MAGNETRON SPUTTERING APPLIED TO THE DEPOSITION OF SILICON-RICH SILICON OXIDE THIN FILMS

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ABSTRACT

The technique of magnetron sputtering is considered for the deposition of silicon rich films. Attention was paid to the possibility to produce light emitting silicon rich films by three different methods, such as reactive magnetron sputtering, co-sputtering from silicon/silicon dioxide targets and a stacked film approach. It was found that photoluminescence of the films deposited in presence of hydrogen was much grater then that for other samples.

A model of reactive sputter deposition was also developed and tested in this work. Results achieved in numerical simulation are compared with experimental data and show a good correlation.

An experimental unit for magnetron sputtering was designed and built based on a sphere-shaped vacuum chamber equipped with a commercially available magnetron sputter gun, RF generator as power supply unit, vacuum controllers, mass flow controllers, in-situ thickness monitor, temperature controller and other supplemental equipment.

Characterization of deposited film was made using Profile Measurement, ellipsometry, Rutherford Back Scattering measurements, X-Ray Diffraction measurements and photoluminescence measurements.

The achieved results show the principal possibility of getting microcrystalline silicon films and light emitting silicon nanocrystals embedded into silicon dioxide matrix by the sputter deposition technique.

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CHAPTER 1. INTRODUCTION

1.1 Light emitting silicon

Since in 1948 Bardeen, Brattain and Shockley invented the transistor in the Bell Laboratories in the USA silicon microelectronic devices have changed our life and defined future investigation in theoretical and applied physics of semiconductors. Some of the properties of silicon such as a band gap of 1.12eV are perfect for creation of the semiconductor devices working at room temperature. At the same time, the indirect band gap of the bulk silicon did not allow counting on invention of effective light emitting sources.

However, in the last decade significant steps were made towards effective light emitters based on silicon. Very promising results were achieved in getting visible light emission by different groups of researches who employed silicon for that goal. This gives hope to create real silicon based light sources and even the lasers fully integrated into existing silicon technology.

In 1990, bright light emission of porous silicon [1] was reported and stimulated efforts on getting light emission from silicon. Such a behavior of silicon was connected with quantum effects in nanometer-sized silicon structures presented in porous silicon as well as in so-called quantum wells, wires and dots. In contrast to etching as in production of porous silicon, there are several ways to get silicon nanometer-sized clusters by growing them within a dielectric matrix. The most popular approach is to use some of the Chemical Vapor Deposition (CVD) processes and to grow silicon nanometer-sized clusters within a silicon dioxide matrix. Within CVD (PECVD – plasma enhanced CVD, ECRCVD – electron cyclotron resonance CVD and others) there are two main steps to

get silicon nanocrystals which are responsible for the light emission. In the first one, deposition of the silicon dioxide film is conducted under those conditions that allow getting excess silicon in the film. Then, sub-stiochiometric silicon dioxide is treated by annealing at high temperatures for up to a couple of hours. The annealing causes a separation of phases between silicon and silicon dioxide, forming the silicon nanocrystals.

As I mentioned above, silicon nanocrystals were widely investigated mainly because of their interesting luminescent properties [2-5]. Explanation of the luminescence given by different authors [6] for porous silicon can be used for any nanometer-sized silicon structures. According to [5] models of luminescence can be combined into six big groups.

1. Hydrogenated amorphous silicon model: Luminescence is caused by hydrogenated amorphous phase (a-Si:H) because hydrogenated amorphous silicon possesses a photoluminescence.

2. The surface hydrides model: It was discovered that decreasing in hydrogen concentration leads to decreasing in photoluminescence that is why silicon hydrides were suggested to be responsible for luminescence.

3. Defect model: Luminescence originates from carriers localized at defect centers such as defects in silicon or silicon dioxide matrix.

4. Siloxene model: A Si:H:O based polymer called siloxene probably is responsible for luminescence because of its visible photoluminescence band.

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5. Surface states model: Giant specific surface of nanometer-sized silicon clusters leads to deep involvement of surface states in their behavior. In this model, radiative recombination involves localized surface states.

6. Quantum confinement model: Luminescence in this model is explained by appearance of measurable quantum effects, which reflect the change of the band gap structure in dependence on the size of silicon clusters.

Various interpretations of the origin of photoluminescence (PL) clearly show that the origin of PL is still under discussion or at least different explanation of PL can be applied to the different samples. Besides, very often PL signal combines a few signals with different origin. These entire make the physics of nanometer sized silicon clusters very interesting.

Despite the fact that there are no commercially available photonics devices based on silicon yet, many expectations and hopes still exist.

1.2 State of affairs with deposition of nanocrystalline silicon film

As was described earlier, there are several ways for deposition of silicon rich $(SiO_x, where x<2)$ films which are the first step towards creation of silicon nanocrystals embedded into silicon dioxide matrix. Besides very popular CVD processes which includes PECVD processes there are such laboratory-tested approaches [5] as laser ablation [7], aerosol technique [8], ion implantation [9] and sputtering [10].

Silicon nanocrystals have been intensively investigated over the last years because of their luminescence in the visible part of spectrum. That is why most of the works are concentrated on optical properties of the silicon nanocrystals and their structural features applied again to optical properties. It was clearly shown that luminescent samples contain silicon nanocrystals with the size distributed in accordance with a Gaussian curve [5]. The higher the temperature of the annealing is the wider is the Gaussian curve. Besides, the mean diameter of the crystals increases with increasing the annealing temperature. Initial concentration of the silicon in silicon rich films is also very important. It was shown that the samples annealed at the same temperature during the same time period had bigger nanocrystals if the initial concentration of silicon was higher [5]. All of these facts are very important in terms of luminescence. Although all of the silicon nanocrystals produce light in the range of 600-1100 nm, there is a dependence of the maximum of emission curve on the silicon concentration in the film and on crystal size. The position of the luminescence peak has been connected with passivation of the nanocrystals surface.

Investigations of the luminescence of silicon nanocrystals are carried out for both photoluminescence (PL) and electroluminescence (EL). They have shown that in order to clarify the origin of luminescence the control of the size of nanocrystals is very important. Gaussian distribution of sizes of nanocrystals defines the physical constraint on the possibility to get very narrow size distribution. However, recently new ways of narrowing the size distribution have been developed [11]. The main idea was to construct superlattice of sequentially deposited layers of silicon and silicon dioxide to limit the growth of the nanocrystals during annealing. Typical TEM (transmission electron microscopy) images of crystallized amorphous silicon layers between silicon dioxide layers are presented in Fig.1201 (from [12]) and Fig.1202 (from [13]).

Such a stacked film approach can be implemented for different insulating materials instead of silicon dioxide and different techniques such as Molecular Beam

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Epitaxy [14], RF-sputtering [15], Pulsed Laser Deposition [16] and Low Pressure Chemical Vapor Deposition [17].

Demonstrated photoluminescence [11] has shown a dependence of PL peak location on the thickness of silicon layers (Fig.1203). The intensity of the PL is affected by passivation of the surface of silicon layers (Fig.1204).



Fig.1201 TEM images of amorphous layers of silicon (left image); crystallized superlattice (in the middle); crystallized "bulk" silicon rich film (right image) (from [12])



Fig.1202 TEM images of crystallized amorphous Si/SiO₂ superlattice for different layer thicknesses (from [13])



Fig.1203 Photoluminescence from Si/SiO₂ superlattice depending on Si layers thickness (from [11])



Fig.1204 Photoluminescence from Si/SiO₂ superlattice depending on passivation of silicon layers (from [11])

1.3 Short description of the performed work

In the frame of research work, the following tasks were carried out:

- I. Creation of sputter deposition system (Chapter 4)
 - Designing, building and testing a vacuum system (Chapter 4; 4.1; 4.2);
 - Designing, building and installing a sample holder with built-in heater (Chapter 4;
 4.1);
 - Installing a sputtering unit based on a standard magnetron sputter gun (Chapter 4; 4.1);
 - Installing measurement and control equipment (Chapter 4; 4.1)
 - Installing a power supply (RF-generator and matching network) (Chapter 4; 4.1).
- II. Investigation of deposition process (Chapter 2; Chapter 4; Chapter 5)
 - Development of a reactive magnetron sputtering model (Chapter 2; 2.7, Chapter 5; 5.1);
 - Calibration of the system (Chapter 4; 4.3);
- III. Fabricating samples and their characterization (Chapter 4; 4.4)
 - Deposition of the samples using three different techniques (Chapter 4; 4.4)
 - Reactive magnetron sputtering (Chapter 4; 4.4.1);
 - Stacked film approach (Chapter 4; 4.4.2);
 - Co-sputtering of silicon and silicon dioxide (Chapter 4; 4.4.3);
 - Characterization of the films by various techniques (Chapter 4, Chapter 5)
 - Scanning Electron Microscopy (Chapter 4; 4.4);
 - Ellipsometry (Chapter 5; 5.2);

• Rutherford Backscattering Spectrometry (Chapter 5; 5.2);

o X-Ray Diffraction Technique (Chapter 5; 5.3);

o Luminescence Spectroscopy (Chapter 5; 5.4);

CHAPTER 2. PRINCIPLES OF MAGNETRON SPUTTERING

2.1 Plasma physics

The term "plasma" was first used in works of Langmuir and Tonks in 1929 [18]. By this term, they meant as we call it now, the plasma of a gas discharge. Although there are many types of plasma such as electron-positron plasma in astrophysics or electronhole plasma in the physics of semiconductors, I will pay attention in this chapter to elements of the gas discharge plasma.

In this context "plasma" is a mixture of electrons, ions and neutral particles, which is generally neutral. "Generally" means that if we take large enough region of plasma it will be neutral. However, small regions of the plasma cannot be exactly neutral due to movement of plasma particles.

To define how small the region of plasma can be under condition of neutrality let us apply Poisson equation

$$\Delta \varphi = -4\pi e \Delta n \,, \tag{1}$$

where φ is the electrical potential, *e* is charge of the electron, $n=n_e=n_i$ is density of plasma, electrons and ions, respectively. Besides, we should take into account that concentration of charged particles in the electrical field with potential φ has spatial distribution in accordance with Boltzmann's law

$$n_{e,i} = n_0 \exp(-\frac{e\varphi}{kT_{e,i}}).$$
⁽²⁾

Here index e corresponds to electrons, i to ions; k is Boltzmann's constant, T is the temperature. Solving both equations together, we will yield the solution as follows

$$\varphi = \frac{e}{r} \exp(-\frac{r}{r_D}) \,. \tag{3}$$

The value $r_D = \sqrt{\frac{1}{4\pi e^2 n_0 (\frac{1}{kT_e} + \frac{1}{kT_i})}}$ defines the so-called Debye length, which is the

distance in plasma within which the neutrality of plasma can be disturbed. Besides, it can be seen that the potential of a particular charged particle in the plasma drops much faster then the potential of free particle. This effect is known as Debye shielding, see Fig.2101.

Besides spatial fluctuations of density, the time of existence of such fluctuations can be estimated. It shall be the time $t \approx \frac{r_D}{v_e}$, where v_e is thermal velocity of electrons, so

that $t \approx \sqrt{\frac{m_e}{4\pi ne^2}}$. In plasma physics the plasma frequency ω_p is used more often,

$$\omega_p = \sqrt{\frac{4\pi n e^2}{m_e}} , \qquad (4)$$

which is also called Langmuir frequency.

The processes on the border of plasma – substance surfaces have special meaning in plasma physics. These processes if there is no applied electrical field can be described in diffusion approximation. However, ions and electrons cannot move independently of one another and their common diffusion (so called "ambipolar" diffusion) defines the potential of isolated body located in plasma.

At the steady-state regime the impingement rates Γ for electrons *e* and ions *i* at the isolated body in plasma are:

$$\Gamma_e = -\mu_e n_e E - D_e \nabla n_e \tag{5}$$

$$\Gamma_i = \mu_i n_i E - D_i \nabla n_i \tag{6}$$

Using condition of neutrality of the plasma $n_e = n_i = n$ and steady-state condition $\Gamma_e = \Gamma_i$ gives $-\mu_e nE - D_e \nabla n = \mu_i nE - D_i \nabla n$. Substitution of value *E* from this expression into the ion flux equation gives $\Gamma_i = -D_a \frac{dn_i}{dx}$ in a one-dimensional problem. Here

 $D_a = \frac{\mu_i D_e + \mu_e D_i}{\mu_i + \mu_e}$ is the coefficient of the ambipolar diffusion. Taking into account the

Einstein relation $\frac{D}{\mu} = \frac{kT}{e}$ we have

$$D_a = D_i \left(1 + \frac{T_e}{T_i} \right) \tag{7}$$

Plasma physics is not limited of course by given above very short description. It is manifold, complex and fine. Detailed discussions about plasma physics can be found for example in [19].



Fig.2101 Illustration of Debye shielding

2.2 Diagnostics of plasmas

The fundamental plasma parameters can be determined by placing a small conducting probe into the plasma and observing the electrical current to the probe as a function of the difference between the probe and plasma potentials.

The current on the probe is actually the sum of the fluxes of all charged components of plasma. $I = A \cdot \sum_{k} n_k \overline{v}_k q_k$, where A is surface area of the probe; n, v, q – are concentration, average velocity and charge of the species k respectively. For a Maxwell-Boltzmann distribution of the energy of particles,

$$f_k(\mathbf{v}) = \left(\frac{2\pi kT_k}{m_k}\right)^{-3_2} \cdot e^{\left(-\frac{m\mathbf{v}^2}{kT_k}\right)} , \qquad (8)$$

the expression for the current of each species can be written as $I_k = nq_k A \int_{v_{min}}^{\infty} f_k(v) v dv$. For

simplicity, we suppose here that the probe is a planar disk with the normal along to X direction. Sometimes a piece of a wire is used as the probe; however, the principle of a calculation remains the same.

If the probe potential is much higher than the plasma potential all, electrons are repelled and such a regime is called ion saturation regime. In this case the saturated ion current is

$$I_{\rm s} = neA \left(\frac{2kT_e}{m_{\rm r}}\right)^{1_2}.$$
(9)

If the probe potential is much lower then plasma potential all electrons are collected by the probe and such a regime is called electron saturation regime. In this case the saturated electron current is

$$I_{es} = -neA \left(\frac{kT_e}{2\pi m_t}\right)^{1_2} . \tag{10}$$

In between these two regimes the total current can be defined by the expression,

$$I = I_{is} - neA \left(\frac{kT_e}{2\pi m_i}\right)^{1_2} e^{\frac{eV}{kT_e}},$$
(11)

where $V = V_{pl} - V_{pr}$ is the difference between plasma and probe potential. A typical I-V graph of Langmuir probe is given in Fig.2201.

In particular, for the determination of the electron temperature we just need to

know the slope of the straight section AB, because from $I = I_{is} - neA \left(\frac{kT_e}{2\pi m_i}\right)^{1_2} e^{\frac{eV}{kT_e}}$ it

follows that $\frac{d(\ln(I))}{dV} = \frac{e}{kT_e}$. Next, using $I_{es} = -neA \left(\frac{kT_e}{2\pi m_i}\right)^{1/2}$ gives the plasma density *n*.



Fig.2201 Current-Voltage characteristic of a Langmuir probe

2.3 Elementary processes in plasmas

For a plasma in thermal equilibrium when $T_e = T_i$, the ionization coefficient $\alpha = \frac{n_i}{n_a}$ is defined only by temperature and can be calculated with the Saha formula

$$\frac{n_i n_e}{n_a} = \frac{g_i g_e}{g_a} \frac{\exp(-\frac{e\varphi_i}{kT})}{\lambda_B^3}.$$
(12)

Here n_a is the concentration of neutrals in plasma, g is the statistical weight of corresponding species, φ_i is potential of ionization of neutral atom, T is plasma temperature, λ_B is the De Broglie wavelength of the electron at temperature T.

However, plasma cannot always be in an equilibrium state. In such cases, elementary processes in the plasma like ionization, recombination or charge exchange have to be considered.

The ionization of neutral species A by electron impact can be written as follows $A + e \rightarrow A^+ + e + e$. This process can be mathematically described by input of the cross section of ionization, which defines the probability of the process. It is given in the easiest case by the Thompson equation

$$\sigma_{i} = \frac{\pi e^{4}}{W^{2}(e\varphi_{i})} (W - e\varphi_{i}), \qquad (13)$$

where *W* is the energy of incident electron and φ_i is the potential of ionization of neutral atom. Increasing the electron density due to ionization will be thus described by equation

$$\frac{dn_e}{dt} = n_a n_e \langle \sigma_i v_e \rangle, \qquad (14)$$

where v_e is the velocity of the incident electron.

When the quantity of electrons becomes large enough, three body recombination starts to be significant. This process looks like $A^+ + e^- + e^- \rightarrow A^- + e^-$. Decreasing of the electron density due to recombination is described by equation

$$\frac{dn_e}{dt} = -\beta n_e^2 n_i.$$
(15)

Here β is a proportionally coefficient.

In plasma, the following processes can also play a significant role:

• photo ionization $A + h\omega \rightarrow A^+ + e$

$$\frac{dn_e}{dt} = \mu n_a \tag{16}$$

• photo recombination $A^+ + e \rightarrow A + h\omega$

$$\frac{dn_e}{dt} = -\gamma m_e n_i \tag{17}$$

Resulting kinetic equation of ionization should be written as follows

$$\frac{dn_e}{dt} = n_a n_e \langle \sigma_i v_e \rangle - \beta n_e^2 n_i + \mu n_a - \gamma n_e n_i.$$
⁽¹⁸⁾

2.4 Types of discharges

All known gas discharges can be roughly described in terms of the diagram below, see Fig.2401. Three general regions are identified on this chart; these are the dark discharge, the glow discharge, and the arc discharge. Each of these general regions discloses many interesting phenomena.

2.4.1 Dark Discharge

The regime between A and E on the voltage-current characteristic is called a dark space because, except for corona discharges and the breakdown itself, the discharge remains invisible to the eye.

A - B: During the background ionization stage of the process, the electric field applied along the axis of the discharge tube removes the ions and electrons created by ionization produced by background radiation. Background radiation from cosmic rays, radioactive minerals, or other sources, produces a constant and measurable degree of ionization in air at atmospheric pressure. The ions and electrons migrate to the electrodes in the applied electric field producing a weak electric current. Increasing voltage wipes out an increasing number of these ions and electrons.

B - C: If the voltage between the electrodes is increased far enough, eventually all the available electrons and ions are moved away, and the current saturates. In the saturation region, the current remains constant while the voltage is increased. This current depends linearly on the radiation source strength. This regime is useful in some counters of radiation.

C - E: If the voltage across the low-pressure discharge tube is increased beyond point C, the current will rise exponentially. The electric field is now high enough so that the electrons initially existed in the gas can collect enough energy before reaching the anode and ionize the neutral atoms.

VOLTAGE, VOLTS



Fig.2401 General current-voltage characteristics of a gas discharge

When the electric field becomes stronger, the secondary electrons may also ionize other neutral atoms that lead to an avalanche of electrons and ions production. The region of exponentially increasing current is called the Townsend discharge.

 $\mathbf{D} - \mathbf{E}$: Corona discharges as a part of Townsend dark discharges occur in regions of high electric field near sharp points, edges, or wires in gases prior to electrical breakdown. If the coronal currents are high enough, corona discharges can be technically called "glow discharges", visible to the eye. For low currents, the entire corona is dark, as appropriate for the dark discharges. Related phenomena include the silent electrical discharge, an inaudible form of filamentary discharge, and the brush discharge, a luminous discharge in a non-uniform electric field where many corona discharges are active at the same time and form streamers through the gas.

 $\mathbf{E} - \mathbf{F}$: Electrical breakdown occurs in the Townsend regime with the addition of secondary electrons emitted from the cathode due to ion or photon impact. At the breakdown, or sparking potential V_B, the current might increase by a factor of 10⁴ to 10⁸, and is usually limited only by the internal resistance of the power supply connected to the electrodes. If the internal resistance of the power supply is very high, the discharge tube cannot draw enough current to break down the gas, and the tube will remain in the corona regime with small corona points or brush discharges being evident on the electrodes. If the internal resistance of the power supply low, then the gas will break down at the voltage V_B, and move into the normal glow discharge regime. The breakdown voltage for a particular gas and electrode material depends on the product of the pressure and the distance between the electrodes, *p*·*d*, as expressed in Paschen's law (1889).



Fig.2402 Paschen's Law for air, from [75]

2.4.2 Glow Discharge

The glow discharge regime took its name from the fact that the plasma is luminous. The gas glows because the electron energy and density are high enough to generate visible light by excitation collisions. The applications of glow discharge include fluorescent lights, DC parallel-plate plasma reactors, "magnetron" discharges used for deposition of thin films, and plasma sources based on electron bombardment.

 $\mathbf{F} - \mathbf{G}$: After a discontinuous transition from \mathbf{E} to \mathbf{F} , the gas enters the normal glow region, in which the voltage is almost independent on the current over several orders of magnitude in the discharge current. The current density on the electrode is independent of the total current in this regime. This means that the plasma is in contact with only a small part of the cathode surface at low currents. As the current is increased from \mathbf{F} to \mathbf{G} , the part of the cathode occupied by the plasma increases, until plasma covers the entire cathode surface at point \mathbf{G} .

G - H: In the abnormal glow regime, which occurs above point G, the voltage increases significantly with the increasing total current in order to force the cathode current density above its natural value and provide the desired current. Starting at point G and moving to the left, a form of hysteresis is observed in the voltage-current characteristic. The discharge manages itself at considerably lower currents and current densities than at point F and only then makes a transition back to the Townsend regime.

2.4.3 Arc Discharges

H - K: At point H, the electrodes become sufficiently hot so that the cathode emits electrons thermally. If the DC power supply has a sufficiently low internal resistance, the discharge will transform from a glow to arc type (H-I). The arc regime, from I through K is one where the discharge voltage decreases as the current increases, until large currents are achieved at point J. After that point, the voltage increases slowly with increasing the current.

2.5 Plasmas in thin film deposition

Methods of thin film preparation can be roughly divided on two big groups: a) chemical methods and 2) physical methods. Modern techniques of thin film deposition use plasmas in both of them. The first group covers such processes as Chemical Vapor Deposition (CVD), Deposition from Aqueous Solutions and Thermal Spray Deposition; however, plasma as enhancer of chemical reactions is mostly in use in CVD processes. The second group is presented by Physical Vapor Deposition (PVD), which includes Evaporation, Sputter Deposition Processes and Ion Plating where the latter two use plasmas in their mechanisms of film deposition.

2.5.1 Chemical Vapor Deposition

Chemical Vapor Deposition is a process, which uses the chemical reactions, which transform gaseous molecules, called precursors, into a solid material, in the form of thin films or powder, on the surface of a substrate. Gaseous compounds of the materials to be deposited are transported to a substrate surface where a thermal reaction/deposition occurs. Reaction byproducts are then exhausted out of the system. CVD is a very versatile process used in the production of coatings, powders, fibers and monolithic parts. With CVD, it is possible to produce almost any metallic or non-metallic
element, including carbon and silicon, as well as compounds such as carbides, nitrides, borides, oxides, inter-metallic and many others. The process is widely used to fabricate semiconductor devices. Implementation of plasma into the CVD process gives new possibilities to form the thin films. It is connected with separating the substrate from the area of precursor dissociation. In the process called Plasma Enhanced CVD (PECVD), dissociation of a precursor is causing by electron impact and the temperature of the substrate play only additional positive role in film formation.

In accordance with the method of plasma generation in PECVD, the plasma sources are presented in most cases by Inductively/Capacitively Coupled Plasma (ICP) sources or by sources in Electron Cyclotron Resonance (ECR), see Fig.2501 a), b).

In the ICP method, the time varying Magnetic Field creates a time varying Electric Field. This Electro Magnetic Field is used to ignite the plasma (Fig.2502). The precursor can be introduced into the discharge area or just behind it. Accordingly, the substrate is placed within the glow zone or out of it.

In ECR systems an electro magnetic field at Larmor frequency, which is equal to $\omega = \frac{eB}{m}$, where *e* is electron charge, *B* is magnetic field and *m* is electron mass, will be in phase with the electron motion and add the energy to the electron on any orbit (Fig.2503). In order to obtain silicon-based films in both ICP and ECR configurations the gaseous silicon tetra hydride called silane (SiH₄) is used as the precursor. The substrate temperature is shown to be above 450 $^{\circ}$ C [21] for polycrystalline silicon formation.

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Fig.2501 PECVD in a) - ICP configuration, and b) - ECR configuration



Fig.2502 Electromagnetic Field in ICP



Fig.2503 Electron in Electromagnetic Field in ECR

A key advantage of the PECVD process as all CVD processes lies in the fact that the reactants used are gases, thereby taking advantage of the many characteristics of gases. One result is that CVD is not a line-of-sight process as are most other coating processes. In addition, PECVD offers excellent control in film composition, possibility to cover large areas with grate uniformity and low substrate temperature.

2.5.2 Thermal Spray Deposition

Advanced Thermal Spray Deposition is suitable for almost any material that can be melted without decomposing. The key of this method is the heating of depositing material just to the point of its melting and directing that material toward the substrate. For most applications, the temperature of substrate does not exceed 150^oC. Thickness of coatings usually ranges from 0.05 to (for some cases) 5 mm.

In accordance with the source of heating, the Thermal Spray Deposition can be divided into the following groups: 1) plasma deposition, 2) detonation gun deposition, and 3) high velocity oxy-fuel deposition. In the first case, the depositing material presented as a powder is directed into the high temperature plasma flux formed usually by an electric-arc plasmatron. Using special nozzles, the supersonic velocity of the plasma can be achieved. The temperature of the plasma core may exceed 30000 ⁰C. The efficiency of heat transfer from the plasma to the powder particles can be increased by the inclusion of diatomic gases such as hydrogen or nitrogen into the discharge.

The control of substrate temperature is very important in all mentioned schemes. Usually it is desirable to have the temperature not more than 150° C. It can be achieved by limitation of deposition rate or/and extra cooling by air or CO₂. Despite the fact that, in many applications the coating deposited by the Thermal Spray Deposition method may

be used as-coated, most applications require a finished coating before use. This fact has general character and defines the limitation in using Thermal Spray Deposition. Besides the main disadvantage of the all droplet transfer processes is the porosity in the final deposit, which affects the properties.

2.5.3 Physical Vapor Deposition (PVD): Ion Plating

Ion Plating is part of PVD processes but distinguished by artificial bombardment of the substrate with energetic ions. This bombardment causes the changes in properties of deposited film. In terms of Ion Plating, it does not matter which source of particles for deposition is used. It can be source based on simple vaporization or sputtering. It can be also the plasma of chemical species in PECVD. Any way, the main reason for Ion Plating is to modify the film composition, morphology, microstructure and properties of the deposited film by its ion bombardment during growth.

This bombardment during adatom deposition increases the nucleation densities and may enhance the surface mobility of atoms [22, 23]. Particle bombardment is interesting also because of the ability to clean the surface before deposition, providing enough energy to the surface region to enhance diffusion of adatoms, clusters, and chemical reactants. During the ion bombardment, a re-deposition of depositing material should be taken into account. Additional ion bombardment can modify the film properties such as stress, stoichiometry, grain size and orientation, hardness density, adhesion [24].

The Ion plating technique gives additional levels of freedom for thin film formation and can be used for specific applications.

2.5.4 Physical Vapor Deposition (PVD): Sputter Deposition

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In sputtering systems, positive ions formed in a glow gas discharge bombard the target (cathode) and dislodge its atoms, which are later depositing onto the substrate.

The erosion of the cathode in a glow discharge was first discovered in 1852 by W.R. Grove [25]. Since that time, there have been published hundreds of manuscripts reporting different aspects of sputtering. Particularly the magnetron sputtering was first presented in the early 1970's and has now general meaning in thin film production and coating. In many cases, magnetron sputtered films now have better performances than films deposited by other PVD processes. Consequently, magnetron sputtered films have applications in hard, wear-resistant coatings, low friction coatings, corrosion-resistant coatings, decorative coatings and coatings with specific optical or electrical properties [26].

2.6 Magnetron sputtering

The sputter deposition process combines in general several simple processes:

- Obtaining an ion or atom/molecule beam;
- Transferring kinetic energy to the beam so that it has an impulse directed towards the sputtering target;
- Sputtering a target material by ion/atom/molecule bombardment;
- Transferring the target material towards a substrate;
- Growing a film on a substrate;

In the general case, the source of ions is not connected in any way with the target, but in magnetron sputter systems the target works as a cathode above the surface of which the specially configured magnetic field is formed. The core idea of a magnetron sputter system is to use the drift of electrons in crossed electrical and magnetic fields (Hall Effect), see Fig.2601. The trajectory of the electron movement is called cycloid.

No one electron can escape from that electro-magnetic trap without collision with atoms of the plasma forming gas. That is why the magnetron systems are very effective plasma sources with ionization coefficients close to unity. Electrons can move freely along the magnetic lines but the movement across them is possible only due to collisions with atoms of the plasma forming gas. It means that mobility of electrons along/parallel magnetic field is much higher then across it.

The ratio of mobility across and along the magnetic field is usually presented as the following equation

$$\frac{\mu_{\perp}}{\mu_{\pm}} = \frac{1}{1 + (\omega_e t)^2},$$
(19)

where μ is mobility of electrons along (=) or perpendicular ($^{\perp}$) to the magnetic field, $\omega_e = \frac{eB}{m}$ is the Larmor frequency of electron and *t* is the time of electron relaxation. Low

perpendicular mobility defines the drop of potential in the cathode layer, which acts therefore as accelerator of ions.

Incident ions produce sputtering of target atoms, which leave the target with certain distribution of velocities as follows from [27], see Fig.2602. Sputtered material of the target then moves from the target. If the substrate is placed on that way, it will be covered by sputtered material.



Fig.2601 Movement of electrons in the magnetic trap of the magnetron

There are many types of magnetron sputtering systems. The type of applied power mostly distinguishes them but generally, they always contain crossed electrical and magnetic fields. Currently, two types of power supply are used in magnetrons, RF and DC power supplies. However, in the first case, despite applied RF power the bias on the target is on average negative in steady-state regime, see Fig.2603. It happens due to higher mobility of electrons compared to ions that causes effective charging of the target by electrons during the positive half-of-wave of the RF power and leads to the process shown in Fig.2603. That is why RF magnetron sputtering is essentially sputtering in DC discharge.

Further developing the magnetron sputtering technique, the balanced magnetrons [28, 29] were introduced and became an important step forward in coating techniques. However, in the late 1980s [30-32] the unbalanced magnetron was developed and its incorporation into multi-source unclosed-field systems in the early 1990s [33, 34] has transformed the capabilities of this technique, and has subsequently been responsible for its rise in importance. Closed-field unbalanced magnetron sputtering (CFUBMS) is an exceptionally versatile technique, suitable for the deposition of high quality, well-adhered films of a wide range of materials at commercially useful rates. The pulsed magnetron sputtering (PMS) process is another very important recent development in the field of sputtering [35].

The deposition of complex compounds such as insulating materials, oxides, nitrides and others is highly problematic in reactive sputtering. The problems connected with the reactive magnetron sputtering of highly insulating materials are widely reported in [35-42]. Generally, they can be divided into two categories 1) problems connected

with instability of gas discharge caused by hysteresis phenomena (Fig.2604 from [43]) and arc events on the target [44]. The second class of problems can be solved relatively easily by employment of a pulsed power supply [35].

The first problem has definitely high scientific interest but can be also easily solved. It is described in [35, 45-49] that if the pumping speed exceeds a certain critical rate according to $S \ge -\frac{\partial \Phi}{\partial p}$ [49] the hysteresis effect is never present. Here, S is the pumping speed, Φ is the flow rate of reactive gas (RG) consumed by sputtered material, p is the partial pressure of reactive gas. Another method to avoid hysteresis effects is to use simple s feedback loop in which a sensor controlling the reactive gas pressure gives a signal to the flow controller. Thus, the pressure remains stable, see Fig.2605.

The reason of appearance of hysteresis is that during the deposition process, some areas on the target become covered with an insulating layer, as result of chemical reaction between active gas and material of the target. This coverage of the target is known as target poisoning.

The experimental parameters such as applied power, dimensions of the target, distance to the sample, working pressure and many others are changing from one experimental unit to the other. Any experimental unit needs to be calibrated. It takes a lot of time and effort. The model of reactive sputtering described below can help to reduce the number of experiments and to achieve the best results in the fastest way.



Fig. 2602 Energy distribution of sputtered species



Fig.2603 The potential on the target as a function of time for the first several RF cycles



Fig.2605 Schematic set up of a feedback loop, which allow to avoid the hysteresis effect

2.7 Reactive magnetron sputtering

Reactive magnetron sputtering is distinguished from simple magnetron sputtering by the presence of chemical reactions, which occur if chemically active gas is introduced into the vacuum chamber together with inertial plasma forming gas. Let us consider the sputter deposition of a material of a target M in an atmosphere of the inertial gas I (usually Ar) and the reactive gas R_2 (usually with the two atoms per molecule). The reactions presented in Tab.2701 reflect interactions among particles in plasma area.

##	1 st step		##	2 nd step	
1	$I + e \rightarrow$	$I^+ + 2e$	1a	$I^+ + e \rightarrow$	$I^{2+} + 2e$
			1b		$I^{+*} + e$
2		I*+e	2a	$I^* \rightarrow$	I + hv
			2b		$I^+ + e$
			2c	$I^* + e \rightarrow$	$I^+ + 2e + hv$
3	$R_2 + e \rightarrow$	$R_2^+ + 2e$	3a	$R_2^+ + e \rightarrow$	$R_2^{2+} + 2e$
			3b		$R_2^{+*} + e$
			3c		$R^+ + R + e$
4		R+R+e	4a	$R + e \rightarrow$	$R^+ + 2e$
			4b		$R^* + e$
5		$R_2^* + e$	5a	$R_2^* \rightarrow$	$R_2 + hv$
			5b		R + R + hv
			5c		$R_2^+ + e$
			6a	$I^* + R_2 \rightarrow$	$R_2^+ + I + e + hv$
			6b	$R_2^* + I \rightarrow$	$I^+ + R_2 + e + hv$
			6c	$I^* + R_2 \rightarrow$	$R_2^* + I + hv$
			6d	$R_2^* + I \rightarrow$	$I^* + R_2 + hv$
			6e	$I^* + R_2 \rightarrow$	R + R + I + hv

Tab.2701 – Some of the possible reactions in the plasma zone

Here e represents electron, sign *- represents atom/molecule/ion in excited state, sign +- represents one (+) or two (2+) times ionized atom.

The analysis of the probability of above reactions is important to understand which of them are responsible for current of discharge, luminosity of plasma or chemical process. To define the flux of target material molecules which is the key factor for the Master Thesis – E. Chelomentsev

film growth we need to pay our attention to the reactions 1, 1a, 1b, 2b, 2c, 3, 3a, 3b, 3c, 4a, 5c, 6a, 6b because they reflect an ion source, as result the current on the target and finally the flux of sputtered material.

In order to make a correct assumption about the probability of each reaction we need to define gases I and R_2 and the material of the target M. However, even without their exact definition we can say that 1a and 3a will go with low probability because of high potential of ionization for the one time ionized ions. 1b, 3b, and 3c do not lead to a change of quantity of the ions and can be eliminated from consideration. The probability of reactions 2b and 5c is low, because among reactions of this type, 2a and 5a are more preferable. We will not consider 2b and 5c in the calculation of current of discharge. Less strict assumptions are connected with the reactions 2c, 4a. As second-step reactions, they are less probable than the reactions of the first step. That is why we will not consider them. The same conclusion can be reached by comparing of corresponding potentials of ionization and energy of excited states of the most of materials for reactions 6a and 6b.

Following to our supposition, let us calculate the current of discharge. According to Ohm's Law written for the model of two liquids for a one-component plasma [19]

$$\frac{d\bar{j}}{dt} = \frac{ne^2}{m}\vec{E} - \frac{e}{mc}\left[\vec{j}\vec{H}\right] + \frac{e}{m}\nabla p_e - \frac{\vec{j}}{\tau}.$$
(20)

In last equation j is a current, n is a plasma concentration, e is a charge of an electron, E is an electrical field, H is a magnetic field, m is an electron mass, τ is relaxation time for electrons.

For the case of a homogeneous plasma and DC-type current it can be written as

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$$\vec{j} + \omega_e \tau \left[\vec{j} \vec{h} \right] = \frac{ne^2}{m} \tau \vec{E} \,. \tag{21}$$

Here ω_e is Larmor frequency and *h* is unit vector of magnetic field. Thus, we have in plasma across magnetic field

$$\vec{j} = \frac{1}{1 + \omega_e \tau} \frac{ne^2}{m} \tau \vec{E} .$$
⁽²²⁾

Taking into account that we have two components (I and R₂) plasma and for it $\frac{1}{\tau} = Q_I n_I u_{I-e} + Q_{R_2} n_{R_2} u_{R_2-e}, \text{ where } Q \text{ is an ionization cross section of species } I \text{ and } R_2, n$ is their concentration and u is a relative velocity of mentioned species. Denoting that for isothermal plasma $u_{I-e} = u_{R_2-e} = u$ we can write

$$\vec{j} = \frac{1}{1 + \omega_e \tau} \frac{ne^2}{m} \vec{E} \frac{Q_I n_I u + Q_{R_2} n_{R_2} u}{(Q_I n_I u + Q_{R_2} n_{R_2} u)^2} \text{ or } \vec{j} = \vec{j}_I + \vec{j}_{R_2}.$$
(23)

Thus, we have for the current of species *I*:

$$\bar{j}_{I} = \bar{j} \frac{Q_{I} n_{I}}{Q_{R_{2}} n_{R_{2}} + Q_{I} n_{I}} .$$
⁽²⁴⁾

Influence of a magnetic field is significant only for electrons in case of magnetized plasma for which the condition $\omega_e \tau >> 1$ holds. However, we should consider it only if we suppose to get voltage – current characteristic of magnetron. In our case, we suppose that total current *j* as well as target voltage, is known from measurement.

In accordance with the Berg theory [50], the current on the target defines the following processes on it:

- Chemical reaction between material of the target and reactive part \vec{j}_{R_2} of total current;
- Sputtering the pure material of the target by the current \vec{j}_i ;
- Sputtering the chemical compounds of material of the target and reactive gas R_2 by \vec{j}_i ;

It means that the initial flux rate of the pure target material can be calculated as follows

$$j_{0_M} = j \frac{Q_I^2 n_I^2}{(Q_{R_2} n_{R_2} + Q_I n_I)^2} Y_{M-I}, \qquad (25)$$

or under definition $\frac{n_{R_2}}{n_l} = \chi$ as

$$j_{0M} = j \frac{Q_I^2}{(Q_{R_2} \chi + Q_I)^2} Y_{M-I}.$$
(26)

Here Y means sputtering yield of species M if it is bombarded by species I. During propagation though the chamber, the flux j_M is changing due to reaction with gas R₂ that is being absorbed by the sputtered target material as it is shown in Fig 2701.

This can be described by the differential equation

$$-\frac{dj_{M}}{dx} = j_{M} n_{R_{2}} Q_{M-R_{2}}.$$
 (27)



Fig.2701 Flux change in an active layer

The solution of this equation is written below.

$$j_{M} = j \frac{Q_{I}^{2}}{(Q_{R_{2}}\chi + Q_{I})^{2}} Y_{M-I} \exp\left(-\frac{nQ_{M-R_{2}}d}{1 + \frac{1}{\chi}}\right).$$
(28)

Here $n = n_1 + n_{R_2}$ - total concentration, d - distance between target and substrate.

The difference between j_{0M} and j_M is the flux of compound MR₂.

$$j_{MR_2} = j \frac{Q_I^2}{(Q_{R_2}\chi + Q_I)^2} Y_{M-I} \left(1 - \exp\left(-\frac{nQ_{M-R_2}d}{1 + \frac{1}{\chi}}\right) \right).$$
(29)

In fact the compound MR₂ may not exist [51]. Besides, the growing film can absorb some quantity of reactive gas so that film on the substrate is usually presented by compound MR_x. Despite the flux of the pure target material, is presented on the substrate in any case; the value of x can be not only lower but also higher then 1. That is why it is more correct to use the last equation for the flux j_{MRx} and cross section Q_{xM-R_2} , where Q_{xM-R_2} describes the probability of reaction M+R₂ \rightarrow MR_x. This chemical reaction can proceed not only in the atmosphere of the chamber but also on the surface of substrate. However, in the frame of the presented model it is important that the most part of reactive gas molecules/atoms is being absorbed by pure target material flux just on its way from the target to the substrate. Master Thesis – E. Chelomentsev

According to equations above, we can estimate the ratio of atomic concentration

in the film on the substrate. Obviously, $\frac{n_R}{n_M} = \frac{j_R}{j_M}$. So we can get the following

equation
$$\frac{n_R}{n_M} = \frac{x J_{MR_x}}{j_{MR_x} + j_M}$$
 or finally,

$$\frac{n_R}{n_M} = x \left(1 - \exp\left(-\frac{n Q_{x_M - R_2} d}{1 + \frac{1}{\chi}}\right) \right).$$
(30)

The total deposition rate $V[m^3/sec]$ which is volume of deposited film per unit time can also be estimated and the value should be proportional to $xj_{MR_x}\mu_{R_x} + j_{MR_x}\mu_M + j_M\mu_M$.

$$V = \left(j \frac{Q_{I}^{2}}{(Q_{R_{2}}\chi + Q_{I})^{2}} Y_{M-I} \frac{n_{R}}{xn_{M}} (x\mu_{R_{x}} + \mu_{M}) + j \frac{Q_{I}^{2}}{(Q_{R_{2}}\chi + Q_{I})^{2}} Y_{M-I} \left(1 - \frac{n_{R}}{xn_{M}} \right) \mu_{M} \right) \frac{S \cdot 10^{-3}}{\rho_{IR_{x}} N_{A} e}$$
(31)

Here S is the sputtering area.

If the deposition rate is spatially distributed under the law v = kf(x,d), it is true that $\iint_{x,\alpha} kf(x,d)xdxd\alpha = V$, where integration should be done for all possible values of x

and α . In other words, $2\pi k \int_{0}^{+\infty} xf(x,d)dx = V$. It means that deposition rate on the distance

d from the target in the point with coordinate x from the central axes i.e. in the point

$$A(x,d)$$
 is $v = \frac{V \cdot f(x,d)}{2\pi \int_{0}^{+\infty} xf(x,d)dx}$, according to Fig.2702.



Fig.2702 Illustration to distribution function calculation

For magnetron sputtering the distribution function f(x,d) can be written as

$$f(x,d) = \frac{\left(d^2 + (r+x)^2\right)}{\left(d^2 + (r+x)^2\right)^{3/2}} + \frac{\left(d^2 + (r-x)^2\right)}{\left(d^2 + (r-x)^2\right)^{3/2}}$$
(32)

according to geometry presented in Fig.2702 and based on cosine law of emission.

The equations (30), (31), and (32) describe mainly the process of material transfer but give no idea about the structure and the morphology of the growing film. That is why it is necessary to pay attention to the processes of film formation, which are important in the context of the present work.

CHAPTER 3. PRINCIPLES OF THIN FILM GROWTH

3.1 Models of thin film formation

The material of this chapter does not claim to be full and systematic and reflects only some of the interesting aspects of thin films growth. Complete description under this theme can be found in references below.

It is generally agreed, that there are three possible modes of film growth on surfaces. They are illustrated schematically in Fig.3101 [52]; θ represents the coverage in monolayers.

The layer or Frank-van der Merwe mode is reflected on Fig.3101a. It is supposed in this regime that the atoms are more strongly bound to the substrate than to each other. The first condensing atoms form a complete monolayer on the surface. It becomes covered with a less strongly bound second layer. Monotonically decreasing in the binding energy toward the value for a bulk crystal of the deposited material gives the layer growth mode. This growth mode is observed in the case of adsorbed gases, such as rare gases on graphite and on several metals, in some metal-metal systems, and in semiconductor growth on semiconductors.

In the island, or Volmer-Weber mode (Fig.3101c), small clusters are nucleated directly on the substrate surface and then grow into islands of the condensed phase. This happens when the atoms (or molecules) of the deposit are more strongly bound to each other than to the substrate. This mode happens in many systems of metals growing on insulators.

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The layer plus island, or Stranski-Krastanov, growth mode (Fig.3101b) is an intermediate case. After forming the first monolayer (ML), or a few ML, subsequent layer growth is unfavorable and islands are forming on top of this intermediate layer. There are many possible reasons for this mode to appear, and almost any factor, which disturbs the monotonic decrease in binding energy (characteristic of layer growth), may cause it. For example, the lattice parameter, symmetry, orientation of molecules of the intermediate layer may not be able to be continued into the bulk crystal of the deposit. It results in a high free energy of the surface of deposited intermediate layer, which favors subsequent island formation. There are many examples of its occurrence in metal-metal, metal-semiconductor, gas-metal and gas-layer compound systems.

These three different growth modes have their thermodynamic counterparts in three different forms of adsorption isotherms illustrated in Fig.3102 [53, 54]; $\Delta\mu$ represents the chemical potential of the growing deposit relative to the bulk material and θ is the coverage in ML. In (b) two stable intermediate layers are indicated.

In island growth (Fig.3102a), the concentration of adsorbed atoms is often very low, due to fast re-evaporation from the weakly binding substrate. That is why a large positive chemical potential change $\Delta\mu$ or super saturation S, is needed to nucleate the deposit. However, the first two-dimensional (2D) layers in layer growth can exist in equilibrium with the dilute three-dimensional phase at negative $\Delta\mu$ (under saturation), as illustrated in Fig.3102c. Here we are concerned with growth from the vapor, and illustrated adsorption isotherms are seen. It happens, for example, in rare-gas adsorption (e.g. Kr, Xe) on graphite. In the Stranski-Krastanov case, the adsorption isotherm is as



Fig.3101 Schematic representation of the crystal growth modes (from [52])



Fig.3102 Adsorption isotherms related to Fig.3101 (from [52])

illustrated in Fig.3102 b), where the $\Delta \mu = 0$ line is cut at some finite thickness, or coverage θ . Beyond this coverage, island growth is preferable thermodynamically.

3.2 Principles of crystal growth

The atomic processes which provide adsorption and crystal growth on surfaces are given on Fig.3201 [55], where evaporation energies are E_a , diffusion energies are E_d , binding energies of small clusters of size *j* are E_j , and for critical nucleus of size *i* are E_t . For vapor deposition from an ideal gas at pressure *p*, the impingement rate *R* at the substrate is given by the Langmuir equation $R = p \cdot (2\pi m kT_s)^{1_2}$, where *m* is the molecular weight, *k* is Boltzmann's constant and T_s is the source temperature. This flux creates single atoms on the substrate. These single atoms may then diffuse over the surface until they are lost by one of several processes. These processes include re-evaporation, nucleation of two-dimensional (2D) or three-dimensional (3D) clusters, capture by existing clusters, possibly dissolution into the substrate, and capture at defects such as steps. On an ideally flat, inert substrate, these last two processes would be excluded, though they may often be present in practice.

The processes illustrated in Fig.3201 are re-arrangement processes. The clusters that are initially formed at defects are not necessarily set in their most stable form and can be re-arranged in many different ways. Such processes can include mixing of species, shape changes caused by diffusion and/or coalescence, annealing of defects, etc. Diffusion processes thus occur at several stages of thin film formation: the motion of single atoms in forming small clusters, the motion of these clusters themselves and the re-arrangement of larger clusters (islands) after coalescence.

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Fig.3201 Scheme of processes and characteristic energies in nucleation and growth (from [52])

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In thermodynamic equilibrium, all processes go in opposite directions at equal rates. However, crystal growth is non-equilibrium, but kinetic process and the final macroscopic state of the system depends on the route taken among the various reaction paths indicated in Fig.3201. The state, which is obtained is not necessarily the most stable, but is kinetically determined. In general, certain parts of the overall process may be kinetically forbidden (e.g. dissolution into the substrate), others may be in local thermodynamic equilibrium, and some will have limited kinetic rate. In the second case, equilibrium arguments may be applied locally, i.e. to the adsorption-desorption cycle so that density of single atoms is $n_1 = R\tau_a$, where τ_a is characteristic time of evaporation which is given by expression $\tau_a = v^{-1}e^{\frac{E_a}{kT_s}}$. Here v is attempt frequency ($\approx 10^{12}$ 1/s), E_a is desorption barrier, T_s is substrate temperature.

Considering growth of small clusters, which decay rapidly, the Walton relation [56], can be derived for the concentration of clusters *j*:

$$\frac{n_j}{N_0} = \left(\frac{n_1}{N_0}\right)^j \sum_m C_j(m) e^{\frac{\Gamma_j(m)}{kT_s}},$$
(33)

where $C_j(m)$ are statistical weights, N_0 is density of absorption sites of the substrate, E_j is the cluster binding energy.

The equilibrium form of crystals of substance A condensed on surface B can be described in terms of the surface free energies, γ_A , γ_B and the interfacial free energy γ^* between A and B. The equilibrium form can be then calculated via the Wulff theorem; the arguments for growth of crystals on surfaces are given in [54]. In such arguments,

island growth is favored when $\gamma_A + \gamma^* \ge \gamma_B$ and layer growth is favored when $\gamma_A + \gamma^* \le \gamma_B$.

The form of the free energy $\Delta G(j)$ vs. the number *j* of atoms in the cluster is given in [54]:

$$\Delta G(j) = -j\Delta\mu + j^{2_3}X, \qquad (34)$$

for 3D clusters, where $X = \sum_{k} C_{k} \gamma_{k} + C_{AB} (\gamma^{*} - \gamma_{B})$, C_{k} and C_{AB} are geometrical constants

describing the surface area.

$$\Delta G(j) = -j\Delta\mu + (\gamma_A + \gamma^* - \gamma_B) \cdot \Omega^{2_3} + j^{1_2}X, \qquad (35)$$

for 2D clusters, where $X = \sum_{e} C_{e} \gamma_{e}$, Ω is atomic volume of A, γ_{e} is edge energy of the

cluster.

The size i of the cluster for which the free energy has maximum value is known as

critical size. I.e. for 3D cluster we have $i = \left(\frac{2X}{3\Delta\mu}\right)^3$; for 2D cluster we have

$$i = \left(\frac{X}{2\left(\Delta\mu - (\gamma_A + \gamma^* - \gamma_B)\Omega^{2_3}\right)}\right)^2.$$
(36)

Following Zinsmeister [57-61] and Vanables [62] the kinetic rate equations needed to describe nucleation and growth behavior can be written as follows:

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$$\frac{dn_1}{dt} = R - \frac{n_1}{\tau_a} - \frac{d(n_x w_x)}{dt}$$
(37)

$$\frac{dn_j}{dt} = 0, \quad \left(2 \le j \le i\right) \tag{38}$$

$$\frac{dn_x}{dt} = J - U_c - U_m \tag{39}$$

In the first equation, the last term represents the loss of single atoms to n_x stable clusters with an average number of atoms w_x per cluster. The second equation is a consequence of the detailed balance arguments ($U_J = 0$) for the sub critical clusters which leads to the Walton relation. The last two terms in equation (39) reflect the coalescence process. If stable clusters impinge on each other by growth factor U_c or by mobility factor across the substrate U_m so the number of stable clusters will be reduced.

The term J in the last equation presents the nucleation rate which can be written as $J = D\sigma_i n_i n_i$, where D is diffusion coefficient for diffusion of single atom along the surface, σ_i is the so called capture number widely discussed in [62] which has its value in the range 2-4. For example, the solution of (37-39) for high temperature substrate where re-evaporation processes have place has the following form:

$$J = \sigma_{I} D(R\tau_{a})^{I+1} C_{I} N_{0}^{1-I} e^{\frac{E_{I}}{kT_{v}}}.$$
(40)

3.3 Features of microcrystalline film formation in magnetron sputtering

The main advantage in magnetron sputtering in terms of microcrystalline film growth lies in high energy of sputtered atoms. If for standard CVD processes or thermal evaporation the average energy of deposited spices is about 0.1 eV, for magnetron sputtering it is around 5 eV. It gives additional freedom for film forming species to diffuse along the substrate surface. It can give also additional advantage if the surface of the substrate is tilted relatively to main axes of the magnetron. In this case the total velocity of the impinging species is distributed a between parallel to the surface part and a perpendicular part. The leveling of the temperatures of the surface and impinging species will go lower and they will get additional time for migration. During this time, the species more probably will be attached to already form microcrystalline grains rather than form new one. Besides, high energy of species allows them to overcome the potential barrier between amorphous state and microcrystalline state of already combined species and take the level with lower energy, i.e., to form microcrystal.

It is also important that applying a negative bias on the substrate will increase the ion bombardment of the growing film. Such a bombardment gives more energy to the diffusion process and leads to preferred formation of micro crystals. This is described in reviews [63-65]. Besides, the positively charged ions on the surface play the role of the centers of crystallization. Presence of such centers makes easier the initial stage of crystallization and leads to directional crystal grow. Appropriate impingement rate will allow getting the balance shifted towards deposition of the film rather then its sputtering. It means, that critical value for additional ion bombardment can be estimated from the following formula $\frac{j_{hombardment} \cdot y}{e} < \frac{v \cdot N_A \cdot \rho}{\mu}$. Here *e* is the electron charge, *v* is the molar mass of depositing species, *y* is the sputtering yield of the depositing film by bombarding ions. For a silicon film depositing at 1 A/sec and affected by additional argon bombardment at a bias of 500 V (*y*=0.5) the critical flux of argon ions *j*_{hombardment} is $3.2 \cdot 10^{-6} \text{ A/m}^2$.

CHAPTER 4. EXPERIMENTAL DETAILS

4.1 Deposition system

To proceed to the experimental part of the project on magnetron sputtering of silicon, the deposition system was designed and built. Schematically it is shown in Fig. 4101. The vacuum part of the system combines the vacuum sphere-shaped chamber of one foot in diameter. It is connected with a diffusion pump (BocEdwards) with minimally achieved pressure less then 10⁻⁹ Torr and announced pumping speed of 180 liters per second. Vacuum system is ended by a fore vacuum piston pump (Leybold) with a pumping speed of 16 cubic meters per hour and minimal possible pressure less then 10^{-4} Torr. The diffusion pump is equipped with a shutter valve, which separates the pump and the vacuum chamber. There is a possibility to switch pumping of the piston pump between the chamber and diffusion pump. A load lock system is not installed. Artificial leakage of gases, which are necessary for the sputtering process, has been provided and controlled by Sierra Mass Flow Controllers. Compressed argon graded "UHP (Ultra High Purity) plus" and delivered by VitalAire Company with the purity 99.99% has been used in the process as plasma forming gas. A Mass Flow Controller calibrated for the rate 200 standard cubic centimeter per minute (sccm) was used to control the argon flow. Compressed oxygen graded "UHP (Ultra High Purity) plus" and delivered by VitalAire Company with the purity 99.99% was used in some deposition processes as a reactive gas. A Mass Flow Controller calibrated for the rate 50 sccm was cut into the oxygen line. The conventional magnetron by Kurt J. Lesker Company was used as a sputtering gun.

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Fig.4101 Schematic of the Magnetron Sputter System

The silicon target with diameter of 3" and thickness of 0.125" was installed. The purity of the silicon target is 99.999% provided by Kurt J. Lesker Company. Cooling water was circulating to cool down the target and diffusion pump.

As a power supply unit a RF (Radio Frequency) generator produced by Advanced Energy Company was installed into the system. The matching network pointed between generator and magnetron was placed to couple the transferred RF power and the discharge. Maximum allowed power of the generator is 620 Watt.

The following controllers were also installed:

- Vacuum gauge Granville-Phillips 316 coupled with thermo-electrical gauge for the pressure measurement above 1.10⁻⁴ Torr;
- Vacuum gauge Granville-Phillips 340 coupled with ionization gauge for the pressure measurement under 1.10⁻⁴ Torr;
- Thickness controller Sycon STM-100 coupled with quartz crystal sensor for insitu measurement of thickness and deposition rate;
- Temperature controller Barnant coupled with a standard K-type thermocouple (from -100^oC to +1370^oC) for in-situ sample temperature measurement and regulation;
- King's water flow meters with range 1 gallon per minute for diffusion pump and magnetron water flow control.

The sample holder specially designed for sputtering system allows fixing and rotating two- and three- inch samples. It is installed close to the ceramic heater with maximum allowed power of 1.5 kW at normal conditions. The sample holder is adjustable also in horizontal movement. It can move from target from 20 to 180 mm.

4.2 Testing the experimental equipment

The ultimate achieved pressure was fixed at $3.4 \cdot 10^{-8}$ Torr. After closing a shutter valve, the time dependence of the pressure in the vacuum chamber was read to get the natural leakage into the chamber, see Fig.4201.

The conditions in the vacuum chamber allow using the Ideal Gas Law $PV = \frac{m}{\mu}RT$ in order to estimate the leakage and actual pumping speed. The formula

for calculation $P_2 = P_1 + \frac{q}{V} \cdot t$ derived from that equation gives the leakage as $4.15 \cdot 10^{-4}$ sccm calculated for the point [t=15 hours, $P_2=8.6 \cdot 10^{-3}$ Torr]. The difference in results on the initial part of the curve is related to the slow response of the convection vacuum gauge on fast changing of the pressure.

On the other hand, the pumping speed can be derived from the same equation and presented as follows:

$$Q = q \frac{P_{atm} \left(1 - e^{-\frac{qt}{V}} \right)}{P_2 - P_{atm} e^{-\frac{qt}{V}}}.$$
(41)

Calculated pumping speed for the diffusion pump gives us the value of 150 liters per second versus announced 180 liters per second. There is no big difference between these two figures that tells that the vacuum system is well configured. It can be seen also that the ultimate vacuum which can be theoretically achieved at the maximum pumping speed



Fig.4201 Pressure in the vacuum chamber vs. time when leaking

of 180 liters per second is $3.2 \cdot 10^{-8}$ Torr (we give the infinite value to the time in equation for pumping speed). However, in order to get the operational pressure at about one tenth of one mTorr, which is necessary for magnetron operation, the shutter valve throttled the pumping line and thus the pumping speed during deposition reduced up to 15 liters per second. Total measured gas flow under this condition was 40 sccm at $3.5 \cdot 10^{-2}$ Torr. This gas flow was divided between argon gas flow and oxygen gas flow in different

proportions for different series of experiments and changed from $\frac{q_{O_2}}{q_{Ar}} = 0$ to $\frac{q_{O_2}}{q_{Ar}} = 0.5$.

The temperature of the sample was calibrated by two K-type thermocouples connected with a Barant temperature controller. The first one was bolted to the heater and the second one had a touch contact with the substrate. The temperature was controlled at the same time and correspondence between both values has been investigated, see Fig.4202.

There were difficulties in direct measurement of the temperature of the substrate during the deposition due to rotation of the substrate holder. That is why that temperature was controlled by the measurement of the heater temperature and was extracted later from the curve presented in Fig.4202. The temperature of the substrate along the substrate was measured. The maximal diversion from 500° C in the center of substrate to the edge was 4° C.

Typical Voltage – Current characteristic of the working magnetron is given in Fig. 4203. This graph was obtained during its operation on pure argon and on the mixture of argon and oxygen. Both curves are given for the same total pressure $3.5 \cdot 10^{-2}$ Torr but


Fig.4202 Difference in temperatures of thermocouples placed on the heater and the substrate



Fig.4203 Current - Voltage characteristics of magnetron

with different oxygen/argon flow ratios as indicated. The current was calculated dividing the absorbed power by the measured target voltage.

In order to avoid cracking the silicon target it was heated up during 30 minutes with increasing RF power. The applied power was increased stepwise by 40 W per step from the point of plasma ignition at 40 W until operational regime. Typical discharge conditions were kept as follows: the total pressure $3.5 \cdot 10^{-2}$ Torr; transferred power minus reflected power 200 W; target voltage 650 - 750 V (depended on gas mixture). The manually operated shutter was always closed during heating up to prevent undesirable deposition.

4.3 Calibration of the system

The system was calibrated in two different regimes. In the first one, only argon as the plasma forming gas was introduced into the vacuum chamber. In the second one, the gas mixture of argon and oxygen was introduced into the vacuum chamber.

The dependence of the deposition rate on the applied power at the fixed partial pressure of $3.5 \cdot 10^{-2}$ Torr is given in the Fig.4301. The sample – target distance was kept at 180 mm during these series of experiments.

The dependence of the deposition rate on the partial pressure at a fixed applied power of 200 W is given in Fig.4302. The sample – target distance was kept also at 180 mm during these series of experiments. The uniformity of the films in this regime was not controlled and the value of deposition rate was calculated dividing the thickness in the center of sample by deposition time. The dependence of deposition rate on the distance between target and sample is given in Fig.4303 for the fixed applied power of 200 W and a fixed partial pressure of $3.5 \cdot 10^{-2}$ Torr.

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The uniformity of the films was easier to measure when polished silicon wafer was covered by transparent silicon dioxide film. Using Ellipsometry technique the spatial uniformity of the film thickness and the refractive index were obtained. These measurements were done during calibration of the system in the second regime. In that case, the working gas was presented as a mixture of argon and oxygen in different proportions. The following results of silicon dioxide film characterization are presented below:



Fig.4301 Deposition rate versus applied power



Fig.4302 Deposition rate versus partial pressure of argon

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Fig.4303 Deposition rate versus sample – target distance

• Dispersion of the thickness of the film on the silicon wafer in dependence on the distance to the target (total pressure $3.5 \cdot 10^{-2}$ Torr; $\frac{q_{Ar}}{q_{O_2}} = 0.2$; deposition time 30

min; RF-power 200 W) Fig.4304;

- Dispersion of the refractive index of the film in dependence on the distance to the target (total pressure $3.5 \cdot 10^{-2}$ Torr; $\frac{q_{Ar}}{q_{O_2}} = 0.2$; RF-power 200 W) Fig.4305;
- Dependence of the refractive index on the gases flow ratio (in the center of sample; total pressure 3.5·10⁻² Torr; distance to target 180 mm; RF-power 200 W)
 Fig.4306;
- Dependence of the deposition rate on the gases flow ratio (in the center of sample; total pressure 3.5·10⁻² Torr; distance to target 180 mm; RF-power 200 W) Fig.4307;
- Relation of the quantity of silicon in the films to the refractive index Fig.4308;
- Dependence of the deposition rate on the applied power (in the center of sample;

total pressure $3.5 \cdot 10^{-2}$ Torr; $\frac{q_{Ar}}{q_{O_2}} = 0.2$; distance to target 180 mm) Fig.4309.



Fig.4304 Dispersion of the thickness for different distances to the target







Fig.4306 Dependence of the refractive index on the gases flow ratio



Fig.4307 Dependence of the deposition rate on the gases flow ratio



Fig.4308 Relation of the quantity of silicon in the films to the refractive index





4.4 Fabricating samples and their characterization

Fabricating samples (below as "silicon rich films") with repeatable performances is always a challenge when they are going to be deposited by reactive magnetron sputtering. This depends on the fact that the parameters of deposition such as partial pressure of plasma forming gas and the reactive gas, target voltage, sputtering yield, applied power are tied with each other in a magnetron discharge. Even small changes of one of them immediately affect the others and in fact, change the film properties. For example the regime for the deposition of silicon rich films with silicon concentration at 42% was set up as follows: RF power of 200W (absorbed power); distance from target to substrate at 180 mm; temperature of the substrate of 200^{9} C; total pressure in the chamber at $1.5 \cdot 10^{-2}$ Torr; oxygen to argon flow ratio 1:10. This regime lies within the area of hysteresis (Chapter 2) and very strong experience was needed to keep the regime stable.

This is one reason why the stacked film approach was taken as other method of getting silicon rich films (below as "stacked silicon rich films") as well as co-sputtering of silicon and silicon dioxide target (below samples called "co-sputtered silicon rich films"). Comparison of the samples obtained by the mentioned methods was done for samples with equal silicon concentrations for refractive index, photoluminescence, and size of crystallites.

The stacked film approach is the method of multilayer film deposition, in which the resulting film combines many sequentially deposited ultra thin films. It is reported that the superstructure of the film does not affect the film properties if thickness of one sub layer is less than 50 Angstroms [66]. For the case of silicon-rich films, the sub layers of pure silicon and silicon dioxide should be sequentially deposited, see Fig.4401. Silicon dioxide layers were deposited by reactive magnetron sputtering of the silicon target in the stable state of the magnetron. Working regime of the magnetron gun during those depositions was set up to get stiochiometric silicon dioxide film at the largest deposition rate, as follows:

- Total pressure 3.5·10⁻² Torr;
- Oxygen : Argon flow ratio 1:5;
- Transferred RF power 230W;
- Reflected RF power 30W;
- Target voltage 650 V;

Silicon layers were deposited by simple sputtering of a pure silicon target in an argon atmosphere. Working regime of the magnetron gun during those depositions was set up as follows:

- Total pressure 2.9·10⁻² Torr;
- Oxygen : Argon flow ratio 0:5;
- Transferred RF power 230W;
- Reflected RF power 60W;
- Target voltage 750 V;

The target – substrate distance was not changed during silicon or silicon dioxide deposition and was 180 mm. Temperature of the substrate was kept at 200° C. Total deposition time was 45 minutes. Regimes mentioned above allowed obtaining samples with the silicon concentration of 42% if silicon deposition time per one layer was 2.25 minutes and silicon dioxide deposition time per one layer was 1 minute.

The experiments were run in two series. In both series, the input of oxygen was controlled by switching the oxygen shutter valve of the mass flow controller "on" and "off" (Fig.4101). Total time of every run was set up to 45 minutes. In first series the rotating shutter, see Fig.4101, was open for the whole 45 minutes of the total deposition time. In this series, when the oxygen shutter valve was switched from "on" to "off", some time was needed to pump down the oxygen presented in the vacuum chamber. This time can be considered as a certain transition period between deposition of pure silicon dioxide and pure silicon. For given pump productivity that time was measured as about 30 seconds. During this time, the transition zone in the film was produced but its composition and character of bonds was unclear.

To avoid the appearance of the transition zones in the film a second series of experiments was done. The sample was mechanically shuttered from sputtered material during any action, which produces the transition zone. The sample was exposed to sputtered material only if magnetron worked in steady-state regime. It guaranteed that only pure silicon or silicon dioxide was being deposited. The time point, when mechanical shutter could be opened, was defined according to measurement of partial pressure in the chamber, the voltage on the target and the color of the discharge. This combination of parameters is unique for discharges with and without oxygen. In the current configuration of the system, it was necessary to spend about half a minute to stabilize the discharge parameters in a new regime.

Co-sputtering of silicon and silicon dioxide was done by sputtering of a sectioned target in argon atmosphere, see Fig.4402. For concentration of silicon in the film at 42%, the angle of the silicon sector should be about 45 deg.

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Obviously, in such a configuration we can get any composition on the substrate from pure silicon dioxide to pure silicon by changing the coverage of the silicon dioxide disk by silicon chunk. Achieved film properties are very stable from one run to another. This caused by employment of inert argon only without oxygen. Presence of small steps (less than 0.5 mm in my case) on the border of silicon - silicon dioxide has no effect on stability of magnetron sputter device. Dependence of refractive index on the silicon sector angle is given in Fig.4403. The first point at zero degree means no silicon coverage at all.

The samples of films were deposited always on one side polished two inch silicon wafers, p-type, cut in <100> direction. No additional treatment was done for their cleaning before deposition, so that they were used as delivered.

The thickness of the films for X-Ray Diffraction (XRD) measurements was chosen to be about 1 μ m to get acceptable count rate. In other cases, it varied from 300 to 3000 A.



Fig.4401 Principle of the equity of concentrations



Fig. 4402 Sectioned target for co-sputtering of silicon and silicon dioxide



Fig.4403 Refractive index vs. Si sector angle

The samples deposited by any of the mentioned methods showed their amorphous structure as it follows from XRD pattern. A typical XRD pattern of silicon rich film deposited by the mentioned methods is presented in Fig.4404. Deposition of the films was performed under different temperature of the substrate. However, even heating to 500 degrees Celsius produced no measurable effect on the crystalline structure of the films. Films were always amorphous. In order to crystallize the films, annealing was applied. Annealing conditions were set up as follows: temperature of annealing was 1100^{0} C and the processing time was 2 hours in nitrogen atmosphere. Resulting patterns are given in Fig.4406 for silicon rich films, in Fig.4407 for stacked silicon rich films, and in Fig.4408 for co-sputtered silicon rich films. Patterns are presented for total silicon concentration in the film of 42%. Patterns for silicon rich and co-sputtered silicon rich films with the same concentration of 42% are just equal.

The surfaces of samples obtained by different methods and observed by Scanning Electron Microscope (SEM) in secondary electron mode with 20 kV of accelerating voltage, look similar and one of the images presented in Fig. 4405.

Ellipsometry methods were used to measure the thickness and the refractive index of grown films. The plot presented in Fig.4409 reflects the dependence of the refractive index on the composition of the films for three methods of deposition. Spatial distribution of thickness and refractive index along the sample surface is given in Fig.4410 and Fig.4411 for silicon rich films, in Fig.4412 and Fig.4413 for stacked silicon rich films, and Fig.4414 and Fig.4415 for co-sputtered silicon rich films, all with 42% of silicon.



Fig.4404 XRD pattern of stacked silicon rich film (as deposited)



Fig.4405 SEM image of stacked silicon rich film surface (as deposited)





Fig.4408 XRD pattern of co-sputtered silicon rich film after annealing



Fig.4409 Refractive index vs. film composition for different deposition methods

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Fig.4410 Spatial distribution of thickness for silicon rich films



Fig.4411 Spatial distribution of refractive index for silicon rich films



Fig.4412 Spatial distribution of thickness for stacked silicon rich films





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Fig.4414 Spatial distribution of thickness for co-sputtered silicon rich films





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CHAPTER 5. DISCUSSION OF RESULTS

5.1 Reactive sputtering model

Some of the samples were prepared to examine the model of reactive sputter deposition described in Chapter 2, Part 2.4. Those samples were deposited under different conditions. They were then characterized and results were compared with predictions of the mentioned theoretical model. The comparisons were done for deposition rate, silicon concentration in the film, spatial distribution of the film thickness in dependence on applied power, distance to the substrate, and gas flow ratios.

Let us pay attention first to the deposition rate of silicon rich films. In Fig. 5001, the solid line presents the theoretical curve and separate triangles present experimental data. Despite the wide distribution of experimental data, the trend of them is clearly seen. As it was said earlier, keeping the discharge parameters stable is a trick in reactive sputtering when a feedback loop is not used. This feedback loop is a very simple technique yet very expensive and it was not employed in my case. The behavior of the curve given in Fig. 5001 looks understandable if one recalls that the quantity of sputtered species depends on ion current on the target and sputtering yield proportionally $j_{sputtered} \propto j_1 \cdot y$ (according to Chapter 2). In the literature [67], it is shown that the sputtering yield y has a very complex functional dependence on the energy of incident ions. However, in a small region around 500eV, which is mostly used in magnetron, sputtering this dependence can be simplified by linear dependence on applied voltage, so that the quantity of sputtered species depends absorbed on power

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Fig.5001 Deposition rate vs. applied power. Substrate-target distance 180 mm; Oxygen:Argon flow ratio 1:5



Fig.5002 Deposition rate vs. substrate-target distance. Applied power 200W; Oxygen:Argon flow ratio 1:5

as $j_{sputtered} \propto j_1 \cdot y \propto I \cdot V = W$. This assumption was used in the model of reactive sputter deposition (equation 31, where $Y_{M-I} = (0.5f_{S_I} + 0.23f_{S_IO_2})\frac{U}{500})$ and found to be in good correspondence with experimental data, see Fig.5001. In expression for *Y*: *f* means the fraction of the target covered by *Si* or *SiO*₂, *U* means the target bias; 0.5 and 0.23 are the sputtering yield for *Si* and *SiO*₂ at 500 V.

Change of the distance d from substrate to target causes corresponding change in deposition rate as well. In most cases, Cosine Law of emission (number of particles per unit time per unit solid angle in direction θ is proportional to $\cos\theta$) can describe a material emission from the point-like source. Besides, it is obvious that number of particles per unit time per unit area in any direction is proportional to d^2 . Calculation for magnetron geometry made in Chapter 2 under the equation (31) gives the theoretical curve presented as solid line in Fig.5002; triangles present experimental data. General behavior looks the same, but in details, experimental data have definitely higher value. Explanation of this fact lies in simplifications accepted for creation of reactive sputter deposition model. First of all, it was supposed that there is no deposition caused by sputtering of the target by reactive gas (oxygen). Secondly, deposition of silicon dioxide, which partially covers the target, was not taken into account at all. That is why total actual deposition rate should be higher than in theory for the gases mixture with higher ration of argon to oxygen. Therefore, when the plasma is formed only by oxygen, the target is totally covered by silicon dioxide, and deposition rate is defined by sputtering of silicon dioxide by oxygen.

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Fig.5003 Deposition rate vs. gas flow ratio. Applied power 200W; target-substrate distance 180 mm.



Fig.5004 Concentration of silicon calculated and measured in experiment (Applied power 200W; target-substrate distance 180 mm)

That means that the experimental curve of deposition rate should be constant for high argon : oxygen ratio. It is reflected in Fig.5003 for the deposition rate plotted versus argon : oxygen ratio. When the quantity of oxygen is small enough, ion current produced by the oxygen is fully absorbed by the target and there is almost no deposition caused by oxygen. Besides, coverage of the target by silicon dioxide is also relatively small and argon sputters mostly the silicon. That is why we see good match between experimental and theoretical data in the range of small values of argon-to-oxygen ratios.

The presence of a maximum in Fig.5003 indicates that on the left shoulder of it the sputtered silicon absorbs more and more oxygen so that growing film contains more oxygen per one silicon atom. Taking into account that densities of silicon and silicon dioxide are close we get higher deposition rate for higher argon-to-oxygen ratios. On the right shoulder of the curve (Fig.5003) the target is widely covered by silicon dioxide. Sputtering yield of silicon dioxide by argon is significantly lower (0.23 for silicon dioxide against 0.5 for silicon sputtered by 500V argon atoms) so there is much less sputtered species per unit time. Relatively constant deposition rate after argon/oxygen gas flow ratio is 0.3 means that the target is fully covered by oxygen and we cannot expect obtain silicon rich films in this region.

A similar situation regarding the silicon concentration in the film is shown in Fig.5004. As expected, we obtain the stoichiometry earlier in real films, than in theory, see equation (30). In order to obtain a pure silicon dioxide film the target must not be fully covered by it. Pure silicon sputtered from the target will absorb free oxygen during its movement to the substrate.

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Fig.5005 Comparison of results of calculation under theoretical model of reactive sputtering with factual distribution of the film thickness along the surface of the sample; substrate-target distance -20 mm



Fig.5006 Comparison of results of calculation under theoretical model of reactive sputtering with factual distribution of the film thickness along the surface of the sample; substrate-target distance -100 mm

As result the species impinged the substrate are only silicon dioxide. We can expect even over stoichiometry (x>2 in SiO_x films) in some films obtained under high oxygen pressure. In fact, the minimal achieved refractive index for silicon dioxide films was 1.35, which by implication, shows exceeding a quantity of oxygen in the film over stoichiometry.

However, investigations of such films were beyond of focus of the present research and detailed characterizations were not conducted.

An example of thickness distribution along the surface of the sample plotted together with results of calculations for theoretical model is presented in Fig.5005 and Fig.5006. Calculation of the thickness *h* was done under formula $h = \frac{V \cdot f(x,d)}{2\pi \int_{0}^{+\infty} xf(x,d)dx}t$ from Chapter 2 by the method of finite elements, where t is the

deposition time.

Obviously, the position of the sample close to the target causes very high dispersion in thickness of deposited film. The maximum of the thickness is expected to be a circle with the diameter equal to that one of the erosion zone of the target. Measurement of the diameter of the erosion zone done after long time of target usage gave a value of about 30 mm. It is clearly seen that the maximum of thickness for real film has the position exactly 15 mm off the center of the substrate (Fig.5005). With increasing the distance between target and substrate, the influence of the geometry of the sputtering zone diminishes and uniformity of the films becomes much better (Fig.5006). At the same time, the deposition rate slows down. It is generally possible to create a

special substrate holder with a mechanism of the movement, which would provide perfect uniformity even very close to the target, but in that case, the influence of radiation from the target, of electron bombardment, of magnetic field should be investigated in terms of film quality. In the context of this research, the distance between target and substrate was taken as 180 mm for the most of the samples as it is recommended in some articles [68].

The graphs presented in Fig.5005-5006 show that the reactive sputtering model gives us acceptable results compared to experimental data. This model can be used for initial modeling of the sputtering processes in magnetron configuration. Using the model of reactive sputtering will allow reducing an expenditure of the time on the calibration of any magnetron sputtering system.

5.2 Refractive index

In following part of this chapter we will discuss in some details the results of film characterization obtained for the films deposited by reactive sputter deposition, by cosputtering of silicon and silicon dioxide target and deposited using stacked film approach.

First of all it follows from analysis of characterization data that films deposited by reactive sputtering and co-sputtering are very close in their properties. The films with the same percentage of silicon have shown the same value for refractive index (Fig.4409, Fig.4411 and Fig.4415). The main difference is a much more flat distribution of the refractive index for co-sputtered films. The films deposited in co-sputtering mode were deposited in the atmosphere of pure argon and composition of growing films was depended only on composition of the target and was not affected by chemical reaction in vacuum chamber. That is why the composition of the film repeats that one of the target. In opposite, there was the strong dependence of the film composition on chemical

reaction in vacuum chamber for the films obtained by reactive sputtering. The longer is the distance to the substrate, the more probable the silicon from the target is oxidized by the oxygen from the atmosphere of the vacuum chamber. It caused higher oxidation rate on the edges of silicon wafer comparing to the center of the substrate. As a result, the refractive index decreases toward the edge of the wafer following to decreasing silicon concentration.

The films deposited according to stacked approach display different behavior. As it is seen from Fig.4409, the films with the same percentage of silicon can have refractive indexes different from the films deposited by other methods. In practice, in the extreme case of very thick sub-layers results of ellipsometric measurements could show the refractive index of 1.46 (with pure silicon dioxide deposited as upper layer) or 3.86 (with pure amorphous silicon deposited as an upper layer). However, we have to keep in mind that this stacked film approach was implemented exactly to try getting the films with properties equal to that of standard silicon rich films. That is why the most important fact is that it is possible to deposit the silicon rich-like films by stacking silicon and silicon dioxide layers. However, the same silicon concentration in the films does not mean the same refractive index. The sensitivity of properties of the stacked films to the thickness of silicon layers are very high and reflected in Fig.5007. In this plot, time means the time of deposition of every single silicon layer when the time for deposition of silicon dioxide layers was kept the same during all depositions. For example, if the silicon dioxide layer deposition time compared to that of silicon was longer as much as 2.25 times, this approach allowed depositing the films with 42% of silicon concentration. This concentration was first calculated based on total deposition time for silicon and silicon

dioxide layers (Chapter 4) using the simple approximation

$$C_{S_{l}} = \frac{z \cdot \rho_{S_{l}} \cdot \mu_{S_{l}O_{2}} + \rho_{S_{l}O_{2}} \cdot \mu_{S_{l}}}{z \cdot \rho_{S_{l}} \cdot \mu_{S_{l}O_{2}} + 3 \cdot \rho_{S_{l}O_{2}} \cdot \mu_{S_{l}}}$$
(42)

where $z = \frac{n_{S_{IO_2}} - n}{n - n_{S_I}}$ (here C is a concentration; ρ is a density; n is a refractive index; μ is a

molar mass) and then measured by RBS, see Fig.5008 (41.9%). Quantification of RBS results were carried out using the program "Quark" provided by University of Western Ontario.

The first edge at channel 550 in Fig.5008 is associated with silicon in the film. The next edge at 530 is associated with the silicon in the substrate. The peak of oxygen starting at 350 and ending at 310, which is clearly seen over the signal from the substrate, indicates the presence of oxygen in the investigated film.

The sensitivity of the used equipment was not high enough to detect the periodicity in the given films. It tells us that the sub layers are acceptably thin in terms of homogeneity of silicon concentration throughout the film. For short times of deposition of each layer, there is good correspondence of the curves in Fig.4308 and Fig.4409 to simulation based on Bruggemann formula [69]. However, for longer deposition time, the refraction index is higher then it was predicted by theory. It can be explained in terms of phase separation between silicon and silicon dioxide. For short periods, there are in fact no phase separations and stacked films behave as homogeneous silicon rich film with uniform distribution of silicon atoms in silicon dioxide matrix. For longer periods, we can predict the formation of silicon and silicon dioxide. As it was shown in [69], increasing phase

separation leads to increasing refractive index. It can also be confirmed if we compare the curves for samples deposited with and without transition. Higher refractive index was achieved for the samples without transition zone, i.e., for samples with grater phase separations.



Fig.5007 Time dependence of refractive index for stacked films



Fig.5008 RBS spectrum of stacked silicon and silicon dioxide films with total thickness of 1450 Å; 42% of silicon concentration and refractive index of 1.9

5.3 XRD measurements

It was noted earlier that all as deposited films had amorphous structure, which was confirmed by XRD measurements. There are two broad peaks in respect to 2 θ , one at about 28 degrees and second one at about 50 degrees (the example in Fig.4404 presents the XRD pattern for a stacked silicon rich film). At the same time for most of the polycrystalline silicon films there should be observed three different peaks within the same range at 28.408, 47.287 and 56.08 degrees corresponding to <111>, <220> and <311> crystallographic directions respectively.

It is generally accepted that if XRD patterns for silicon containing film show one broad peak at about 50 degrees instead of two the peaks at 47.287 and 56.08 degrees and besides one more broad peak at about 28 degrees, such a film contains silicon in the amorphous state. Of course, it is not totally amorphous silicon, for which we would not see any peaks, but the crystallographic order of each crystal is limited by very small space. That is why two broad peaks at 47.287 and 56.08 degrees are merged and form one peak at 50 degrees. High temperature annealing of deposited samples has shown the change in the XRD patterns for all films. Results of annealing at 1100^oC for 2 hours in nitrogen atmosphere are presented in Fig.4406, 4407 and 4408 for silicon rich, stacked and co-sputtered films, respectively. Such a transformation of the XRD patterns is also considered as an evidence of amorphism of as deposited films.

Estimation of the crystalline size z of silicon crystals after annealing was carried out using well-known Scherrer formula:

$$z \cong \frac{0.9\lambda}{d\cos\theta},\tag{43}$$

where λ is X-ray wavelength of a base beam, *d* is the half width of the peak, and θ is diffraction angle. All films show similar crystalline size of about 4-5 nm. However, the width of the peaks indicates a wide distribution of sizes of nanocrystals. A detailed investigation of how exactly the sizes are distributed was not carried out.

5.4 Photoluminescence

None of the as deposited samples showed photoluminescence (PL). Even annealing at 1100°C during 2 hours did not improve the situation. Only samples deposited using the stacked film approach showed a small PL signal for silicon concentrations of about 42 at.%, see Fig.5009. As it was discussed in [11], the main problem in terms of PL for all silicon nanocrystals embedded into a silicon dioxide matrix is the passivation of the surfaces of the nanocrystals. In case of a superlattice, which was actually produced in the stacked film approach, the passivation of nanocrystalnanocrystal grain boundaries is also essential. At the grain boundaries between silicon nanocrystals, some defects such as silicon dangling bonds can play a positive role in PL or can act as non-radiative recombination centers for electron-hole pairs. That is why there are different PL peak positions from one sample to another with significantly lower PL intensity compared to conventionally fabricated samples. In my case, as-deposited films show no significant PL in visible spectrum as films with no silicon nanocrystals and hence with just no ability to emit light. Annealed samples with concentrations less or more than 42 at.% also show no PL. At the same time, the PL peak for 42% of silicon is broad indicating large diversion of the crystal size in the sample.
As was already mentioned, passivation of the surface of silicon nanocrystals is essential. In case of deposition of silicon rich films in atmosphere of argon and hydrogen, the latter can act as passivator of dangling bonds of silicon. In Fig.5010, the PL signal from a not passivated sample deposited as stacked films is compared with PL signal of a passivated sample deposited by co-sputtering in argon and hydrogen atmosphere. The grain size in both cases was calculated from XRD measurements and gave 4 nm crystal sizes as most probable. However, the peak position is different, which likely is an indication of different PL origins. In the frame of this work it was not deeply investigated which of the possible effects (quantum confinement, surface states, defects or others) is leading in PL. Nevertheless, quantum confinement is found by some authors to be dominant in cases close to stacked films and the defect model is found to be dominant for the films obtained by co-sputtering [11].

The PL spectrum for stacked films presented in Fig.5009 can be composed from two peaks: first at about 550 nm and second at about 750 nm. If we take into account that silicon in the layer is crystalline (according to the XRD pattern) and the quantum confinement is effective, we can construct a model of visible photoluminescence similar to that one described in [70].

The above mentioned transition layers between silicon and silicon dioxide should be taken into account in this model. PL is supposed to originate from exciton (electronhole pair) recombination within silicon layer and within transition zone.

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Fig.5009 PL signals from as deposited (no peaks) and annealed stacked films



Fig.5010 PL intensity from annealed samples of stacked film (low intensity) and of the film obtained by co-sputtering in argon and hydrogen atmosphere

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For the energy diagram proposed in Fig.5011 (from [70] the following equations for the exciton wave function can be written (m* implies $m^*=1/m_e+1/m_h$ – reduced mass of the exciton as a function of electron and hole masses) as:

$$-\frac{\hbar^2}{2m^*}\frac{\partial^2\Psi(x)}{\partial x^2} = \Psi(x)(E)$$
(44)

$$-\frac{\hbar^2}{2m^*}\frac{\partial^2\Psi(x)}{\partial x^2} = \Psi(x)(E-V_1)$$
(45)

$$-\frac{\hbar^2}{2m^*}\frac{\partial^2\Psi(x)}{\partial x^2} = \Psi(x)(E - V_2)$$
(46)

Taking into account that wave functions and their derivatives should be equal at the boundaries we can get following authors of [70] for the permitted wave vectors k:

$$kt \cdot Tg(kt) = \frac{ptCosh(qe) + ptSinh(qe)}{Cosh(qe) + \frac{p}{q}Sinh(qe)}$$
(47)

and for the eigenvalues of the particles

$$E = \frac{\hbar^2 k^2}{2m^*},\tag{48}$$

where $q^2 = \left| \frac{2m^* V_1}{\hbar^2} - k^2 \right|$ and $p^2 = \left| \frac{2m^* V_2}{\hbar^2} - k^2 \right|$.

Results presented in [70] show that the peak at 550 nm from Fig.5009 reflects photoluminescence from the transition layer between silicon and silicon dioxide. The main peak at 750 nm can be also explained in terms of quantum confinement as mentioned above.





CHAPTER 6. CONCLUSIONS AND SUGGESTIONS FOR FUTURE WORK

The main goal of proposed work was to show the possibility to create silicon based thin films deposited by magnetron sputtering which can emit light in the visible range. In the first stage of this work, the experimental system was created based on standard components such as a vacuum chamber, sputtering gun and control equipment.

The system was installed and tested in a laboratory of the Engineering Physics Department at McMaster University. The vacuum part of the system showed good performance, which allowed working with a background pressure less then $4 \cdot 10^{-8}$ Torr. At the same time, the vacuum part of the system could provide a working pressure up to one tenth of a millitorr. The power supply unit used in the system was combined from an RF generator workable up to 600 W and a matching network. A magnetron sputter gun was the load.

The magnetron sputtering system was tested on different regimes in particular in the reactive sputtering mode. In this case, the plasma forming gas was combined from inert argon and chemically active oxygen. Exactly for this kind of operation conditions, the reactive sputter deposition model for thin film deposition was developed in the frame of the presented work. Checking of that model on given magnetron sputtering system has shown its good correspondence to experimental data up to oxygen : argon flow ratios as high as 0.4. For grater values, results of the experiments diverge with those of the model. It is caused by certain simplifications accepted for the developed model. Nevertheless, the model of reactive sputter deposition can be successfully used for corresponding systems.

During carrying out of the work, three methods of silicon-rich film deposition were proposed and tested. The first one was simple reactive sputter deposition of silicon; the second was deposition of stacked films of silicon and silicon dioxide; and the third was co-sputtering of silicon and silicon dioxide in one run.

It was shown that all as-deposited films have amorphous structure. However, annealing at high temperatures caused phase separation with creation of silicon nanometer-sized crystals inside of a silicon dioxide matrix. The size of the nanocrystals was estimated as 2-4 nm.

The percentage of silicon in silicon rich films can be easily controlled in cases of co-sputtering and stacked films. Obtaining silicon rich films by reactive sputtering with repeatable quality was highly problematic. However, as it was mentioned earlier, it is possible using additional feedback loop closed on in-chamber pressure.

The most intensive effect of photo luminescence was clearly observed only if some hydrogen was introduced into the chamber during deposition. Due to specific conditions of depositions, only co-sputtering was used to check how hydrogen influences on the PL of deposited films. In other cases, the presence of hydrogen and oxygen in discharge zone could cause the undesirable chemical reactions between those gases and such experiments were not done. Very poor PL was observed for stacked films with concentrations of silicon only as high as 42%. No other sample showed significantly high PL.

There are many aspects concerning the place of sputter deposition in silicon nanocrystals technique, which are not addressed in this work, however, there are plans to pay attention to co-sputtering as a prospective method of deposition of thin films.

The idea to use the target combined from different materials looks very promising in terms of obtaining the films of silicon dioxide enriched by silicon and doped by other elements like that from Rare Earth group. The emission of light from Rare Earth elements embedded into SRSO (silicon rich silicon oxide) films which is now intensively investigated can cover the spectrum from blue to red. Combination of different emitting layers can even give the emission of whole structure in white light. However, the emission of Rare Earth ions is provided by energy transfer from silicon nanocrystals to the ions. The usual way to form the nanocrystals is to anneal the as-grown films at a high temperature for a long time. Fortunately, so called "chemical annealing" was recently discovered as very promising. It is reported in [71-73], that if even small amount of hydrogen is introduced into the vacuum chamber during the sputtering, the as-grown films show the presence of the crystallized silicon. The more hydrogen is introduced into the discharge, the larger amount of crystalline phase of silicon will be found in the deposited film. From other hand, sputtering of the silicon dioxide target in presence of hydrogen can lead to the deposition of pure silicon. However, that silicon is always amorphous. Nevertheless, co-sputtering of silicon and silicon dioxide in the presence of hydrogen can lead to formation of certain amount of the silicon nanocrystals in as-grown films. In addition to this, one can apply the magnetic field in parallel to the substrate. It is reported [74] that microcrystalline films of silicon were deposited using this approach.

Additional bombardment of a growing film by argon can also be helpful in terms of the crystalline silicon film formation.

In my future work, I hope to find the optimal regimes of the film formation for the effective emission of Rare Earth elements embedded into SRSO obtained by reactive sputtering.

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