to the PL spectra for sample T025 in Figure 6.23(b), a slight increase in the PL is then seen at 1000 °C before decreasing again. As discussed, at 1000 °C

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oxidation effects were observed for the sample. Due to this oxidation it is difficult to consider the sample annealed at 1000 °C when considering the general trends of the PL with annealing. The high energy emission seen at all anneal temperatures is commonly associated with recombination between the confined energy levels of the Si-nc and N-related defects such as N-dangling bonds. The initial increase in intensity for this peak is attributed to the formation of Si-ncs, following a growth pathway similar to that shown in Figure 6.24, and the breaking of N-H bonds to produce such defects, as evidenced through FTIR, with annealing. After annealing at 700 °C or higher, however, the structural reordering of the films tends towards a stoichiometric structure, reducing such bonds and leading to a decrease in the PL intensity.

For the thinner sample, T016, the PL shows a peak at 700 °C, however, on the basis of the results from T025 it is likely that the optimal anneal temperature for this sample could have been slightly lower. At higher anneal temperatures the PL decreases in intensity while showing a blue-shift in the emission energy of the more intense peak. This can be interpreted in a similar manner to that of the thicker sample, excluding the case of T025 annealed at 1000 °C.

The broad peak seen in the PL from these samples at ~600 nm is commonly associated with recombination through Si- dangling bonds. The peak decreases in intensity with annealing in a similar manner to the high energy peak. With the structural reordering of the films and H-passivation the number of Si dangling bonds decreases, resulting in the decrease of the PL intensity from this peak.

Finally, the PL spectra from the interim Si-content films, samples T022 and T027, are shown in Figure 6.25. Unlike the most and least Si-rich films analyzed in this work, which both show an increase and then a rapid decrease in PL, the luminescent intensity of these samples increases and then remains more or less constant, although some fluctuations are observed in the total intensity. Within the range of 700-1100 °C the two samples (thick and thin) show similar behavior with increased annealing temperatures. No clear shift in the emission peak can be assigned to sample T027 due to the oscillatory nature of the peaks. A clear shift to lower energies is observed for sample T022. As discussed for the previous samples, an initial increase in PL can be tied to the structural reordering, removing non-radiative defects. As the anneal temperature is increased, evidence of a higher energy emission is observed for sample T022. In fact, it appears that there are 2 higher energy emission bands (at ~400 and 470 nm) that concurrently appear in the spectra. No evidence of this behavior is seen for sample T027 though, which appears to show only a single broad emission peak. The generally increasing PL signal from the sample correlates with the increasing Si-clustering in the films seen through the analysis of the Si K-edge. An increase in the anneal temperature can cause the formation of more Si-nc nucleation centers, leading to the increased emission observed. As mentioned previously, the broad emission peak in this energy range is commonly associated with recombination through Si dangling bonds. It is possible that an increasing number of such defects occurs due to the formation of more Si-ncs, however, one would

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 expect H-passivation of the samples to then decrease this emission, a result that has not

 been observed.

Sample T022 was odd in that evidence of Si-ncs was clearly observed in the asgrown film. However, as Si-ncs form in all the films after annealing, the presence of the peak at 470 nm cannot be attributed to them. In addition to the observation of a Si-Si related peak in the as-grown film, the structure of the Si-N peak at the *L*-edge in this sample is consistently unique at all anneal temperatures. The behavior of this peak is likely tied to the presence of a nitrogen related defect which leads to the observation of the two high energy peaks seen for this sample. We cannot expect it to be tied to the presence of nitrogen dangling bonds, or the peak should be seen to reduce with annealing. While it is clear that there is a structural tie between this Si-N peak and the observed luminescent behavior, the detailed nature of the PL peak at 470 nm remains to be resolved. PhD Thesis – T. Roschuk



Figure 6.25: Photoluminescence spectra for samples T027 and T022. Spectra are shown for samples T027 annealed at (a) low and (b) high anneal temperatures and for (c) T022. The y-scale is the same for (a) and (b). The as-grown PL has been plotted in (a) and (b) as a reference.

6.1.4 XEOL Studies of SRSN Thin Films

In the above discussion the PLY-XAS spectra have not been presented. Ideally, PLY and XEOL can provide more detailed information on the origin of the luminescence in materials; however, several difficulties were encountered in relation to PLY and XEOL studies of the silicon nitrides. Although XEOL was observed from the samples, under the influence of the x-ray beam it was seen to decay quite rapidly. As has been discussed in these films no nanocrystals were observed, only amorphous nanoclusters. Hydrogen passivation of the samples is therefore considered key in order to remove non-radiative defect states from the films. Initial passivation is obtained from bonding with residual hydrogen in the deposition chamber or through the incomplete disassociation of silane, as evidenced by the FTIR spectra. Increased PL is then observed through a combination of nanocluster formation and hydrogen passivation within the films, as has been discussed in this and the previous chapter.

Under X-ray excitation Si-H bonds may be broken. The use of UV-irradiation to break and remove hydrogen from a SRSO sample was used in [75] in order to analyze details of the luminescence. The high flux and energy of the synchrotron beam can easily be expected to produce the same result, although in a localized area⁵¹. In this case the

⁵¹ In fact PL studies of the luminescence from these samples after XAS shows 2 localized 'dead' areas, one where the sample was aligned under the zero order beam, and one where the XAS measurement was taken. If a simple method of measuring these areas could be found one could, in principle, obtain information regarding the signal generation area for comparison with the slit settings at the beamline. The difficulty in measuring the areas is that there is no change in the sample visible to the naked eye, only when the areas are passed under a UV-laser source.

<u>PhD Thesis – T. Roschuk</u><u>McMaster University– Engineering Physics</u> number of radiative nanoclusters in the films rapidly decreases and eventually XEOL from the samples is lost. For this reason over the course of a XAS scan the PLY from a sample can have degraded before the scan approaches an absorption edge. Even had the scan been started at the edge the XEOL will have been lost within the first couple of data points and even measurements conducted at select energies could not be reasonably compared.

Similar problems were not observed in SRSO samples where nanocrystals are known to form. In such a case, however, it is possible that the observed XEOL is only from Si-ncs that did not require H-passivation to be optically active. To the author's knowledge there are no studies of the PLY and XEOL behavior of SRSO samples containing only a-Si-ncs, however, given the importance of hydrogen passivation to the luminescence of such a system, a study of this nature could confirm the breaking of H-bonds as the source of XEOL decay. Similarly, if Si-nanocrystals can be formed in future deposited SRSN films (either as-grown or after annealing) then one could expect an observable PLY. On this note, recent work using a PECVD system to fabricate SRSN materials (led by Patrick Wilson) has produced some samples using NH₃ as the nitrogen source, which has been seen in the literature to lead to *in-situ* nanocrystal formation [80]. The structure of these films still requires investigation to confirm whether nanocrystals have indeed formed.

It is interesting to note that after the XEOL from the sample had decayed, if the X-ray beam is turned off and then back on the XEOL is observed to partially recover,

<u>PhD Thesis – T. Roschuk</u> <u>McMaster University– Engineering Physics</u> suggesting that not all of the hydrogen has diffused out of the sample and that some may be reincorporated. The degree to which the XEOL recovers is dependent on the amount of time that the sample had been exposed to the X-ray beam. Furthermore, the decay of the PL signal from SRSO films under a UV-laser with time has been observed in [23],

which may be due to a similar effect.

6.1.5 A comparison of ICP-CVD, ECR-PECVD, and PECVD-grown SRSN

Structure and photoluminescence from SRSN samples has so far been discussed only for the case of the ICP-CVD system. In this section the luminescence and structure of SRSN samples grown using two other deposition systems will be presented for comparison with the results from the ICP-CVD system. The intent here is not to perform a comprehensive analysis of the results from these other systems, but rather to illustrate that similarities and differences appear in the PL and structure of these films depending on the method of preparation. A full comparison of the effects of fabricating SRSN thin films using different methods is the subject of a current, ongoing research project.

The PL for the as-grown PECVD (Table 5.4 on pg. 162) and ECR-PECVD (Table 5.3 on pg. 161) samples is shown in Figure 6.26. PL for the ICP-CVD samples was shown in Figure 6.2 on pg. 173. The PL spectra show similar characteristics between the three systems. Only in samples with low excess Si is a high energy shoulder observed. Unlike what was observed for sample T016 none of the samples grown using the PECVD or ECR-PECVD system exhibit luminescence where this high energy shoulder is the dominant emission from the samples. While a substantial decrease in intensity was

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 observed for the most Si-rich samples grown using the ICP-CVD system, neither the

 PECVD or ECR-PECVD system show as large a decrease. In fact, the emission

 intensities are comparable for both of the ECR-PECVD samples considered here.



Figure 6.26: PL Spectra for the as-grown (a) PECVD and (b) ECR-PECVD films. As with the ICP-CVD grown films the PL peak position red-shifts with increased Siconcentrations.

The Si *K*-edge XANES is shown for the as-grown PECVD samples in Figure 6.27. Figure 6.28 shows the $L_{3,2}$ edge structure after annealing for sample TFNH3-11. For the as-grown samples the XANES at the Si *K*-edge is as one would expect for homogenous RBM type structures, extending to lower energies as the Si-concentration is increased. At the $L_{3,2}$ –edge a defined Si-Si₄ related bonding peak can be seen at 99.5 eV, even for the case of the as-grown sample. As the film is annealed the structure at the Si-edge is observed to become more defined. It is possible that Si-nanocrystals are present in these films, however, this has yet to be confirmed with XRD or TEM-based measurements.





Figure 6.27: Si K-edge XANES for the PECVD as-grown samples⁵². As the Siconcentration of the films is increased there is an increase in Si-Si bonding.



Figure 6.28: Si $L_{3,2}$ -edge XANES for the annealed sample TFNH3-11. In contrast with the ICP-CVD grown films a prominent Si-Si₄ related shoulder is observed in the spectra after annealing.

⁵² The Si₃N₄ reference sample shown here was grown with the ICP-CVD system. The noise seen in the spectrum is an issue with the beamline during this run and not due to issues with the samples.

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Finally, the Si $L_{3,2}$ -edge XANES is shown in Figure 6.29 for the ECR-PECVD samples. Here the TEY must be used, as the films are thinner and the FLY signal is dominated by the substrate. We can see that at the Si-Si₄ edge a shoulder is apparent for sample SRSN4, the more Si-rich of the two. Conversely, the Si-N peak is not readily seen in this more Si-rich sample, however, the lack of structure in this region (104.5 eV) was previously shown to occur for the ICP-CVD grown samples as the samples became more Si-rich. Note that the refractive index for ECR-SRSN4 was 2.32, indicating that the sample is quite Si-rich in comparison with the ICP-CVD grown samples. Given that for samples T018 and T026, the most Si-rich ICP-CVD grown samples, the PL intensity was quite low it is interesting that PL is observed at all for ECR-SRSN4.



Figure 6.29: Si $L_{3,2}$ XANES for the as-grown ECR-PECVD samples. A clear shoulder is observed at the Si-Si₄ edge for sample SRSN4, the more Si-rich of the two samples.

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Some of the structural differences between samples grown using different deposition systems have been outlined here along with some of the differences in the luminescent nature of these films, even though the luminescent signals have similar qualitative features. As mentioned previously, the results are not intended to be comprehensive, simply to illustrate that such differences exist and that further study is necessary in order to determine how these structural differences correlate with the observed luminescent nature of the films. Such work is particularly necessary if these materials are to be used for device fabrication, where consistency will be required. The analysis of XANES for even this limited set of samples demonstrates that XAS has substantial potential to resolve issues related to these differences. Additional work is required in this area for all forms of luminescent Si-based materials where a range of results exist.

6.1.6 EFTEM Imaging and EELS of SRSN Thin Films

STEM ADF images of sample T016 and T026 are shown in Figure 6.30. Note the presence of dark spots in the images. EELS scans conducted over these regions show a decrease in the overall EELS signal. The results are consistent with what one would expect in an area of lower density. Recall that contrast in the annular dark field is primarily Z-contrast. Z-contrast is however, not particularly intense between elements of low atomic number. However, if there is a significant variation in the density of two regions, as can be expected to occur between Si_3N_4 and Si, one can expect more

PhD Thesis – T. Roschuk McMaster University– Engineering Physics scattering elements in the dense region, resulting in the increased (brighter) signal for the denser medium. In such a case the dark regions could potentially be attributed to the Si ncs. It can also be seen that the darker regions are larger in sample T026, as one would expect since it is the more Si-rich of the two. In a SRSO thin film no such contrast has been observed in the Si-nc regions in the ADF images. ADF images.



Figure 6.30: STEM images illustrating the presence of *a***-Si nanoclusters in SRSN systems.** Shown are sample T016 annealed at 700 °C (left) and sample T026 annealed at 1100 °C (right). The Si-substrate appears as the white area on the right in the right hand picture. The red arrows highlight features examined in more detail using EFTEM.

Although this is a compelling line of thought, as it would indicate that STEM alone provides a reasonable method to determine the presence of *a*-Si-ncs for SRSN materials, one should not be too hasty in making the association between a low density region and the presence of Si-ncs. I have been critical of work where contrast is assigned

PhD Thesis – T. RoschukMcMaster University– Engineering Physicsto Si-ncs without a reasonable justification and the same caution must be exercised here.One notes that in the images above the Si substrate appears brighter than the Si $_3N_4$, eventhough Z-contrast from the substrate should be comparable to that of the Si-ncs. Althoughin the ADF Z-contrast is the dominant mechanism of contrast there may also be somediffraction contrast contributing to the Si signal. Let us then consider EFTEM for theseregions in order to determine if a more substantial assignment can be made. Figure 6.31shows an EFTEM image extracted at the Si plasmon energy from the signal integralregion (the rectangular gray box) shown in Figure 6.30 for sample T026. Si-ncs willappear lighter in these images. The Si plasmon intensity in the Si-rich regions is quitesmall and it is just possible to make out all four of the spheres. Furthermore, it is apparentthat the host matrix still remains partially Si-rich.



Figure 6.31: An EFTEM image extracted from 14.3-18.2 eV. The image contrast has been adjusted in order to better illustrate the Si-rich regions in the films. The Si-substrate is on the right.

There is cause for both optimism and pessimism with these results. On the one

hand, it is clear that the regions are Si-rich confirming that they are Si-ncs. On the other hand, the result is difficult to attain. The Si-plasmon provides only a marginal increase over the background nitride plasmon. The extraction of such an image is strongly dependent on background fitting in order to extract the Si-plasmon. The TEM samples

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 were, however, thick in this region. It is possible that with further work thinning the samples the Si-plasmon would become more prominent.

EELS analysis of the Si $L_{3,2}$ edge in these films, shown in Figure 6.32, showed only a slight Si-shoulder though, another reason for not being too optimistic about the result. Again, this may, however, be due to the thickness of the films. As was seen in XAS, the Si-Si₄ signal can be difficult to resolve. The EELS spectra do show, however, that within the films no clear Si-O bonding signal is observed, confirming that the oxide signal seen in the XAS data likely arises primarily from the surface of the films.



Figure 6.32: EELS spectrum from sample T026 annealed at 1100 °C. A small edge, associated with Si-Si bonding, is seen at ~99 eV. The spectrum shows no evidence of Si-O bonding within the film itself.

6.2 Silicon Oxynitrides

One of the goals in fabricating SiON films was to tune the influence of defect states related to nitride or oxide bonding in order to assess their contributions to the observed PL. To do so the SRSN film with the bluest emission was used as a baseline material, as the Si=O double bond exhibits a red to near-infrared emission, which should make the PL between nitride and oxide defects distinguishable. As with the SRSN thin films no evidence of Si-nanocrystal formation has been observed in the SiON samples considered in this work, however, only a single sample was prepared for TEM analysis. As will be shown XAS measurements do not indicate the presence of Si-clustering in this set of films, a detail that will be considered from a structural aspect. In spite of this, luminescence was observed for the SiON films.

The XANES at the Si *K*-edge for sample T028 is shown in Figure 6.33 while that at the Si $L_{3,2}$ edge is shown in Figure 6.34. For annealing temperatures up to 1100 °C the spectra show that the film is tending towards the formation of a homogenous silicon oxynitride, with a shift towards Si-O bonding. At 1200 °C a sudden change in the structure is observed and the edge structure again resembles that of a silicon oxynitride. At this temperature there may be a phase change in the film, resulting in the sudden reobservation of a more characteristic nitride phase. Results at the $L_{3,2}$ edge show the same type of behavior. In neither case is a separate phase related to Si-Si₄ bonding clearly observed.





Figure 6.33: Si *K*-edge XANES for sample T028. The evolution of structure up to 1100 °C is shown in (a) while the effects of annealing at 1200 °C are shown in (b). The inset in (a) shows the Si-shoulder region to illustrate that although a Si-shoulder appears to be present for the sample, its intensity is below that of the stoichiometric Si_3N_4 reference sample.

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Figure 6.34: Si $L_{3,2}$ edge XANES for sample T028. The spectra show the evolution of film structure with annealing. No evidence of Si-Si bonding is observed in the spectra and structural changes within the film relate primarily to Si-O and Si-N bonding.

The $L_{3,2}$ XANES for sample T017, which was grown under similar conditions to T028, is shown in Figure 6.35⁵³. Differing XANES can be expected between the two samples for three reasons. One is the slightly differing growth conditions; the second is some inhomogeneity of the samples, as discussed for the SRSN films. Finally, sample T028 was annealed along with the thick SRSN samples. Possible issues related with the

⁵³ The conditions were intended to be the same, however, for sample T028 the mass flow controllers began to have difficulties maintaining a stable oxygen flow rate. The flow rate was increased to a stable value before the deposition was started.
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annealing treatments, such as the oxidation effects observed for the SRSN samples, can be expected to influence the results. Nevertheless, the behavior of the samples is similar, yet, for T017 the peak related to Si-N bonding is not seen to reduce to the same degree as that which was observed for sample T028. The differing behavior between the films is exemplified through the analysis of the lower energy peak of the Si-O related doublet. For sample T028 one can see that this peak is increased in intensity as the Si-N related bonding peak is reduced. The peak is suddenly reduced in intensity after the 1200 °C anneal and a distinct Si-N related peak is observed. This behavior is not seen at all for sample T017, where the oxide and nitride peaks retain a more distinct character.





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For sample T028 these results indicate that with annealing up to 1100 °C the sample is tending towards a homogenous SiON structure, skewed towards an oxide. After annealing at 1200 °C the sample breaks down and separate Si-N and Si-O phases form. Only through the analysis of both the K and L-edges is the complete picture of the phase separation seen, as at the K-edge separate peak structure is not clearly resolved.

The behavior of sample T028 at the O and N K-edges is shown in Figure 6.36. At low anneal temperatures there is a decrease in the absorption at the N K-edge, however, it is not too substantial. At anneal temperatures greater than 800 °C a large drop off is seen in the intensity of the nitrogen edge. After a 1200 °C anneal only a weak broad edge is seen which correlates with the decreased intensity the Si-N related peak seen at the Si-edges. Although the behavior at the Si-edge seems to indicate the formation of an oxynitride phase, no clear resonant line associated with N-dangling bonds is observed indicating that nitrogen is not incorporating substitutionally for O within the matrix.

At the Si-O edge there is an initial increase in the absorption with annealing up to 700 °C. At higher anneal temperatures absorption at the edge decreases, approaching the same intensity as was seen for the as-grown case. At the higher anneal temperatures a low energy tail forms. The tail decreases with annealing up to 1100 °C and then increases substantially. The tail correlates with the structural reordering of the films observed at high temperatures and may be associated with the presence of O-N bonds.





Figure 6.36: N and O K-edge XANES for sample T028. (a) N K-edge and (b) O K-edge.

FTIR spectra are shown for sample T017 in Figure 6.37. The data in the FTIR plots reflects that of the XAS data. A main broad absorption peak, from ~800-1100 cm⁻¹, is seen in the spectra. The peak is a convolution of Si-O (1050 cm⁻¹) and Si-N (890 cm⁻¹) absorption bands. With annealing, increases are primarily seen in Si-O related absorption peak, however, a Si-N related peak is always apparent in the spectra. The results show that in the case of T017 the Si-N and Si-O related phases appear to remain distinct, in contrast to T028 where a Si-O-N related structure appears until annealing at 1200 °C.



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Figure 6.37: FTIR spectra for sample T017 annealed at the temperatures shown. Difference spectra between the annealed and as-grown sample are shown in the bottom plot illustrating the increase in Si-N and Si-O bonding with annealing.

H-bonding in the films (not shown) was found to be primarily in the form of N-H bonding. No clear peak associated with Si-H bonding was observed. The N-H related peak was found to disappear at 800 °C, reappear at 900-1000 °C, and then to disappear again. The results may be due to variations in diffusivity of H with temperature or

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 variations in the gas flow during the anneal process and further reveal the need for a controlled analysis of hydrogen incorporation in these materials.

Through the combination of XAS data it is now possible to consider the observed PL from these samples and to attempt to determine their correlation with the structural properties. The PL for sample T017 is shown in Figure 6.38. A bright broad PL is observed for the as-grown samples. The PL is primarily the result of defects within the as-grown films, however, one can see similar elements to the spectral shape as for the annealed samples. With annealing the PL decreases. At 1000 °C the PL then begins to increase again, peaking at 1100 °C before dropping off at 1200 °C. The PL slightly redshifts from the as-grown case with the initial annealing and then blueshift with annealing at higher temperatures. The decrease in PL at 1200 °C is associated with the phase separation that occurs in the films resulting in the presence of distinct Si-N and Si-O related bonding peaks. At this anneal temperature only a weak PL remains, possibly associated with oxide or nitride defects. With annealing up to 1100 °C one can see in the XANES spectra that the sample is tending towards a more homogenous SiON structure. There is no clear method to distinguish whether the peak is associated with Si-N or Si-O bonding, as there are defects in this energy region associated with luminescence from these materials.



Figure 6.38: Photoluminescence spectra for sample T017, a SiON sample, annealed at the temperatures shown.

PL from the thicker sample T028 is shown in Figure 6.39. A significantly different behavior is seen with annealing in comparison with sample T017. Note that the PL from the thicker samples is blue-shifted in comparison with the thin film T017. At low anneal temperatures there is a moderate increase in the PL. After annealing at 700 °C the PL decreases. The PL is substantially reduced at 800 °C and is only just detectable at higher anneal temperatures. One can see that a similar trend is observed for both the N and O *K*-edges (Figure 6.36). Analysis at the Si *K*-edge (Figure 6.33 on pg. 234) shows that this behavior is also well inversely correlated with the evolution of the Si-related structure in the film. At 600 °C the peak intensity of the Si-O_xN_{4-x} bonding structure increases in intensity, indicating that more Si bonds with both O and N atoms are forming, likely as a

PhD Thesis – T. RoschukMcMaster University– Engineering Physicsresult of a reordering from the as-grown case to a more homogenous SiON film. Afterannealing at 700 °C one can see that there is a decrease in the peak intensity, after whichthe XAS peak begins to increase again and shift towards the Si-O peak position.Similarly, the trend follows the loss of Si-N related structure at the Si $L_{3,2}$ -edge (Figure6.34 on pg. 235). Finally, we see for the sample that the peak intensity also follows thebehavior of the N K-edge (Figure 6.36), being almost absent after annealing attemperatures of 900 °C or higher. The PL from this sample can be seen to be similar innature to that of some of the SRSN films and is more blueshifted than that of sampleT017.



Figure 6.39: Photoluminescence spectra for sample T028. (a) Low and (b) high anneal temperatures. The PL spectrum for the as-grown sample is shown in (b) for reference.

While the goal was to form SRSON materials for this work to try and tune the emission from these samples, in hindsight, the lack of Si-nc formation films could have been predicted. By choosing the bluest emitting silicon nitride in order to try and optimize the analysis of defect PL emission, the samples with the least excess Si were chosen. The introduction of oxygen into the system sets up a scenario where this excess Si can be easily depleted within the films. Nevertheless, PL was observed in the films and has been attributed to the presence of defect states within the film structure.

6.3 Rare Earth Doped Silicon Oxides

The luminescent behavior of the Ce and Tb-doped samples considered in this work has been previously reported and was discussed in Chapter 2 [38]. Of particular interest is the differing nature of the luminescence observed between SRSO and ORSO samples. This section will begin with a discussion of the SRSO and ORSO Tb-doped films and will conclude with a discussion of the ORSO Ce-doped sample.

The discussion in this section will proceed in a manner different from the previous two sections. While little or no XEOL and PLY were observed for the SRSN and SiON samples, strong signals were seen for the RE-doped samples. This section will focus less on the XAS structure of these films and its correlation with the luminescence properties, and more on the site specific excitation that can be performed with XEOL.

6.3.1 Tb-doped SRSO and ORSO

XAS spectra for the as-grown Tb-doped samples are shown in Figure 6.40. Recall that sample Tb012 is the only SRSO, while Tb015 and Tb016 are ORSO samples, with Tb015 containing more Tb. The figures show both the TEY and PLY for the samples. The PLY signal has been renormalized in order to better allow for the comparison of spectral features. It should be noted that although the detector used for collecting XEOL and PLY was cooled there is a thermal drift in the PLY over the course of a scan. This can lead to artifacts in the PLY spectrum. In cases where peaks are observed the XEOL spectra will be considered in order to illustrate that a resonant excitation of luminescence has or has not occurred.

One can see immediately that the two materials behave very differently. In the SRSO material only a weak resonance is observed near the Si-O related edge and just beyond the M_5 edge. These resonances will be reconsidered in a moment. In both ORSO films a strong resonance is seen at both the Si-O related peak and the O *K*-edge. Some resonance with the Tb M_5 -edge for sample Tb016 is also seen, however, this too will be reconsidered in a moment.

The Tb $M_{5,4}$ peak structure is similar for all samples, indicative that Tb is in the luminescent 3+ state through comparison with the spectra shown in Figure 4.6 on page 118.

In all of the Si K-edge spectra a peak associated with Si-Si₄ bonding may be seen. This is a result of the thinness of the films, resulting in a contribution to the XAS signal

PhD Thesis – T. Roschuk McMaster University– Engineering Physics from the substrate. As such it is not possible to easily analyze changes in the Si bonding structure for this particular set of films. Nevertheless, the presence of a peak here provides a clear reference for analysis of resonant XEOL excitation at Si-related energies.

One can see that similar behavior is observed for the two ORSO samples in the as-grown case. As such, for simplicity, it will suffice to discuss the behavior of sample Tb016 in comparison with sample Tb012 in order to resolve the differing nature between ORSO and SRSO samples. Details of the comparison between the two ORSO samples, which relate to differing film compositions and Tb concentrations, will be discussed outside of this work.





Figure 6.40: TEY and PLY-XANES spectra for as-grown Tb-doped samples. (a) Tb012, (b) Tb015, and (c) Tb016. The extensions, .1, .2, and .3, refer to the Si K-edge, the O K-edge, and the Tb $M_{5,4}$ edges, respectively. The spectra are offset for clarity.

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Let us now consider the XEOL spectra at the resonant energies observed for the two samples. Furthermore, XEOL spectra will also be shown at key excitation energies regardless of whether a resonant peak was seen or not. These include the Si-Si₄ peak (1840 eV), the Si-O₄ peak (1847 eV) and at the Tb edges (1244 and 1276 eV). At the Si-Si₄ edge, 1840 eV is used instead of 1839 eV in order to insure that we are just beyond the onset of the edge, which can shift as a result of quantum confinement.

Figure 6.41 shows the XEOL spectra at the energies indicated for the as-grown sample Tb012. One can see that there are no excited luminescence peaks. Several features, seen across all XEOL spectra (sharp lines), are artifacts of the CCD detector. As the PLY is the integral of the XEOL signal the lack of any clear luminescence peaks illustrates that peaks in the PLY for this sample are primarily an artifact of the detector, likely arising due to the charging of certain pixels which produces the sharp lines seen in the spectra. Thus, for the as-grown sample Tb012 there are no identifiable resonant luminescent peaks. This corresponds well with the PL behavior of the sample, which showed no significant luminescence in the as-grown case.



Figure 6.41: XEOL spectra obtained at the energies shown for the as-grown sample Tb012. In the as-grown sample no Tb-related XEOL is observed.

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XEOL spectra for the as-grown sample Tb016 are shown in Figure 6.42. In contrast to the SRSO sample one can see that the excitation energies examined here lead to the characteristic emission from Tb ions. XEOL is most efficiently excited at the O K-edge⁵⁴. There is, therefore, a Tb-O related complex formed in the as-grown film. Weak excitation at the Si-Si₄ edge and a stronger excitation at the Si-O₄ peak indicate that the chemical structure responsible for the luminescence has some Tb-O-Si character. The structure may then be related to the formation of a Tb-silicate or a Tb-oxide structure within the films. Although the exact complex is not yet known the results definitively demonstrate that it is not related to Si-nc excitation but is instead closely tied to a Tb-O related structure. Tb-O₆ (Tb coordinated with 6 O atoms) has previously been found to lead to an enhanced Tb-emission and has been suggested as a possible reason for the observed luminescence in these samples [120].

The XEOL spectra, excited at 540 eV, for sample Tb016 annealed at 700 and 1100 °C are shown in Figure 6.43. After annealing at 700 °C the brightest PL was observed from this sample. Similarly, the brightest XEOL is observed after excitation at 540 eV for the sample annealed at 700 °C. The increase in both PL and XEOL can then be tied to a structural reordering of the film, increasing the number of Tb-oxide bonds and likely forming more Tb-O₆ complexes. Annealing at higher temperatures leads to a dissociation of the Tb-O₆ complexes, potentially forming Tb-O₂ structures.

⁵⁴ Although the plots are not on the same scales this is evident from the greater SNR observed after excitation at the O K-edge.

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Figure 6.42: XEOL spectra obtained at the energies shown for the as-grown sample Tb016. Tb-related luminescence peaks are clearly observed in the spectra and are most efficiently excited at O-related energies.



Figure 6.43: XEOL spectra excited at 540 eV for sample Tb016 after annealing at the temperatures shown. The decrease in XEOL is associated with the dissociation of luminescent Tb-O₆ structures at high anneal temperatures.

The results so far have shown that Tb ions incorporated in ORSO films are efficiently excited due to the formation of Tb-O related complexes. Although possible sensitizers have previously been sought in order to try and interpret the Tb-luminescence in these films, it is possible that these complexes are directly excited during the PL process. The results yield a second possibility, however, as Tb luminescence was also efficiently excited at Si-O related energies. Although the Tb-O₆ complex may be the luminescent center, one should also consider the second nearest neighbors which are
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 likely to be Si atoms given the structure of the films. In such a scenario the sensitization

 mechanism can be through excitation of Si-O related bonds.

Having demonstrated that luminescence in the Tb-doped ORSO sample is tied to a Tb-O related phase let us now return to the Tb-doped SRSO sample. In Tb012 little luminescence was seen prior to annealing at 1100 °C. At this anneal temperature luminescence associated with Si-nanocrystals formed in SRSO materials was seen. Only after annealing at 1200 °C was a luminescence associated with Tb³⁺ observed. In the XAS-PLY and XEOL spectra no resonant behavior or luminescence (either from Si-ncs or Tb) was observed at any of the edges considered for this work. It is, therefore, not possible with this film to discuss the nature of the Si-nc luminescence. The TEY and PLY XANES for the sample annealed at 1200 °C are shown in Figure 6.44. We see here an interesting result, although the film is Si-rich, the PLY is closely tied to O-related edge structures. The results indicate that luminescence from Tb in Si-based materials is tied to the formation of Tb-O related complexes. In an ORSO sample such structures are easily formed due to the abundance of O-atoms in the host matrix, being present even for asgrown films. In the SRSO samples, however, it is more difficult for such structures to form, as Si-O bonds must be broken. Only at sufficiently high anneal temperatures does a structural transformation occur resulting in a luminescent Tb-related phase.



Figure 6.44: TEY and PLY XANES for a Tb-doped SRSO sample annealed at 1200 °C. The data is shown at the O (top) and Si (bottom) *K*-edges. The PLY is strongly resonant with O-related energy states.

At high temperatures quenching of the luminescence attributed to Si-ncs was simultaneously observed with an enhancement of the Tb luminescence. There are several aspects related that must be considered. The first is that the excess Si in this film was insufficient to observe Si-nc related XEOL from these samples. As the Si-ncs were not efficiently excited it is not possible to say that there is no energy transfer from Si-ncs to the Tb-ions. Secondly, the formation of Tb-O related structures must result in a PhD Thesis – T. Roschuk McMaster University– Engineering Physics

significant disturbance of the host structure, particularly when Tb-O₆ complexes are formed. Such behavior may require the breaking of Si=O double bonds to which the NIR PL is attributed. In such a scenario luminescence from the Si-ncs may be quenched or could shift to the blue, as the main defect responsible for the NIR emission is now removed. This would then explain the broad background underneath the Tb-related emission for this sample (Figure 2.16, page 70) which could arise directly from the Si-ncs. Although the energy of the Si-nc emission in this case would be sufficient to excite the Tb-ions, the PLY and XEOL results show that Tb luminescence is primarily related to the formation of Tb-O structures.

Luminescence from Tb-ions is, therefore, definitively tied to an oxide related structure in both ORSO and SRSO materials. In ORSO materials the excess oxygen in the matrix leads to the formation of such structures in the as-grown film. In an SRSO film the formation of such structures occurs only after annealing at high temperatures. The influence of Si-ncs on Tb-luminescence of SRSO films has, however, not been completely resolved. While they may act as sensitizers, they are likely sensitizers of Tb-O related complexes, not directly of the Tb ions.

6.3.2 Ce-doped ORSO

The XAS spectra for sample Ce031 at the Si and O K-edges and the Ce $M_{5,4}$ edge are shown Figure 6.45. The Si K-edge signal at 1839 eV observed in (a) is likely from the substrate due to small thickness of the film. At 1850 eV a peak is observed in the TEY-XAS signal which is not related to Si-Si or Si-O related bonding structures. This peak is PhD Thesis – T. RoschukMcMaster University– Engineering Physicsassociated with Si-Ce related bonding, clearly indicating that a Ce-silicate has formed inthe films. The Ce $M_{5,4}$ TEY-XANES is indicative of the Ce in this sample being primarilyin the luminescent 3+ state.

The PLY can be seen to be strongly resonant with the XANES only at the O *K*-edge. Although there appears to be some resonant luminescence at the Si and Ce edges, this is in fact largely an artifact arising from drift and charging in the detector over the course of a measurement. This is confirmed by looking at the XEOL spectra at select resonant energies near and at the edges, as is shown in Figure 6.46. Efficient XEOL is observed only for resonant excitation at oxygen related energies, including excitation at the Si-O edge, although the XEOL signal is quite weak at this edge.



Figure 6.45: XAS spectra for Ce-doped ORSO annealed at 1200 °C. TEY and PLY signals at (a) the Si-K-edge (b) the Ce $M_{5,4}$ -edge, and (c) the O K-edge. The PLY signal has been renormalized to allow for comparison with the XAS peaks.



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Figure 6.46: XEOL spectra for Ce-doped ORSO annealed at 1200 °C. The spectra have been collected at the energies indicated near the (a) the Si *K*-edge (b) Ce $M_{5,4}$ -edge, and (c) O *K*-edge.

The results indicate that Ce-luminescence in these samples is related to the formation of an oxide related phase which is consistent with the previous results ascribing the luminescence to the formation of a Ce-silicate [38]. Note that Ce-luminescence is not even efficiently excited directly, indicating that it is the formation of such an oxide structure that is closely tied with the origin of luminescence in these samples. The results are similar to those observed for Tb, however, the lack of a Ce-doped SRSO for

PhD Thesis – T. Roschuk McMaster University– Engineering Physics comparison means that additional work is required to determine if Ce-doped SRSO luminescence is also strongly related to the presence of an oxide related structure.

Similar behavior has been observed at the Si $L_{3,2}$ edge, not shown here, where there is no efficient excitation of the Ce at the Si-Si₄ edge while a weakly excited XEOL signal is seen at the Si-O related edge.

The results demonstrate unambiguously that the luminescence does not originate from the presence of Si-ncs too small to clearly detect by techniques such as HREM. Although such a result has not been confirmed for Er-doped samples, the results demonstrate that in principle oxide related energy states are capable of leading to luminescence in these materials.

With a larger data set it should become possible to unambiguously determine the origin of luminescence in RE-doped samples and to determine differences in Ce-doped SRSO and ORSO materials. The Ce-data presented here is only an extremely limited data set yet it demonstrates that the technique is quite powerful in this area.

Chapter 7: Conclusions and Future Work

7.1 Structure and Luminescence of the Silicon Nitrides

Using XAS the local chemical environment and electronic structure of luminescent Si-nanostructure embedded materials has been analyzed as a function of thin film composition and annealing parameters. Analysis of the XANES at the Si *K* and *L*-edges has shown that as the Si concentration of the films is increased there is in an increase in Si-Si related bonding, however, the film has primarily a RBM like structure. After annealing evidence of a phase separation of the films into Si-ncs embedded within a Si₃N₄ has been shown. The anneal temperature at which the phase separation onsets is dependent on the film composition, occurring at lower temperatures in more Si-rich films. Analysis of the XANES and FTIR spectra has been used to illustrate the reordering of the silicon nitride host towards a stoichiometric Si₃N₄ structure.

PL observed from these samples has a complex nature, being associated with the presence of several types of defects. As the films are annealed all samples show an initial increase in luminescence. This behavior is associated with the structural reordering of the nitride host, removing defects, along with the onset of phase separation of Si and Si₃N₄. There is a general shift of the PL to higher energies with decreasing Si concentrations, leading to the observation of higher energy radiative defect states. Analysis of the PL and

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 XAS data suggests that the luminescence originates from confinement in Si-rich regions

 and Si-ncs but proceeds through recombination at defects.

7.2 Structure and Luminescence of the Silicon Oxynitrides

Two SiON films (one thick and one thin) were analyzed in this work. Through the use of XAS and FTIR spectroscopy it was found that with annealing the films tend to form a RBM like oxynitride structure, however, in this structure, a substantial increase in Si-O bonding was found.

Through the analysis of the structural evolution of these films it was possible to determine how the luminescence from these samples correlates with changes in the host structure. PL from the samples showed primarily a single sharp blue emission band, although the nature of the peak was found to differ between the two samples. The SiON films analyzed here had low excess Si-content, a result of their deposition conditions, and XAS data shows no evidence of Si-Si₄ related bonding. It is, therefore, unlikely that PL from these samples arises due to quantum confinement, but rather is through the excitation of defects in the SiON matrix. The production of an oxynitride phase with annealing in these samples was found to quench the PL of a thick sample, likely due to the removal of nitrogen related states through which the recombination occurs. In a thin film it was not possible to determine whether the PL was tied to the oxide or nitride phase as the PL correlates with changes in both phases. As the thin film had less oxygen than

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 the thicker film, it is likely that the luminescence in the sample is associated with the Si

 N related defects.

7.3 Structure and Luminescence of the RE-doped oxides

Through TEY-XANES, PLY-XANES, and XEOL the luminescent nature of rare earth doped materials was studied. Luminescence from Tb was found to be strongly related to the formation of Tb-oxide structures, even for the case of an SRSO film. In the ORSO films such structures form in the as-grown film due to the abundance of excess oxygen while in the SRSO films a high temperature anneal is needed in order break Si-O bonds to form Tb-O complexes. The exact influence of Si-ncs on the luminescence remains unknown, however, the results demonstrate that Tb luminescence is primarily related to the formation of Tb-oxide complexes and not due to direct excitation.

In a Ce-doped ORSO film similar behavior to the Tb-doped ORSO was found, that being that the luminescence was strongly related to the formation of oxide related complexes. Evidence of Si-Ce related bonding was also seen, suggesting the formation of a Ce-silicate. The incomplete nature of the Ce-doped sample set means, however, that future work is required before definitive conclusions can be drawn as to the comparative nature of Ce-doped ORSO and SRSO.

7.4 Future Work

A controlled study of hydrogen incorporation within sets of thick and thin films and a comprehensive study of hydrogen diffusion in the nitrides with annealing are necessary.

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Although H-passivation has been seen to lead to an increase in the PL in comparison with annealing in a pure N_2 ambient, the specific details of H-incorporation have not yet been considered. Of course, this is an area where the details will be system and material dependent, but such only highlights the need for cross-system comparison in order to develop consistency in interpreting results between different groups.

In order to obtain SRSON thin films it will be necessary to increase the silane flow to add more Si to the films, as the oxygen flow cannot be lowered any further without experiencing instability in the flow rates. This creates a scenario where extensive calibration will be required. Furthermore, among the samples grown for this work, luminescent SRSN samples were only produced under low silane flow/growth rates. As such the change in silane flow, which has a significant impact on the growth rate, may have significant consequences for the fabrication of luminescent SRSON films and may impact the ability to tune the relative contributions to the PL from N and O-related defects. An alternative possibility is to intentionally attempt to oxidize the samples during the anneal process to introduce O-related defect states to the film.

As mentioned several times in the text it has long been known that the behavior of these materials is strongly system dependent. The results that have been discussed so far in the literature have focused on sputtering vs. PECVD of SRSO thin films. Because the nitride host matrix acts as limiting factor in how SRSN thin films can evolve one can expect that the deposition method for SRSN thin films may play an even stronger role. Regardless of whether the focus is on SRSO or SRSN thin films XAS provides a unique

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method through which the details of the phase separation process can be clearly analyzed. Furthermore, ion implantation has not yet been analyzed in these schemes. A comparative study of PECVD-based, sputtered, and ion implanted SRSN films would greatly enhance the understanding of the system dependence of SRSN materials.

XAS reflects the DOS of the conduction band. This has yielded information on the electronic structure of this band and details of the local bonding environment of the constituent atoms of these films. X-ray emission spectroscopy (XES) is a complementary technique to XAS. In XES, a fixed excitation energy is used in order to excite an electron from a core shell. As the material then relaxes and high level electrons drop down to fill the vacancy left by this excitation they release their energy in the form of X-rays. As with the X-rays absorbed during XAS, these X-rays have characteristic energies related to the electronic structure of the materials. In this case the emission spectrum structure reflects the DOS at the valence band edge of the material, not the conduction band. The complementary nature of these two techniques can, therefore, be used to provide a more complete picture of electronic band structure of these materials.

XAS research on the rare earth doped samples has only just begun. The results discussed in this work illustrate that the nature of luminescence, details of rare earth incorporation, and information on the thermal evolution of RE doped films are complex subjects and the nature of luminescent sites for the RE-ions is often not fully considered. Here the luminescent sites for Tb, and to a lesser degree Ce, were shown to depend on the presence of RE-oxide structures. Further work is required to expand on the results

<u>PhD Thesis – T. Roschuk</u><u>McMaster University– Engineering Physics</u> presented here to provide a more complete understanding of these materials⁵⁵. If the oxide complex is indeed significant for the luminescence of Tb in Si-based materials this raises the question of what will occur in RE-doped SRSN materials. To date rare earth doping has been primarily explored for silicon oxide based films. In silicon nitrides, reports are just now being presented on Er incorporation, however, other rare earths remain to be explored. Using the ECR-PECVD system at McMaster there are no technical barriers to the fabrication of RE-doped nitrides.

Finally, if Si-nc based light emitters are to be used in optical interconnect schemes for integrated photonics more work is needed in the area of actually integrating these materials into devices. The Ph.D. work of J. Milgram presents some of the first work in this area [23, 34, 203]. In that work the coupling of luminescence from a Si-nc layer to a silicon nitride waveguide was studied. There is still vast room for studying the electronic and electroluminescent properties of these materials if an electrically pumped device is to be made.

⁵⁵ Work in this area is already planned. At the time of writing two proposals to the Canadian Light Source focused primarily on the study of RE doped systems will remain active allowing for a substantial extension to the work that has been done thus far.

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