THE DAMAGE LAYER PRODUCED

IN

ION BOMBARDED SILICON*

*A study of the layer, and its usefulness in the study of radiation damage itself.

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ION BOMBARDED SILICON

By IAN REID, B.Sc.

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In this thesis a study is made of the damage layer (as defined by its solubility in a $HF-H_2O_2$, or concentrated HF solution) produced by ion bombardment of Si. This thesis is concerned with not only the layer but also its usefulness in the study of radiation damage itself.

The layer is examined with respect to the adverse effects it has upon the anodic oxidation and stripping technique, to the dose of incident ions required to produce it (ie the threshold dose), and to its relationship to the amorphous layer which has been observed with ion bombardment of Si.

Annealing of the damage has been approached from two points of view. First the temperature dependence of the threshold dose is used to obtain information about the annealing of the damage that occurs between the formation of a discrete damage zone and the formation of a layer. Secondly using gas release of the radioactive Kr⁸⁵ the annealing of the fully formed amorphous damage layer is followed.

The solubility of the damage layer in a $HF-H_2O_2$ solution is shown to be a very useful tool in the study of radiation damage.

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Firstly it provides a convenient means of obtaining the mean range of the damage distribution as a function of incident ion energy. Secondly it is used to obtain the threshold dose for the formation of the damage layer, and thirdly it is used in the gas release experiments to give more detailed information about the Kr^{85} motion.

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SECTION I: ANODIC OXIDATION OF ION BOMBARDED SILICON

Introductory Comments

Essential to the anodic stripping technique used in range studies, diffusion work, and device characterization, is the requirement that only the anodic oxide be removed in the dissolution step. Experiments conducted on high $(3.74 \times 10^{15} \text{ ions/cm}^2)$ and intermediate $(10^{14} \text{ ions/cm}^2)$ dose Kr⁸⁵ bombarded p-type Si wafers reveal that this criterion is not met.

The samples were anodized in an electrolyte of 0.4 gm KNO_3 , 96 ml ethylene glycol, and 4 ml of distilled water.⁽¹⁾ A 0.03 N solution of HF was used to dissolve the anodic oxide; however no distinction could be made between the dissolution of the anodic oxide and the underlying amorphous Si.

By anodizing before bombarding it is shown that the lack of any observable dissolution rate change is not due to an unexpected deep anodization of Si which is amorphous.

¹E. F. Duffek, E. A. Benjamini and C. Mylroie, Electrochemical Tech. <u>3</u>, 75 (1965).

Introduction

Anodic stripping of bombarded Si is a widely used technique in the investigation of property changes such as concentration of implantant, concentration of diffusant, carrier concentration and mobility, and defect concentration with depth⁽²⁾. The reliability of the technique is based on the assumption that the stripping solution attacks only the anodic oxide and not the underlying Si, or at least attacks the latter at a very slow rate. Even though the technique is widely used, direct experimental evidence is seldom presented to show that this criterion is satisfied. The reason for this probably lies in the fact that most of the work has been done either on crystalline Si, which has a slow dissolution rate in HF, or on Si which was amorphized by bombarding particles only in the vicinity of the mean range of the particles, thence not at the surface. However, high-dose bombardments at lower energies (<40 keV) cause an amorphous layer to be produced which commences at the surface, and difficulty may arise due to the solubility of the amorphous Si in HF. This property of amorphous silicon, which has itself been used as a tool in probing silicon^(3,4) and will be discussed elsewhere here*, at first appears to offer no difficulty because of the high HF concentrations used to dissolve amorphous silicon as compared to the low concentrations used to dissolve anodic oxides of silicon.

The purpose of the present work is to investigate the feasibility of using the anodic stripping technique for probing amorphous silicon.

²J. W. Mayer, L. Eriksson, J. A. Davies, "Ion Implantation in Semiconductors", Academic Press, New York, 1970.

Jech, Phys. Stat. Sol. 27, 573 (1968). F. Gibbons, E. O. HechtT, T. Tsurushima, App. Phys. Letters 15, 117 (1969) and T 111

Experimental Method

Silicon wafers (p-type, <111> orientation, and $\rho = 5-10 \ \Omega$ -cm) were bombarded with 40 kv Kr⁸⁵ ions to doses of 10¹⁴ and 3.74 x 10¹⁵ ions/cm². The samples were anodized in the apparatus shown in Fig. 1.1 using an electrolyte of 4 gm KNO₃, 96 ml ethylene glycol, 4 ml distilled water. The anodic oxide was formed at constant current, the process being terminated when the preset voltage was reached. The voltage measured is actually the voltage across the oxide plus the voltage across the silicon and electrolyte; however, by keeping the current density small the latter two become a negligible part of the total.

Fig. 1.2 shows the calibration of the anodizing process obtained using a large silicon wafer anodized to the required voltage and stripped in HF. The thickness of silicon removed was obtained by comparing the weight before anodizing to that after stripping, giving a value for the thickness of silicon removed of 3 A/volt. The wafer was then broken and the pieces used in the subsequent experiments.

Results and Discussion

In the first set of experiments the normal procedure for obtaining a range distribution was followed, i.e., the sample was bombarded $(40 \text{ kv}, 3.74 \times 10^{15} \text{ ions/cm}^2)$, anodized, and placed in the stripping solution. However, rather than assume that after a certain period of time the anodic oxide had been removed and the underlying silicon left intact the residual activity was recorded as a function of time in the stripping solution. If only the anodic oxide is dissolved then the residual activity of the sample should decrease to some value and remain there. The results are shown in Fig. 1.3 for anodic oxides of 80, 50, 10 and 5 volts (i.e. 250, 150, 50 and 40 $\stackrel{\circ}{A}$ of Si). Since at 40 kv Kr⁸⁵ has a mean projected range of 260 $\stackrel{\circ}{A}$ (5), less than 50% of the activity should be lost in the dissolution of these oxides.

We note from Fig. 1.3 that no distinction can be made between the dissolution rates of the anodic oxide and the underlying amorphous silicon. The knee in the dissolution curves at $\approx 0.15\%$ residual activity is a result of the change in dissolution rate between the amorphous or anodize Si and crystalline silicon, and confirms the usually assumed slow dissolution rate of the crystalline silicon. The appearance of this knee at $\approx 0.15\%$ for the 50, & lov anodize also confirms that the anodic oxide has not penetrated deeper than the amorphous-crystalline interface. Although no distinction can be made between the dissolution rate of the oxide and the underlying silicon, the thickness of the oxide does govern the rate at which the two dissolve. The increased dissolution rate of the oxide with thickness may be related to the stoichiometry of the oxide, but this does not explain the effect upon the underlying amorphous silicon. The investigation of this effect is, however, outside the scope of this thesis.

If the apparently similar dissolution rate for the anodic oxide and underlying amorphous silicon is due to unexpectedly deep anodization of silicon which is amorphous (i.e. such that the calibration line is steeper than in Fig. 1.2), it should be eliminated by anodizing before bombarding. Fig. 1.4 shows the results of a 120, 10 and 5 volt anodize followed by a 3.7 x 10^{15} ions/cm² 40 keV Kr⁸⁵ bombardment. The 40 keV Kr⁸⁵

⁵W. S. Johnson and J. F. Gibbon, "Projected Range Statistics in Semiconductors", Stanford University Bookstore (1970).

ions have not penetrated the 120 V oxide and thus all the activity is lost within 30 minutes. This result is expected since a 120 V anodize will produce at most a 800 Å oxide layer (assuming the oxide to be SiO_2) and the mean range of 40 keV 85 Kr in SiO_2 is 210 Å $^{(5)}$. The 10 and 5 voltanodizes, however, will give only a 100 and 80 Å oxide respectively. Most of the Kr 85 has thus penetrated the 10V and 5V oxides but as in Fig. 1.3 no distinction can be made between the dissolution of the anodic oxide and the underlying amorphous silicon.

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The dissolution rate of amorphous silicon produced by ion bombardment has been found⁽⁶⁾ to increase with ion dose. At lower doses it thus might be possible to distinguish between the dissolution of the anodic oxide and the underlying amorphous silicon. Two samples were therefore bombarded with 40 keV ⁸⁵Kr to $\approx 10^{14}$ ions/cm², one was anodized at 10 volts (50 Å Si), the other at 20 volts (80 Å), and both were stripped in a 0.03 N HF solution. The dissolution curves (Fig. 1.5) like those of Fig. 1.3 and L4 show no dissolution rate difference between the anodic oxide and the underlying amorphous silicon. The knee due to the slow dissolution rate of crystalline silicon has moved up to $\approx 1.5\%$ activity as a result of the decreased dose, presumably because the amorphous-crystalline interface is nearer the surface. This is an important effect, and will be discussed in detail later⁽⁶⁾.

Dearnally et al.⁽⁷⁾ have discussed range distributions in amorphous silicon bombarded with 40 keV P^{32} ions, an anodic stripping technique with an electrolyte of 0.1 M aqueous solution of boric acid

⁶See Section II.

⁷G. Dearnally, M. A. Wilkins, P. D. Goode, J. H. Freeman, G. A. Gard, "Atomic Collision Phenomena in Solids", ed. by Palmer, Thompson and Townsend, North-Holland Press, Amsterdam (1970).

and sodium tetraborate having been used. An experiment was therefore conducted using this electrolyte. A sample was bombarded with 40 keV 85 Kr ions to 3.74 x 10¹⁵ ions/cm², followed by an anodize of 10 V in the boric acid plus sodium tetraborate electrolyte. This electrolyte gives a high \hat{A} /volt relation and thus we expect from the calibration of Wilkins⁽⁸⁾ $\simeq 200$ Å of Si to be anodized. The dissolution curve like those of Fig. 1.3. 1.4 and 1.5 revealed no knee as a result of a dissolution rate difference between the anodic oxide and the underlying amorphous silicon.

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Davies et al.⁽⁹⁾ have reported ranges of Xe^{125} in Si using an anodic stripping technique with an electrolyte of 0.04 M KNO_2 in Nmethylacetamide and a stripping solution of 1.0 N HF. The decreased ranges they observed at high doses $(1.2 \times 10^{14} \text{ ions/cm}^2)$ may be in part a result of dissolution of more than the anodic oxide; however, their anodization calibration curve for silicon bombarded to 2×10^{14} ions/cm² is the same as that for silicon which was unbombarded. A major inconsistency would appear to be indicated.

Conclusions

Before employing the anodic stripping technique it should first be demonstrated that in the dissolution step only the anodic oxide is removed. It has been shown that it is not sufficient to look at the dissolution rates of the anodic oxide and the material of interest separately, instead the two must be looked at together as they will be in the actual experiment.

The standard anodic stripping technique for Si using dilute HF as the stripping solution is not applicable for the probing of amorphous ⁸M. A. Wilkins, Harwell Report R-5875, 1968.

⁹J. A. Davies, G. C. Ball, F. Brown, and D. Domeij, Can. J. Phys., 42 1070 (1964).

silicon, owing to the solubility of the amorphous silicon even though it is only moderately soluble when investigated by itself.

This indistinguishability between the anodic oxide and the underlying amorphous silicon is found at intermediate and high doses $(\geq 10^{14} \text{ ions/cm}^2)$. The test should be extended into the low dose region $(\simeq 10^{12} \text{ ions/cm}^2)$ where an amorphous layer is not produced so that the applicability of the technique in the region where it has been used most extensively can be tested. Our present accelerator makes such low doses very difficult to obtain, since the lowest convenient dose is $10^{13} \text{ ions/cm}^2$.







Fig.1.2. Calibration of anodic oxidation using KNO3-ethylene glycol electrolyte.



Fig.1.3. Stripping curves for Si samples bombarded with 40 kev Kr^{85} ions to 3.7 x 10^{15} ions/cm², followed by anodization. The insert shows the anodizing voltage and current.



Fig.1.4. Stripping curves for Si samples anodized before bombardment with 40 kev Kr^{85} ions to 3.7 x 10^{15} ions/cm². Insert shows anodizing voltage and current.



SECTION II: MEAN RANGE OF DAMAGE FOR 10 AND 40 KEV Kr⁸⁵ BOMBARDMENT OF SILICON

Introductory Comments

In section I the solubility of amorphous Si in an HF solution was shown to be detrimental to the anodic stripping technique for probing ion-bombarded Si. In this and subsequent sections we turn our attention to the beneficial nature of this solubility in the study of ion-bombarded Si.

In this section the enhanced solubility of amorphous Si produced by ion bombardment is used to obtain the mean range of damage, $<x_d>$, for 10 and 40 kev Kr⁸⁵ bombardments of Si.

Single crystal wafers of p-type Si (<111> orientation, $\rho = 5-10 \ \Omega$ -cm) were bombarded at 10 kev to doses of 1.87, 3.74 and 18.7 x 10^{14} ions/cm² and at 40 kev to doses of 1.0, 18.7 and 37.4 x 10^{14} ions/cm² with a dose rate of 3.12 x 10^{13} ions/cm²-sec (5 μ A/cm²). The amorphous layer was etched in a solution of 2 pts 48% HF and 1 pt 30% H₂O₂, the depth of the amorphous-crystalline interface being deduced by comparing the integral activity after the amorphous layer is removed with a theoretical ion depth distribution curve.

The depth of this interface within the Si will vary with dose but the concentration of damage C_d , at the interface, is postulated to be constant (i.e. equal to the damage concentration required to render the Si amorphous). Assuming the damage distribution function

to be approximately Gaussian the mean range of damage $\langle x_d \rangle$ follows from the variation of the amorphous layer thickness with dose.

The mean range of damage for a true Gaussian damage distribution is found to be 65 ± 10 Å fro 10 kev and 180 ± 40 Å for 40 kev. If deviation from a Gaussian is accounted for by using Edgeworth's expansion then $<x_d>$ is found to be 55 ± 5 Å for 10 kev and 160 ± 20 Å for 40 kev. The theoretical values of $<x_d>$ are 70 and 190 Å for 10 kev and 40 kev respectively. The agreement is thus rather good.

Introduction

Since a large volume of data pertaining to the range distribution of bombarding ions is already available in the literature much attention has been focussed, in recent years, on the problem of the distribution of damage. Such information is valuable not only from the fundamental point of view of providing a better understanding of the collison process but also because of its relevance to the practical problems of device fabrication by ion implantation. The effect of this damage on the electrical properties of semiconducting materials renders its nature and position a subject of high priority.

The production of an amorphous layer (defined by the lack of long range order) by high dose bombardment of Si, has been well documented⁽¹⁾ using optical reflectivity, **mev**-particle channeling, electron-transmission microscopy, electron diffraction and more recently by scanning electron microscopy patterns.⁽²⁾

The enhanced solubility of this amorphous layer in HF, first reported by Gianola,⁽³⁾ provides a convenient means of extracting information from bombarded silicon. This enhanced solubility has been used to strip thin layers of silicon and thus obtain range distributions of low-dose bombarded silicon⁽⁴⁾ and also to obtain the depth of the damage (amorphous) layer.^(3,5) This latter information has subsequently been used

- (1) J. W. Mayer, L. Eriksson, J. A. Davies, "Ion Implantation in Semiconductors". Academic Press, New York, 1970, Chapter 3.
- (2) S. M. Davidson and G. R. Booker, Rad. Eff., <u>6</u>, 33 (1970).
- (3) V. F. Gianola, J. Appl. Phys., <u>28</u>, 808 (1957).
- (4) C. Jech, Phys. Stat. Sol., 27, 573 (1968).
- (5) J. Gibbons, E. O. Hechtl, T. Tsurushima, Appl. Phys. Letters, <u>15</u>, 117 (1969).

to determine the critical initial fraction of displaced atoms to produce amorphousness in $Si_{\cdot}^{(6)}$

It will be shown here how a comparison of the residual activity, after the amorphous layer is removed, with an integral ion depth distribution curve gives two pieces of information: (a) the thickness of the amorphous layer and (b) the dose required to create amorphousness. In this section the variation of the amorphous layer thickness with dose will be shown to provide an easy and inexpensive means of obtaining the mean depth of the damage distribution.

(6) R. Kelly and L. Q. Nghi, Radiat. Eff. (in press).

Experimental Method

Silicon wafers (p-type, $\rho = 5-10 \ \Omega$ -cm), etched in a solution of 3 pts 48% HF, 5 pts 70% HNO₃, 3 pts CH₃COOH, and rinsed in distilled water followed by methyl alcohol,were bombarded with radioactive Kr⁸⁵ ions at 10 keV to doses of 1.87, 3.74, 18.7 x 10¹⁴ ions/cm² and at 40 keV to doses of 1.0, 18.7 & 37.4 x 10¹⁴ ions/cm² at a dose rate of **3.12 x 10¹³ ions/cm²-sec.**(5μ A/cm²). bombardments were done with a radio-frequency (77 megahertz) ion source, the peak voltage being kept below **24** volts to minimize double ionization of the Kr⁸⁵. There is no mass separation or electrostatic deflection of the beam. The ions are focussed by five electrostatic lenses and accelerated up to 40 keV. The basic components and the related electrical circuitry of the accelerator are shown in figure 2.1.

Bombarding Dose

It is very important in these experiments that the bombarding dose be known accurately and that the dose be uniform over the bombarded area, both being important in determining the depth of the amorphous layer.

Since the accelerator doesn't have a provision for beam-sweeping, steps must be taken to insure that the bombarding beam is uniform. A nonuniform beam will result in different regions of the bombarded area obtaining a different dose and thereby a different depth of amorphization. Focussing conditons, which produce a uniform beam under the two accelerating voltages, were obtained by sputtering anodized Ta under various focussing voltages and arrangements. The colours of the anodic Ta oxide vary with thickness, thence with amount of sputtering, and thus any non-uniformity in colour after the bombardment will reveal a non-uniformity in ion beam

density. At 10 keV (+5 kv, - 5 kv) a uniform beam was produced with a focussing voltage (Fig. 2.1) of 0 volts and at 40 keV (+ 5 kv, - 35 kv) with a focussing voltage of 4000 volts. It should be noted that visual observation of the beam on a fluorescent screen was found to reveal only large non-uniformities.

Accuracy of the dose will also be determined by knowing accurately the area of the beam arriving at the target holder. Since the focussing conditons are set to produce a uniform beam the area of the beam at the target can't be adjusted by altering the focussing. A 1.17 cm diameter aperture was therefore introduced into the beam line just before the target, giving a beam area of 1 cm² at the target.

The largest error in the dose occurs as a result of secondary emission of electrons from the target during bombarding.⁽⁷⁾ The current to the target is thus a result of 85 Kr⁺ ions arriving and electrons leaving. In order to use the current to the target as a measure of the ion dose (1 μ A min/cm² = 3.74 x 10¹⁴ ions/cm²) the electron component must be eliminated.

A Faraday cage is therefore placed around the target holder and kept at a more negative potential (Fig 2.), thus suppressing this electron emission. Fig. 2.2, which shows the current to the target as a function of the suppression voltage for 10 and 40 keV accelerations reveals that a suppression voltage of \approx 400 volts is adequate. However, since the aperture and the screen are held at half the Faraday cage potential, 800 volts

⁽⁷⁾ G. Carter and J. S. Colligon, "Ion Bombardment of Solids," Heinemann Educational Books Ltd., London, 1968, Chapter 3.

is used. This provides adequate suppression of electrons both from the operture to the cage and from target to the aperture and screen. If the suppression voltage is too high then the suppression will start to interfere with the focus and thereby reduce the current further. The greater current decrease for the 40 keV case of Fig 2.2 is a result of a greater yield of electrons at the higher energy.

Gas Sputtering Effect

For the activity of the sample to be proportional to the bombarding dose the dose must be kept below the level where interactions between the incident Kr⁸⁵ ions and the Kr⁸⁵ ions already in the target occur.⁽⁸⁾ In the low-dose region where no interaction occurs

 $n_i = S_0 n_T$

where $n_i = number$ of incident ions n_{T} = number of trapped ions

 $S_0 = sticking probability = 1$ for our energies

Samples were bombarded at 10 keV and 40 keV to various doses, the activity being recording as shown in Fig. 2.3. In the region where $n_i = n_T$ the activity of the sample rises linearly. At higher doses interaction between the incident and trapped ions results in gas sputtering, thus reducing the slope of the curve. Beyond a certain dose, which is shown in Fig 2.3 to be a function of energy, the gas sputtering occurs to such an extent that the number of sputtered ions equals the number of incident ions and the activity or number of trapped ions in the sample remains constant. From Fig. 2.3, we see that the dose in the 10 keV bombardments must be kept below 5 μ Amin/cm² (1.87 x 10¹⁵ ions/cm²) and for the 40 keV 64).

bombardments below 30 μ A min/cm² (1.12 x 10¹⁶ ions/cm²). The greater depth of penetration of the 40 keV ions makes higher doses possible, sputtering being a process that is confined mostly to atoms in a region near the surface.

Etching of the Amorphous Layer

After the samples were bombarded the amorphous layer was preferentially etched in a solution of 2 pts 48% HF and 1 pt 30% H_2O_2 . This solution is faster and gives more reproducible results than the more commonly used HF solution.⁽⁵⁾ The activity of the sample was recorded as a function of time in the etchant in order to obtain the position of the amorphouscrystalline interface and also to observe to what extent the crystalline silicon is **insoluble** in the etchant.

Results and Discussion

Fig. 2.4 and 2.5 show the dissolution curves for the 10 keV and 40 keV bombardments, the difference in dissolution rate between the amorphous and crystalline Si being revealed by a knee in the dissolution curve. It is noted however that the crystalline silicon is slightly soluble in the $HF-H_2O_2$ solution (this is also found to be the case for the 48% HF solution). This technique provides a much more sensitive check on the solubility of the crystalline Si than that using the interference microscope since neither Gianola⁽³⁾ nor Gibbons et al.⁽⁵⁾ were able to detect this solubility. As expected the percentage of residual activity below the amorphous layer decreases with increasing dose indicating an increase in the thickness of the layer. The two arrows on the dissolution curves of Fig. 2.4 define the region in which the amorphous layer is visually noted to disappear, as indicated by its milky colour. Not only is this visual technique a very subjective method, but we note from figure 2.4 that it can result in substantial error, especially in the energy range of the present work (10 and 40 keV). Specifically, it tends to overestimate the dose required for amorphization and to underestimate the thickness of the amorphous layer.

The depth of the amorphous layer was obtained directly by comparing the knee activities of Fig. 2.4 and 25 with the theoretical integral ion range distribution curves of Fig. 2.6 and 2.7.* The results are shown in Table2-I. A check on the reproducibility of the dissolution technique is provided by the residual dose (i.e. the number of ions implanted below

^{*}The method of obtaining these curves is shown in Appendix I.

the amorphous layer), which is shown to be approximately constant as expected.*

The dissolution rate of the amorphous layer is shown in Fig. 2.4 and 2.5 (though with one exception in Fig. 2.5) to increase with dose, thus indicating a sensitivity to either the energy distribution or the ion distribution.

Mean Range of Damage

The distribution of deposited energy can be approximated by (9)

$$F(x)dx = \frac{\upsilon(E) [Dose]dx}{[2\pi\mu_2]^{1/2}} \exp \left[-1.33 \left(\frac{x}{< x_d} - 1\right)^2\right] g(\xi)$$

where v(E) is the energy lost in elastic collisions

 μ_2 is the second central moment**

 $\langle x_d \rangle$ is the mean range of damage

g(ξ) is Edgeworth's correction term to the Gaussian distribution** $\xi \equiv (x - \langle x_d \rangle) / \frac{1/2}{\nu_2}$

If the concentration of damage at the amorphous-crystalline interface is postulated to be constant, then at a given energy the quantity

A = (Dose) exp [-1.33
$$(\frac{x}{\langle x_d \rangle} - 1)^2$$
] g(z)

will be constant. From Table 2-I the three values of Dose and x are obtained for each energy. The quantity A is then plotted as a function of $\langle x_d \rangle$, the point or points of intersection defining the values of $\langle x_d \rangle$ that satisfy

^{*}This quantity gives an estimate of the dose required to produce this layer and will be dealt with in section III in greater detail.
(9) P. Sigmund, Phys. Rev., <u>184</u>, 383 (1969)
**See Appendix I of this section.

the condition of constant concentration at the interface.

As a first example, a Gaussian distribution was assumed, i.e. $g(\xi) = 1$. This gives points of intersection of the three equations at $\langle x_d \rangle = 55$, 70 and 75 Å for 10 keV and $\langle x_d \rangle = 150$, 180 and 220 Å for 40 keV. The purpose of the correction terms $g(\xi)$ is to modify the Gaussian distribution in accordance with the calculated moments. ⁽¹⁰⁾ The correction factor $g(\xi)_d$ is shown graphically in Fig. 2.8 using the damage moments of WSS. ⁽¹⁰⁾ If this correction is made then the intersections occur at $\langle x_d \rangle = 50$, 55 and 60 Å for 10 keV and $\langle x_d \rangle = 140$, 150, and 180 Å for 40 keV.

The theoretical value of $\langle x_d \rangle$ was obtained from the ratio $\langle x_i \rangle / \langle x_d \rangle = 1.36^{(10)}$ where $\langle x_i \rangle$ is the mean projected range of the ion distribution) and the tabulated value $\langle x_i \rangle = 94$ Å at 10 keV and $\langle x_i \rangle = 260$ Å at 40 keV,⁽¹¹⁾ thus giving $\langle x_d \rangle = 70$ Å at 10 keV and 190 Å at 40 keV. The various results are summarized in Table 2-II.

At the doses used in the present work the amorphous-crystalline interface is in each case in the tail of the damage distribution curve. The mean range of damage is thus being determined by values in a region where the form of the distribution is least understood, and where it is believed that the Gaussian is thus just as good (or as bad) an approximation as Edgeworth's expansion.⁽¹²⁾ It is therefore not surprising that the agreement between theory and experiment may be better using the Gaussian.

⁽¹⁰⁾ K. B. Winterbon, P. Sigmund, and J.B. Sanders, Mat. Fys. Medd. Dan. Vid. Selsk., <u>37</u>, No. 14 (1970).

⁽¹¹⁾ W. S. Johnson and J. F. Gibbons, "Projected Range Statistics in SEmiconductors", Stanford University Bookstore (1969).

⁽¹²⁾ P. Sigmund, private communication.

Conclusions

The dissolution of the amorphous layer produced in the ion bombardment of Si can provide values for the mean range of damage that agree rather well with the calculated values. The scatter is found to be comparable if a pure Gaussian damage distribution is assumed or if a Gaussian is corrected with Edgeworth's expansion. The pure Gaussian is however found to give better agreement with the theoretical values of $\langle x_d \rangle$.

In its present form the technique is hindered by:

 (a) the depth of the amorphous layer is determined using a theoretical ion depth distribution curve;

(b) the present results were obtained from rather high dose bombardments, thereby placing the amorphous-crystalline interface in the tail of the ion and damage distributions where the Edgeworth correction term is large.

In light of the above, the experimental conditions could be improved firstly by determining the depth distribution of the ions experimentally by means of an appropriate technique such as vibratory polishing;⁽¹³⁾ anodizing and stripping is apparently not reliable, as shown in section I. Secondly the use of lower bombardment doses would be desirable, since they would place the amorphous-crystalline interface in a better defined region of the distribution functions.

The dissolution curves, Fig. 2.4, 2.5, which show a dependence of dissolution rate on dose suggest that the dissolution rate as a function of depth may provide a means of obtaining damage or ion distributions in Si. The dissolution-rate dependence on dose can possibly be

(13) J. W. Whitton, J. Appl. Phys. <u>36</u>, 3917 (1965).

explained as a result of deposited energy or of strains produced by the presence of the implanted ions. In order to get this information from the dissolution rate the concentration of the radioactive species must be constant throughout the sample. This could be achieved by fast neutron bombardment to give Si^{31} , the neutron damage being removed by a $\simeq 600^{\circ}\mathrm{C}$ anneal. The slope of the dissolution curve following non-radioactive bombardment would then provide either the damage distribution curve depending on whether it was damage or ions which affected the dissolution to the greater extent.
Appendix I: Ion and Damage Distribution Functions

The problem of ion and damage distributions in a bombarded material is a transport problem. Ions of a certain energy arrive at the target surface and are subsequently distributed throughout the target in accordance with the transport equation describing the case of interest. The same can be said concerning the energy in that a certain packet of energy arrives, with the ion, at the surface and is also dissipated throughout the target. The integral equations governing the damage distribution will thus be analogous to those governing the ion range. The ion range function F_i ($\overline{v}, \overline{r}$) dv, i.e. the probability that an ion with velocity vector \overline{v} will be in the volume element dv at \overline{r} , is replaced by F_d ($\overline{v}, \overline{r}$) dv, i.e. the amount of energy deposited in the volume element dv at \overline{r} by an ion with **velocity** vector \overline{v} . The normalization of the two functions is of course different, i.e.

 $\int_{V} F_{i}(\overline{v}, \overline{r}) dv = 1$

whereas

$$\int_{U} F_{H}(\vec{v}, \vec{r}) dv = v(E) ,$$

v(E) being the amount of energy available for nuclear collisions.

It is worth noting that F_i (\overline{v} , \overline{r}) dv gives specific information about each ion trajectory in that it <u>averages</u> the position of rest of a large number of incident ions whereas the damage function F_d (\overline{v} , \overline{r}) dv <u>sums</u> the damage distribution produced by a large number of incident ions.

To obtain more detailed information about the damage produced by a single ion requires the use of correlation functions. (14)

(14) J. E. Westmoreland and P. Sigmund, Radiation Effects, <u>6</u>, 187 (1970)

The distribution function $F_i(E,R)$ where E is the energy, R the total path length of the ion and $F_i(E,R)$ dR the probability that an ion of energy E has a path length between R and R + dR is governed by the integral equation⁽¹⁵⁾

$$\frac{\partial F_i(E,R)}{\partial R} = N \int d\sigma_n \{F_i(E-T_n, R) - F_i(E,R)\}$$

where electronic stopping has been neglected,

 σ_n is the scattering cross-section for nuclear stopping and T_n is the energy transfer in a collision

It has still (i.e. in 1971) not been possible to obtain an exact solution of the integral equations governing ion range and damage distribution; however, it is possible to calculate exact expressions for averages over the distribution function for certain classes of scattering potentials, including power law scattering. In power law scattering the Thomas-Fermi potential is approximated by

 $V(r) = (Const) r^{-1/m}$

Using a 20% accuracy as the acceptable limit, the range of validity for m = 1/3 and m = 1/2 is ⁽¹⁰⁾

m = 1/3 for
$$\epsilon \le 0.2$$

m = 1/2 for 0.08 $\le \epsilon \le 2$

 ϵ is Lindhand's dimensionless energy parameter given by

$$\varepsilon = E \frac{aM_2}{Z_1 Z_2 e^2 (M_1 + M_2)}$$

(15) J. Lindhard, M. Scharff, and H. E. Schiøtt, Mat. Fys. Medd. Vid. Selsk. <u>33</u>, No. 14 (1963).

where E is the incident energy

a is the Thomas-Fermi screening length

 Z_1 and Z_2 are the atomic numbers of the projectile and target and M_1 and M_2 are the masses of the projectile and target

For the case of Kr⁸⁵ bombardment of Si

$$\varepsilon = 3.9 \times 10^{-3} E$$

where E is in keV units.⁽¹⁶⁾ This works out to $\epsilon = 0.04$ for 10 keV and $\epsilon = 0.16$ for 40 keV. The moments are thus calculated with m = 1/3 in the power-law potential. These moments contain the information required to construct the distribution function.⁽¹⁷⁾.

The n^{th} moment α_n of the variable x is defined by

$$\alpha_n = \int_{-\infty}^{+\infty} x^n F(x) dx = \langle x^n \rangle$$

when F(x) is the probability distribution of the variable x and $\langle x^n \rangle$ is the mean or expectation value of x^n . If the moments are taken about the mean value α_1 , then the equation becomes

$$\mu_{n} = \int_{-\infty}^{+\infty} (x - \langle x \rangle)^{n} F(x) dx$$
$$= \langle (x - \langle x \rangle)^{n} \rangle$$

and μ_{n} is called the central moment.

The first moment $\langle x \rangle$ of a distribution function gives its position. The position can of course also be described by the median (x_m) , i.e. the point that divides the mass of the distribution in half:

⁽¹⁶⁾ K. B. Winterbon, AECL Report 3194 (1968).

⁽¹⁷⁾ For a more complete treatment of distribution functions and moments see: H. Cramer, "Mathematical Methods of Statistics", Princeton University Press, 1946.

$$\int_{-\infty}^{\infty} F(x) dx = 1/2$$

or by the most probable position or mode (x_p) , which occurs at the maximum of F(x):

$$\left[\frac{dF(x)}{dx}\right]_{x = x_{p}} = 0$$

For a Gaussian distribution $\langle x \rangle = x_m = x_p$. Other information concerning the distribution is obtained from the central moments μ_2 , μ_3 , and μ_4 .

A measure of the spread or dispersion of the distribution is provided by μ_2 (ie, the second central moment) which is always ≥ 0 . If $\mu_2 = \langle (x-\langle x \rangle)^2 \rangle =$ 0 then the whole distribution is concentrated at $\langle x \rangle$. The third moment μ_3 provides a measure of the skewness or asymmetry of the distribution. For a Gaussian $\mu_3 = 0$ and $\mu_3 > 0$ indicates a tail on the positive side of the distribution. The fourth moment provides a measure of the flatness of the distribution near its maximum. For a Gaussian distribution $\mu_4/\mu_2^2 =$ 3, while if $\mu_4/\mu_2^2 > 3$ then this indicates that the frequency curve is more tall and slim than the Gaussian (and conversely for $\mu_4/\mu_2^2 < 3$).

It should be noted that the moments for $n \ge 2$ are normally put in a form, namely

$$\mu_2/\langle x \rangle^2$$
, $\mu_3/\mu_2^{3/2}$, and μ_4/μ_2^2

such that these quantities are unitless and independent of energy. Their values only depend upon the form of the potential used and the mass ratios of the target and incident species, and can be applied directly to Edgeworth's expansion.

A distribution which is Gaussian to a first approximation can always be described to higher approximation by Edgeworth's expansion, which

is an asymptotic expression in terms of the derivatives of the Gaussian or normal distribution.

The distribution function can thus be approximated by N terms in Edgeworth's expansion (18)

$$F(\boldsymbol{\xi}) = \prod_{n=2}^{N} \mathbf{a}_{n} (\boldsymbol{\xi})$$
(1)

where
$$a_2(\xi) = \phi_0(\xi)$$

 $a_3(\xi) = -\frac{1}{6}\phi_3(\xi)$
 $a_4(\xi) = \frac{\tau_2}{24}\phi_4(\xi) + \frac{\tau_1^2}{72}\phi_6(\xi)$

and

$$\Phi_n = \frac{d^n}{d\xi^n} \frac{1}{\sqrt{2\pi}} \exp\left[-\frac{\xi^2}{2}\right]$$

$$\xi = (x - \langle x \rangle) / \mu_2^{1/2}$$

$$\mu_n = \langle (x - \langle x \rangle)^n \rangle = \langle \Delta x^n \rangle$$

$$T_1 = \mu_3 / \mu_2^{3/2}$$

$$T_2^{=} \mu_4 / \mu_2^{2} - 3$$

Taking N=4 in (1), $F(\xi)$, the distribution function, becomes

$$F(\xi) = \frac{1}{\sqrt{2\pi^{2}}} \exp \left[-\frac{\xi^{2}}{2}\right] g(\xi)$$
 (2)

= (Gaussian Dist.) (Correction term),

(18) P. Sigmund, Can. J. Phys., <u>46</u>, 731 (1968)

the correction term to the Gaussian being

$$g(\xi) = 1 - \frac{1}{6} \frac{\mu_3}{\mu_2^{3/2}} (3\xi - \xi^3) + \frac{1}{24} (\frac{\mu_4}{\mu_2^2} - 3) (3 - 6\xi^2 + \xi^4) + \frac{1}{72} (\frac{\mu_3}{\mu_2^{3/2}})^2 (-15 + 45\xi^2 - 15\xi^4 + \xi^6)$$

Ion Distribution Function

Taking $\mu_2/\langle x_i \rangle^2$ from WSS⁽¹⁰⁾ as equal to 0.15, equation (2) becomes

$$F(\xi)_{i} = \frac{1}{\sqrt{2\pi}} \exp \left[-3.33 \left(\frac{x}{\langle x_{i} \rangle} - 1\right)^{2}\right] g(\xi)_{i} \qquad (3)$$

The correction term $g(\xi)_i$ which is shown in Fig. 2.9, is obtained from the central moment ratios $\mu_3/\mu_2^{3/2}$ and μ_4/μ_2^2 which WSS⁽¹⁰⁾ calculate to be equal to 0.606 and 3.33 respectively. The mean projected ion range $\langle x_i \rangle$ is tabulated by Johnson and Gibbons⁽¹¹⁾ as 94 Å at 10 keV and 260 Å at 40 keV. Using equation (3) the theoretical ion range distribution is obtained and subsequently integrated to give the integral ion distribution curves of Fig. 2.6 and 2.7.

Damage Distribution Function Taking $\mu_2/\langle x_d \rangle^2$ from WSS⁽¹⁰⁾ as equal to 0.375, equation (2) becomes

$$F(\xi)_{d} = \frac{1}{\sqrt{2\pi^{2}}} \exp \left[-1.33 \left(\frac{x}{\langle x_{d} \rangle} - 1\right)^{2}\right] g(\xi)_{d}.$$
 (4)

Without the correction term, $g(\boldsymbol{\xi})_d$, this is a Gaussian distribution

$$F(\xi)_{d} = \frac{1}{\sqrt{2\pi}} \exp \left[-1.33 \left(\frac{x}{< x_{d}^{>}} - 1\right)^{2}\right]$$

To use the correction term of Edgeworth's expansion requires, for N=4 in (1), values of $({\mu_3}/{\mu_2}^{3/2})_d$ and $({\mu_4}/{\mu_2}^2)_d$ which are given by WSS⁽¹⁰⁾ as 0.75 and 3.73 respectively. The resulting values of $g(\boldsymbol{\xi})_d$ as a function of $\boldsymbol{\xi}$ are summarized in Fig. 2.8 as use of pre-tabulated values greatly simplifies the application of equation (4) to deducing $<\mathbf{x}_d^>$.

Table 2-I: Amorphous Layer Thickness as a function of dose for 10 and 40 KeV Kr⁸⁵ bombardments of Si

	After Removal of Amorphous Layer			
Bombarding Energy (keV)	Total Dose (ions/cm ²)	Residual Activity (%)	Residual Dose (ions/cm ²)	Thickness of Amorphoys Layer (Å)
10	1.87 x 10 ¹⁴	3.2	6 x 10 ¹²	170
	3.74 x 10 ¹⁴	2.3	8.6 x 10 ¹²	180
	1.87 x 10 ¹⁵	0.33	6.2 x 10 ¹²	210
40	1.0×10^{14}	2.5	2.5×10^{12}	480
	1.87 x 10 ¹⁵	0.45	8.4 x 10 ¹²	560
	3.75 x 10 ¹⁵	0.15	5.6 \times 10 ¹²	600

Bombarding Energy (keV)	Experimental ^{<x< sup="">d> from_oGaussian (A)</x<>}	Experimental ^{<x< sup="">d^{>} from modified Gaussian (A)</x<>}	Theoretical* ^{<x< sup="">d^{>} (Å)</x<>}
10	65 ± 10	55 ± 5	70
40	180 ± 40	160 ± 20	190

*from Johnson and Gibbons $(11)_{WSS}(10)$



Fig.2.1. Radio-Frequency Ion Accelerator



Fig.2.2. Suppression of secondary electron emission.







Fig. 2.4. Dissolution curves for 10 kev Kr⁸⁵ bombardments of Si. Shown on each curve is the bombarding dose and the region, defined by the small arrows, when the milky appearance of the amorphous layer disappeared.





Fig.2.6. Theoretical integral ion range distribution for 10 kev ${\rm Kr}^{85}$ bombardments of Si.



Fig.2.7. Theoretical integral ion range distribution for 40 kev Kr⁸⁵ bombardments of Si.



Fig.2.8. Edgeworth's expansion correction, $g(\xi)_d$, to the Gaussian damage distribution as a function of ξ . The insert shows the value of the damage moments calculated by WSS⁽¹⁰⁾.



Fig.2.9. Edgeworth's expansion correction $f(\xi)_i$, to the Guassian ion distribution as a function of ξ . The insert gives the value of the range moments calculated by WSS.⁽¹⁰⁾

SECTION III: THRESHOLD DOSE FOR THE FORMATION OF A SOLUBLE* DAMAGE LAYER BY ION BOMBARDMENT OF SILICON

Introductory Comments

In section II it was assumed that the solubility was a characteristic of the amorphous silicon and therefore that the knee in the dissolution curve defined the interface between amorphous and crystalline Si. In this section we wish to compare the threshold dose for rendering the Si soluble to that required to render it amorphous as determined by others. Also of interest is the temperature of this threshold dose determined by dissolution of the soluble layer since it provides a convenient technique for studying the annealing process that the damage zones undergo.

The threshold dose is taken as the dose of ions that has come to rest below the soluble layer. Although the bombarding conditions below this layer are rather ill defined, it is shown that this dose agrees with the dose for the first formation of this layer at the damage distribution maximum. The latter dose is calculated from the concentration of damage at the soluble-insoluble interface. At room temperature the experimental threshold dose (Threshold Dose #1) for 10 kev Kr⁸⁵ bombardments is ~8 x 10¹² ions/cm² and the calculated dose (Threshold Dose #2) is ~9 x 10¹² ions/cm². The dose (Threshold Dose #3)

*Soluble in an HF solution.

required for this layer to grow to the surface is calculated as $\sim 3 \times 10^{13}$ ions/cm².

This threshold dose of 8-9 x 10^{12} ions/cm² is shown to be an order of magnitude lower than that determined by others for the formation of an amorphous layer using electron microscopy, Mev-particle back-scattering, and optical techniques.

The annealing of the disorder zones which overlap to provide this soluble layer is treated in an analogus way as amorphous zones. Using the model of Morehead and Crowder, the temperature dependence of the threshold dose can be described by

 $(Bt)_{T} = 8 \times 10^{12} [1-16 \exp \left[\frac{-0.31}{2kT}\right]^{-2}$ where $(Bt)_{T}$ is dose in ions/cm² required to form a soluble layer at temperature T.

The diffusion time contained in the factor 16 must however be taken as 10^{-8} sec. in order to give a reasonable frequency factor. In the spirit of the stabilization of the zones by overlap, this diffusion time should be 10^{-1} sec., a factor of 10^7 higher.

A model based on the competition between the time for the next impact and the time for the disorder to anneal is shown to give

$$(Bt)_{T} = \frac{(Bt)_{0}^{2} k_{0}}{4nB} \exp \left[\frac{-\Delta E}{kT}\right]$$

where

(Bt)_o is the threshold dose at low temperatures
k_o is the attempt frequency of the diffusing species
n is the number of rate controlling jumps required for
annealing of the disorder zone

B is the dose rate of the bombardment

and ΔE^{1} is the activation energy for migration.

This equation is only defined in the high temperature region where the rate of annealing is not small. The equation is shown to fit the experimental data when

$$k_o = 2n \times 10^7 \text{ sec.}^{-1}$$

 $\Delta E^1 = 0.56 \text{ ev}$

and

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thereby giving a more "reasonable" attempt frequency and a higher activation energy.

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Introduction

Amorphous Zones

When an accelerated ion enters a target material it will slow down by a process of collision with the target atoms. In this collision process the struck atom may receive enough energy to be displaced and accelerated within the crystal. This displaced atom can then displace other atoms, thus creating a collision cascade and introducing damage into the target.

As the accelerated atom slows down the collision cross section σ increases and thus the distance between collisions (L) will decrease according to

$$L = \frac{1}{N\sigma}$$

where N is the number density of the target material.

When the distance between displacement collisions becomes of the order of the lattice spacing then each collision can no longer be thought of as a single event but rather a region of violent localized damage is produced. The displaced atoms move out from the center of this region thereby creating a region of excess vacancies surrounded by a shell of excess intersitials, i.e. a displacement spike. ⁽¹⁾ Seeger⁽²⁾ has extended this model to take account of the effect the crystal lattice will have in the process. Specifically the ordered lattice is postulated as aiding in removing interstitial atoms and energy via channeling, focussing, and

⁽¹⁾J. A. Brinkman, Amer. J. Phys., <u>24</u>, 246 (1956).

⁽²⁾ A. Seeger, Proceedings of the Second International Conference on the Peaceful Uses of Atomic Energy, <u>6</u>, United Nations, Geneva, p. 250 (1958).

crowdion mechanisms. The displacement spike is then called a depleted region. Once an accelerated atom has slowed down to an energy below which it can no longer transfer enough energy for displacement, the atom will then become trapped in the lattice. In order to come to thermal equilibrium with the lattice the atom must lose the remaining excess energy in the form of lattice vibrations. This sudden increase in heat content of a small lattice volume, a thermal spike,⁽³⁾ is carried away in the form of phonons.

In principle the thermal spike and displacement spike both offer a means of explaining the formation of amorphous zones in bombarded materials. The thermal spike model would explain these amorphous zones in terms of a rapid cooling of a liquid region to below the glassy-crystalline transition. The displacement spike would lead to an amorphous zone by transformation of the vacancy rich region into an amorphous structure. A more careful consideration of the problem has been made by Parsons,⁽⁴⁾ however, and according to his point of view the production of amorphous zones in oxygen bombarded Ge is explained in terms of a thermal spike superimposed on a depleted zone. Larger amorphous regions at lower temperatures is postulated to be a result of a faster quench of the thermal spike. It is however dif-

ficult to conceive of the thermal spike giving rise to the amorphous region as the conditions for such a process appear to be too stringent. If the thermal spike cools too rapidly it will not have time to disorder in the first place; on the other hand, if the cooling is not rapid enough then the disordered region will have time to anneal. The production of amorphous

⁽⁴⁾J. R. Parsons, Phil. Mag., 12, 1159 (1965).

⁽³⁾F. Seitz and J. S. Koehler, Solid State Phys., <u>2</u>, 305 (1956).

zones in Ne bombarded Si⁽⁵⁾ and GaAs⁽⁶⁾ has been discussed in terms of a displacement spike mechanism. This view has been supported by field-ion microscopy studies of heavy-ion bombarded iridium.⁽⁷⁾

Present understanding of the mechanism for the production of amorphous or damaged zones is therefore in no way complete. In particular, it is not clear why completely different results are obtained by bombardment of different materials. As outlined in Table 3 of (8), some materials that are crystalline become amorphous with bombardment, some that are crystalline remain crystalline, while in three cases $(Ge^{(9)}, SiO_2^{(9A)})$ and $ZrO_2^{(8)}$ th amorphous material becomes crystalline (or partly so). A further complication is brought out in the work of Chadderton. (10) where the mechanism for damage zone formation is postulated to be different for light incident ions. This is explained in terms of preference for a large number of low-energy encounters for light ions thereby eliminating large cascades. Only small groups of displaced atoms are thus produced rather than the large displacement spikes of heavy-ion bombardment. These defects then migrate to form clusters, at first homogeneously and then at higher doses heterogeneously by growth of the existing embryos. The nonlinear dose dependence of damage for room-temperature B bombardments of Si⁽¹¹⁾ and also the observation

- ⁽⁵⁾D. J. Mazey, R. S. Nelson, and R. S. Barnes, Phil Mag., <u>17</u>, 1145 (1968) ⁽⁶⁾D. J. Mazey and R. S. Nelson, Radiat. Eff., <u>1</u>, 229 (1969).
- (7) J. A. Hudson and B. Ralph in "Atomic Collision Phenomena in Solids", Ed. by Palmer, Thompson and Townsend, North-Holland, Amsterdam, p. 85, 1970.
- (8) H. M. Naguib and R. Kelly in "Atomic Collision Phenomena in Solids", Ed. by Palmer, Thompson and Townsend, North-Holland, Amsterdam, p. 172, 1970.
- ⁽⁹⁾J. R. Parsons and R. W. Balluffi, J. Phys. Chem. Sol., <u>25</u>, 263 (1964).
- ⁽¹⁰⁾L. T. Chadderton, Radiat. Eff. <u>8</u>, 77 (1971).
- ⁽¹¹⁾F. H. Eisen and B. Welsh, Radiat. Eff., <u>7</u>, 143 (1971).
- ^(9A)S. Weissman and K. Nakajima, J. Appl. Phys., 34, 3152 (1963).

that non-amorphous damage zones only are formed at room temperature (and only a few were amorphous at liquid nitrogen temperature (12)) give credence to the view that the mechanism for damage-zone formation is different for light ions as opposed to heavy ions.

In the present work, since heavy ions (Kr⁸⁵) are used, we address ourselves to the displacement spike type of mechanism for the formation of amorphous zones. Damage regions are thus created in the lattice as a direct result of displacement spikes which are then subjected to athermal and thermal annealing. The amount of thermal annealing or reordering of the damage region will depend upon the temperature of the sample and the time span over which the reordering can occur.

Reordering of the Amorphous Zones

For the same time span a higher temperature should result in smaller amorphous zones, as a result of a greater amount of annealing, and thereby a greater dose will be required to produce an amorphous layer. The amorphous layer is assumed a result of the overlap of the amorphous zones, and the dose required is called the "threshold dose." The nature of the temperature dependence of this threshold dose provides a means of checking models for the reordering process.

Previous Observation of the Threshold Dose

Experimental observation of the temperature dependence of the dose to create an amorphous layer has been investigated using a visual technique, in which a sample is bombarded until the surface turns milky. Nelson and Mazey,⁽¹³⁾ using 60 keV Ne bombarded silicon, obtained a linear relation for

⁽¹²⁾L. T. Chadderton and F. H. Eisen, Radiat. Eff., <u>7</u>, 129 (1971) ⁽¹³⁾R. S. Nelson and D. J. Mazey, Can. J. Phys., <u>46</u>, 689 (1968).

log (Threshold Dose) vs 1/T with an "activation energy" of 0.3 eV. Irving⁽¹⁴⁾ obtained a similar result with 100 keV P bombardment of Si with an "activation energy" of 0.18 eV. As was shown in section II the visual method is subjective and could lead to substantial error.

MeV-particle backscattering has also been used to obtain the dose to create an amorphous layer at various temperatures. However, the temperature range has not been well covered and it is therefore difficult to assess the nature of the temperature dependence of the dose.

It might be thought that the threshold dose determined by MeV-particle backscattering would be too high since the layer would not be resolved until it was of the order of 200 Å in thickness.⁽¹⁵⁾ However, Chadderton and Eisen⁽¹²⁾ found that it gave too low a dose! They bombarded Si with 200 keV B ions at -150° C to a dose of 1 x 10^{15} ions/cm². Backscattering showed that a buried amorphous layer should be produced but transmission electron microscopy showed the damage zones to be discrete and only a few to be amorphous. This error is probably not encountered in heavy-ion bombardments where such non-amorphous damage zones have not as yet been observed.

Threshold Dose by Dissolution of the Amorphous Layer

A technique for the determination of the dose required to produce an amorphous layer has been mentioned briefly in Section II. Specifically, the dose to create an amorphous layer is given by the dose left in the sample after the amorphous layer is removed. This is based on the assumptions, (a) that the soluble layer and the amorphous layer are the same and (b) that the damage in a layer dx about x (where x is measured along the (14)S. M. Irving, in "Semiconductor Silicon", Ed. by R. R. Haberecht and E. L. Kern, The Electrochemical Society, New York, 1969. (15)E. Bogh, Can. J. Phys., <u>46</u>, 653 (1968).

bombarding direction) is a result of the ions that have a projected range greater than x. The only check on the first assumption will be a comparison of the present results with other data which will be given later. With regards to the second, it is uncertain whether this threshold dose will tend to be too high or too low.

Thus, a threshold dose measured as proposed will tend to be underestimated firstly since some of the Kr^{85} ions that have a projected range less than x may also contribute to the damage at x as a result of the forward motion of the damage. Secondly, ions that suffer high angle collisons after penetrating further than x may pass back and forth across the interface at x and thereby increase the dose that the layer dx about x has received. Some of these ions will come to rest with a projected range less than x and therefore not be counted, while others will come to rest with a projected range greater than x but will only be counted as contributing once to the dose. On the other hand, this threshold dose may tend to be too high due to the energy degradation the incident ions have experienced in getting to x. The energy of the Kr^{85} ions entering the sample below x is not a single energy but a distribution of energies which than the incident energy. At this lower energy, the amorphous are less zones will be smaller (since dE/dx is smaller) and therefore the number of ions that have to pass through x to render the layer dx about x amorphous is greater.

The purpose of the present work is therefore three-fold. Firstly, we want to determine whether or not the damage at the interface, defined by the rapid decrease in solubility, can be represented by the dose of ions that have come to rest below that interface. Secondly, we ask if

there is any difference between the thickness of the soluble layer and that of the amorphous layer. Thirdly, we wish to test some models for the annealing process that occurs after the disorder zone is created and before a soluble layer is formed. Here the temperature dependence of the threshold dose is used.

Experimental

Bombardments

Silicon wafers ([111] perpendicular to the major plane and $\rho = 5-10\Omega$ -cm), etched in a solution of 3 pts. 48% HF, 5 pts. 70% HNO₃, 3 pts. CH₃COOH, and rinsed in distilled water followed by methyl alcohol, were bombarded with radioactive Kr⁸⁵ at 10 kev to a dose of 1.87x10¹⁵ ions/cm² with a dose rate 3.12x10¹³ ions/cm²-sec. (5µa/cm²).

A dose of 1.87×10^{15} ions/cm² was used since it was high enough to enable exploring up into the temperature range of 300-400°C and yet at the same time was low enough that the activity of the sample could be used to represent the bombarding dose as shown in Section II. To insure a uniform beam, the same focusing conditions as given in Section II were used.

Bombardments were done in the temperature interval of room temperature to 360 °C using the hot stage shown in figure 3.1. The heater power supply is floated at the target potential thus enabling the heating to continue during the bombardment. The heater power supply was set at the voltage required to give the desired temperature (12 volts gives ≈ 400 °C). To insure an accurate and stable temperature, the temperature of the target was allowed to come to equilbrium, as indicated by a chart recorder, before bombarding. Equilibrium was established in 3 to 4 hours. After the bombardment the samples were allowed to cool to room temperature before being removed from the vacuum ($\pm 10^{-5}$ torr.).

Dissolution

The "amorphous layer" formed during the bombardment was etched in a solution of 2 pts. 48% HF and 1 pt. 30% H₂O₂ as in Section II. The activity was recorded as a function of time in the solution. The residual fractional activity at the knee in the dissolution curve, when multiplied by the bombarding dose, gives the dose of Kr^{85} that has penetrated to a depth that is below the "amorphous layer"

}

Experimental Threshold Dose

Some of the dissolution curves for samples bombarded in the temperature region of room temperature to 300°C are shown in figure 3.2. As the implantation temperature increases it requires a greater dose to render the Si soluble at a given depth (Fig. 3.3.) and therefore the soluble - insoluble interface moves closer to the surface. The residual activity after the soluble layer is removed therefore increases with temperature. The number of Kr^{85} ions that have penetrated below the soluble - insoluble interface is just the fraction of the initial activity at the knee times the incident dose. This dose of Kr^{85} ions that have come to rest below the soluble-insoluble interface we call Threshold Dose #1. In order to determine how meaningful a value this is, we calculate the threshold dose to create a soluble layer, for 10 kev Kr^{85} ions in Si, using the damage concentration at the soluble-insoluble interface.

Calculated Threshold Doses

What is more pertinent than the dose of ions that have come to rest below the interface is the concentration of damage at the interface. The damage concentration at the interface is the damage concentration that renders the Si soluble Once this damage concentration is known then the threshold dose to create a soluble layer can be calculated by determining what dose of 10 kev Kr^{85} incident in Si will just give this damage concentration <u>at a given depth</u>. (We note that, because a depth must be specified, the dose is not unique). Two threshold doses will be considered: (a) the dose to give the critical damage concentration at the maximum in the damage distribution and (b) the dose that gives the critical damage concentration at the surface. These doses are called Threshold Dose #2 and Threshold Dose #3 respectively.

Threshold Dose #2 will give a layer which will form below the surface of the sample about the maximum of the damage distribution. The existence of such an amorphous layer has been shown by Davidson and Booker⁽¹⁶⁾ using channeling patterns formed in a scanning electron microscope. If the dose is increased further, then the thickness of the layer will increase. When it has reached the surface the dose will be Threshold Dose #3.

To obtain the concentration of damage at the interface it is necessary to know the depth of the interface from the surface and also the distribution of damage. The depth of the interface from the surface was deduced using the same procedure as that used in section II, i.e. the depth is obtained by combining the theoretical integral ion distribution (figure 2.7) with the percentage residual activity at the knee of the dissolution curve. In using the theoretical ion distribution the assumption is made that it represents the actual distribution of ${\rm Kr}^{85}$ ions not only for room temperature implants but also for hot implants up to 360°C. Two problems enter here. Firstly, although the higher substrate temperatures cause greater vibration of the atoms and thereby reduce channeling, at higher temperatures the bombarded sample also has a greater tendency to remain crystalline and thus permit a greater degree of channeling. Secondly, there is the possibility that the implanted ions migrate in this temperature range. However, as will be shown in section IV, the Kr⁸⁵ does not move until $\simeq 650^{\circ}$ C and even then it appears to be swept out by the crystallization of the amorphous Si (rather than migrating in the normal sense).

(16)S.M. Davidson and G. R. Booker, Radiat. Eff., 6,33 (1970).

The damage distribution is assumed to be Gaussian since, as was shown in section II, it is as good an approximation as the more complicated Edgeworth's expansion. The damage distribution can therefore be expressed as $C_d(x) dx = [D] \left[\begin{pmatrix} Dose \\ (incident) \end{bmatrix} \frac{1}{\sqrt{2\pi\mu_2}} \right] \exp[-1.33 \left(\frac{x}{\langle x_d \rangle} - 1 \right)^2 \right]^\circ dx$ for Kr^{85} bombardment of Si, where D is the number of displaced Si atoms per incident ion. For a given incident ion and target material at a set energy, D, μ_2 and $\langle x_d \rangle$ will be constant. As given in section II, $\langle x_d \rangle = 70^{\circ}A$ for 10 kev Kr⁸⁵ bombardment of Si. If the soluble-insoluble interface is located at x' for a 10 kev bombardment to a dose of 1.87 x 10^{15} ions/cm² then the concentration of damage at the interface is given by

$$C_{d} = [D][1.87 \times 10^{14}] \frac{1}{\sqrt{2\pi\mu_{2}}} \exp[-1.33(\frac{x'}{70}-1)^{2}]$$

in units of displacements/ cm^3 , which is the critical concentration of damage to render Si soluble.

The threshold Dose #2 and #3 is then obtained, as outlined in figure 3.4, by asking what doses of 10 kev Kr^{85} ions will give this critical concentration firstly at the maximum of the damage distribution and secondly at the surface. Threshold Dose #2 is thus given by the equation

$$\begin{bmatrix} D \\ T \end{bmatrix}_{\mu_{2}}^{\mu_{2}} \text{ Threshold Dose} \begin{bmatrix} 1 \\ \mu_{2} \end{bmatrix}_{\mu_{2}}^{\mu_{2}} = \begin{bmatrix} D \\ \sqrt{2\pi} \end{bmatrix} \begin{bmatrix} 1.87 \times 10^{15} \end{bmatrix} \frac{1}{\mu_{2}}^{\mu_{2}} \exp \begin{bmatrix} -1.33 (\frac{x'}{70} - 1)^{2} \end{bmatrix}$$

i.e.
$$\begin{bmatrix} \text{Threshold} \\ \text{Dose } \#2 \end{bmatrix} = \begin{bmatrix} 1.87 \times 10^{15} \end{bmatrix} \exp \begin{bmatrix} -1.33(\frac{x'}{70} - 1)^2 \end{bmatrix}$$

Likewise, Threshold Dose #3 is given by

$$\begin{bmatrix} \text{Threshold} \\ \text{Dose } \#3 \end{bmatrix} \exp \left[-1.33\right] = \left[1.87 \times 10^{15}\right] \exp \left[-1.33\left(\frac{x'}{70} - 1\right)^2\right]$$

The temperature dependence of the threshold dose is contained in x'.

The values of the Threshold Doses #2 and #3 are shown in figure 3.5 along with the experimental Threshold Dose #1. The agreement between Threshold Dose #1 and #2 is found to be surprisingly good. The agreement is somewhat better at the lower temperatures than at the higher temperatures, i.e. the ratio of Dose #2 to Dose #1 is \approx 1.2 at room temperature and \sim 2 at 360°C. (One might conclude from this that the agreement is better when the interface is deep within the sample and the error due to the forward motion of damage is small). Threshold Dose #3 is a factor of \approx 4.5 higher than Dose #1 at room temperature and \approx 8 times greater at 360°C.

Previous Experimental Observation of the Threshold Dose for Room Temperature Bombardments

It is useful at this point to compare the threshold dose determined by the present dissolution technique with other estimates. Such a comparison is complicated by the fact that different incident ions and energies as well as different dose rates may have been used. The fact that different incident ions may have been used is often not a problem since results can usually be found for incident ions sufficiently close to Kr in mass and atomic number. The effect of an increase in incident ion energy will be one of producing larger amorphous zones which are more spread out spatially, the net result being that the threshold dose required for overlap could be either larger or smaller. Any dose rate effect will have to be left as an error since the dose rate is not usually reported with the results and the importance of the dose rate is as yet uncertain. Bøgh et al.(17)reported an increase in damage due to an increased dose rate for room temperature 50 keV Sb bombardments of Si at .003 μ A/cm² and 0.2 μ A/cm² to a dose of 3 x 10^{13} ions/cm². On the other hand, no such dose-rate effect was found by Hart⁽¹⁸⁾ also using Sb bombardments of Si at approximately the same dose, dose rate and energy. The present results were obtained with a dose rate of 5 μ A/cm².

The production of an amorphous layer for room temperature bombardments of Si has been studied using the electron microscope, MeV-particle backscattering, and optical properties such as reflection and absorption.

^{(17)&}lt;sub>E. Bøgh, P. Høgild, and I. Stensgaard, Radiat. Eff. <u>7</u>, 115 (1971). (18)_{R. R. Hart, Radiat. Eff. <u>6</u>, 51 (1970).}</sub>

The results and criteria used in obtaining the dose to create an amorphous layer are summarized in Table 3-I.

Matthews⁽¹⁹⁾ using transmission electron microscopy obtained a threshold dose of $\approx 5 \times 10^{14}$ ions/cm² for 100 keV Ar⁴⁰ bombardments of Si and $\simeq 1 \times 10^{15}$ ions/cm² for 40 keV Si²⁹ bombardments. Here the threshold dose is defined by the appearance of diffuse diffraction rings, these rings naving been shown to correspond to the rings produced by sputtered amorphous Si.⁽⁵⁾ Gusev et al.⁽²⁰⁾ used reflection electron diffraction patterns and obtained a threshold dose of 2 x 10^{14} jons/cm² for 30 keV Kr⁸⁴ bombardments of Si, the threshold dose being here defined by the dose necessary to remove all diffraction spots. It should be noted however that the Kikuchi lines had disappeared by a dose of 1.8 x 10^{13} ions/cm². This latter dose may indicate the first formation of an amorphous layer about the maximum of the damage distribution. Davidson and Booker⁽¹⁶⁾ have shown. using channeling patterns from the scanning electron microscope, that the formation of a buried amorphous layer is indicated by the first sign of degradation in the pattern. Using this criterion they obtained a threshold dose of 3-7 x 10^{14} for 80 keV Ne²⁰ bombardments of Si and $\simeq 4-7 \times 10^{13}$ for 100 keV Sb¹²¹ bombardments.

 M_{eV} -particle backscattering has come into extensive use in the study of damage produced by ion bombardment. In this technique the critical dose is obtained by plotting the area under the damage peak as a function of dose. The area, which is a measure of the damage, is assumed to saturate out when the damage regions overlap and the saturation dose is therefore identified with the threshold dose. Mayer et al.⁽²¹⁾ found a threshold

^{(19)&}lt;sub>M.</sub> D. Matthews, Harwell Report, R6802, May, 1971.

⁽²⁰⁾ V. M. Gusev, Yu. V. Martynenko, and C. V. Starinin, "Atomic Collision Phenomena in Solids", Ed. by Palmer, Thompson & Townsend, North-Holland, Amsterdam 1970.

⁽²¹⁾ J. W. Mayer, L. Eriksson, S. T. Picraux and J. A. Davies, Can. J. Phys., <u>46</u>, 663 (1968) .
dose of 3 x 10^{14} ions/cm² for 40 keV Ga⁷⁰ bombardments of Si and Davies et al.⁽²²⁾ 10^{14} ion/cm² for 40 keV Sb¹²¹ bombardments. However, with a depth of resolution of 300 Å these results are expected to be too high.

The damage has also been studied using optical techniques. As was mentioned previously, the milky appearance of the damaged layer has been used as a criterion of amorphousness by Nelson and Mazey⁽¹³⁾ and by Irving.⁽¹⁴⁾ Nelson and Mazey obtained a threshold dose of 10^{14} ion/cm² for 60 keV Ne²⁰ bombardments and Irving the same threshold dose for 100 keV P³¹ bombardments. This technique is rather subjective in that it is very difficult to determine the point at which the milky color disappears. The technique also appears to be rather insensitive to the mass number of incident ion; thus the same threshold dose was reported for Ne²⁰ and P³¹, while Stein et al.⁽²³⁾ have reported a "slightly milky" appearance at 10^{14} ions/cm for 400 keV Sb¹²¹ bombardments of Si.

The change in reflectivity of an ion bombarded sample is probably a better optical technique to study the formation of an amorphous layer. Here the criterion for the production of an amorphous layer is taken as the dose for which the change in reflectivity as a function of dose has reached saturation. At high doses the reflectivity is shown to be close to that of sputtered amorphous Si. McGill et al.⁽²⁴⁾ used photons in the region of 3-6.5 eV and obtained a threshold dose of 10^{14} ions/cm² for 40 keV Sb¹²¹ bombardments of Si. However Hart and Marsh⁽²⁵⁾ using photons in the region

⁽²²⁾ J. A. Davies, J. Denhartog, W. Eriksson, and J. W. Mayer, Can. J. Phys., <u>45</u>, 4053 (1967)
(23) H. J. Stein, F. L. Vook, D. K. Brice, J. A. Borders and S. T. Picraux, Radiat. Eff., <u>6</u>, 19 (1970).
(24) T. C. McGill, S. Kurtin and G. A. Shifrin, J. Appl. Phys., <u>41</u>, 246 (1970).
(25) R. R. Hart and O. J. Marsh, Appl. Phys. Letters, <u>7</u>, 225 (1969)

of 1.8-2.2 eV obtained a threshold dose of 4 x 10^{13} ions/cm² for 40 keV Sb¹²¹ bombardments.

Stein et al.⁽²³⁾ have used infrared light to study the formation of damage in ion bombarded Si. Here the absorption of light of 1.8μ wavelength by divacancies allows the concentration of divacancies to be followed as a function of dose. Samples of Si were bombarded at 400 keV with Sb¹²¹ and the divacancy concentration calculated as a function of dose. The divacancy concentration is found to increase from zero at $\approx 10^{12} \text{ ions/cm}^2$ up to a dose of $\approx 10^{13} \text{ ions/cm}^2$, where it starts to decrease. At $10^{14} \text{ ions/cm}^2$ it has decreased to zero. This may indicate that the disordered zones are not amorphous for doses below 10^{13} , that above 10^{13} the disorder zones have grown to a size that renders them amorphous, and that at 10^{14} overlap of these zones leads to the formation of a continuous amorphous layer.

From the above results, as summarized in Table 3-I, it appears that the threshold dose defined by the knee in the dissolution curve is lower than that obtained using any of the other techniques. The dissolution technique gives a dose of $\approx 10^{13}$ ions/cm² for 10 keV Kr⁸⁵ bombardments of Si at a dose rate of 5 μ A/cm², whereas the other techniques indicate a dose of $\approx 10^{14}$ ions/cm². There are two possible conclusions. Perhaps the damage required to render the Si soluble in the 2 pts.48% HF and 1 pt. 30% H₂O₂ solution is smaller than that required to render the Si amorphous as defined by the absence of long-range order. Alternatively, the other techniques could be at fault owing variously to a lack of sensitivity or to being too indirect.

Models for Temperature Dependece of the Threshold Dose

One of the possible conclusions of the preceding section was that the change in the rate of dissolution between damaged and undamaged silicon occurs at a damage concentration that is insufficient to render the Si amorphous as defined by electron microscopy, MeV-particle backscattering, or optical reflectivity. The boundary defined by the dissolution rate change might thus be occurring in a region where the disordered zones are still discrete. Nevertheless the variation of the dose required to produce this solubility should give insight into the annealing of the disorder zones just the same. This soluble layer will thus be treated in a way analogous to an amorphous layer whether or not it is in fact amorphous.

(a) Morehead and Crowder's Model

Morehead and Crowder⁽²⁶⁾ have proposed a simple model to explain the temperature dependence of the dose to create an amorphous layer. In this model the incident ion produces damage over a uniform radius along the track and thereby a cylindrical damage region, with the incident ion track as its axis, is produced. An amorphous layer is postulated to form by overlap of the disorder zones, i.e. when

$$(Bt)_{T} R_{T}^{2} = 1$$
 (1)

where $(Bt)_T$ is the dose required to produce an amorphous layer at temperature T, B is the dose rate, t is the duration of bombardment, and R_T is the radius of the disorder cylinder at temperature T. The radius of the disorder

⁽²⁶⁾F. F. Morehead, Jr. and B. L. Crowder, Radiat. Eff., <u>6</u>, 27 (1970).

cylinder R_T will depend upon the amount of annealing that occurs after its formation. Immediately after a damage region has formed it will be subjected to athermal and thermal annealing. The athermal annealing has no activation energy and therefore occurs at all temperatures. This annealing is a result of the stress fields around the defects; for example, an interstitial and vacancy will combine athermally provided they come within a few lattice spacings of each other. Since this annealing occurs at all temperatures it will not be a governing factor. What is however of prime importance is the thermal annealing. This thermal annealing or relaxation of the initial damage zone will be a diffusional process. At sufficiently low temperature, as defined by the activation energy for the diffusion, the thermal relaxation will not occur and the threshold dose will be given by

$$(Bt)_{0} = R_{0}^{2} = 1$$
 (2)

where R_0 is the radius of the disorder cylinder with no thermal annealing. At higher temperatures, the cylinder radius R_T can be expressed as

$$R_{T} = R_{0} - \delta R_{T}$$
(3)

where δR_T is the decrease in radius as a result of thermal annealing. Equation (1) becomes, using (2) and (3)

$$(Bt)_{T} = (Bt)_{0} (1 - \frac{\delta R_{T}}{R_{0}})^{-2}$$
 (4)

This equation describes the dose for the formation of an amorphous layer as a result of overlap of the amorphous zones. For the present work we use this same equation, the only variation being in how we perceive the radius of the cylindrical damage regions. If the radius of the damage region is sufficiently large then overlap will result in the formation of a soluble layer and yet the truly amorphous regions inside these cylinders will still be discrete. This approach is reasonable since the damage will not fall off sharply at some distance from the ion track but will decrease continuously.

The thermal annealing which results in relaxation of the disorder cylinder by δR_T will be a diffusional process described by a diffusion coefficient D. A relaxation of δR_T requires that diffusion occur over this distance, whence (according to Morehead and Crowder)

$$R_{T} \simeq 2 (D_{T})^{1/2}$$
,

 τ being the diffusion time. If the diffusion coefficient D is expressed in terms of the migration energy ΔE and the frequency factor D₀ we get

$$\delta R_{T} \simeq 2(D_{0}\tau)^{1/2} \exp\left[-\frac{\Delta E}{2kT}\right],$$
 (5)

and the threshold dose $(Bt)_{T}$ thus becomes from equations (2), (4) and (5)

$$(Bt)_{T} = (Bt)_{0} [1 - Q \exp(-\frac{\Delta E}{2kT})]^{-2}$$
 (6)

where Q = 2 $(\pi(Bt)_0 D_0 \tau)^{1/2}$

Equation (6) is shown in figure 3.6 for Q = 16 and $\Delta E = 0.31$ eV. The experimental points are represented as bars which extend from the experimentally determined threshold doses (Dose #1) to the calculated threshold dose (Dose #2). There is good agreement between the model and the experimental points. Before discussing the values of Q and ΔE it is of interest however, to explore whether or not the assumed shape of the disorder region affects the form of the resulting equation for the threshold dose (Bt)_T and subsequently the values of the parameters of the equation when fitted to the experimental data. In order to investigate any geometry dependence, the equation for the temperature dependence of the threshold dose, $(Bt)_T$, is re-expressed in terms of the volume of the disorder zone. Following Morehead and Crowder⁽²⁶⁾ a soluble layer of thickness W will be produced when

Bt $V_T \ge W$

where V_T is the volume of the disorder zone and W is its length. The threshold dose (Bt)_T will thus be given by

$$(Bt)_{T} V_{T} = W .$$
 (7)

Analogous to $\boldsymbol{R}_{T}^{}$, $\boldsymbol{V}_{T}^{}$ can be expressed as

$$V_{\rm T} = V_{\rm o} \delta V_{\rm T} \tag{8}$$

where δV_T is the relaxation due to thermal annealing. At low enough temperature the threshold dose is given by

$$(Bt)_{o} = \frac{W}{V_{o}}$$
(9)

Combining equations (7), (8), and (9) gives

$$(Bt)_{T} = (Bt)_{0} (1 - \frac{\delta V_{T}}{V_{0}})^{-1}$$
 (10)

As we would expect, for a cylindrical disorder region this gives equation (4)

i.e.
$$(Bt)_{T} = (Bt)_{0} (1 - \frac{\delta R_{T}}{R_{0}})^{-2}$$

using $V_o = \pi R_o^2 W$ and $\delta V_T = \pi R_o^2 W - \pi R_T^2 W$ For a cylindrical region of damage to be produced around the ion track; the energy loss per unit length for elastic collision, dE/dx, would have to be constant. The Thomas-Fermi potential however gives a decreasing dE/dx along the path as the incident ion energy decreases. A conical disorder region may therefore provide a more realistic estimate of the actual disorder geometry. For a conical disorder zone of length W with

$$V_{0} = (1/3) \pi R_{0}^{2} W$$

and

$$\delta V_{T} = (1/3) \pi R_{0}^{2} W - (1/3) \pi R_{T}^{2} W$$

equation (10) becomes eq. (4). Assuming conical disorder zones thus does not affect the model Assuming spherical disorder zones results in eq.(4) having a power -3 instead of -2, though, even here the effect can be shown to be unimportant (ie Q=26 rather than 16 and △E=.38 rather than .31). Thus in no case does the assumed geometry of the disorder zone

affect the model in a significant way.

Significance of the Parameters Q and ΔE

Since the defects are formed by ion bombardment, the activation energy ΔE for the relaxation of the disorder region around the ion will be governed by the migration energy of the defects and not the formation plus the migration energies. The activation energy of 0.31 eV obtained value in the present work agrees well with the 0.33 \pm .03 eV for single vacancy migration in Si (p-type) as reported by Watkins⁽²⁷⁾, though we would regard this as completely fortuitous; that is, there is no reason why single

⁽²⁷⁾G. D. Watkins, J. Phys. Soc. Japan, <u>18</u>, 22 (1963).

vacancies should play the dominant role in the annealing process, and (even if they did) why they should exhibit their normal activation energy. In other studies of the threshold dose in Si, Mazey and Nelson⁽¹³⁾ obtained an activation energy of 0.3 eV, Irving⁽¹⁴⁾ 0.18 eV, and Morehead and Crowder⁽²⁶⁾ 0.12 eV.

Another check of the model is provided by the frequency factor contained in Q. For a reasonable attempt frequency of 10^{12} to 10^{13} sec⁻¹, D_o should be in the region of 10^{-3} to 10^{-4} cm²/sec since for a diamond lattice

$$D_0 = \frac{a^2 v_0}{8},$$

where a is the diffusion jump distance and ν_0 is the attempt frequency. The value of D_0 is given in the present work by

$$Q = 2 (\pi (Bt)_0)^{1/2} (D_0^{\tau})^{1/2}$$

= 16

To obtain D_0 a diffusion time τ must thus be assumed. In order for the attempt frequency v_0 to be $\approx 10^{12}$ Morehead and Crowder⁽²⁶⁾ have taken the diffusion time as 10^{-9} sec, while in the present work a diffusion time of 10^{-8} sec will also satisfy this condition. However, one must ask if these diffusion times are reasonable; i.e. is there any reason why diffusion should stop 10^{-8} or 10^{-9} sec after the disorder zone is formed?

Diffusion Time

Since the criterion used for the formation of an amorphous layer is the overlap of the amorphous zones, it seems reasonable that the diffusion time should be the time for this event to occur. When an amorphous zone is formed it is subject to relaxation until

another ion is incident upon the area of roughly $\pi(2R_0)^2$ around it. Once overlap occurs the zone is stabilized and diffusion is stopped or retarded. This diffusion time is reasonable since the annealing of the individual amorphous zones in Si has been shown to occur at 300-400°C whereas a continuous amorphous layer does not anneal until 600-700°C.

We thus postulate that after a disorder zone is formed, diffusion of defects out of this zone occurs until another ion is incident upon the area $4\pi R_0^2$ around the initial incident ion track. At a dose rate of B ions/cm²-sec the diffusion time τ will thus be given by

$$\tau = \frac{1}{B4\pi R_0^2} = \frac{(Bt)_0}{4B}.$$
 (11)

In the present work, $(Bt)_0$ has been shown to be approximately 8 x 10^{12} ions/cm². Since

B = 5
$$\mu$$
A/cm² = 3.12 x 10¹³ ions
cm²-sec

we finally get

$$\tau \simeq 10^{-1}$$
 sec.

This diffusion time is a factor of 10^8 larger than the time assumed by Morehead and Crowder⁽²⁶⁾ and makes the attempt frequency v_0 far too low to be acceptable.

(B) Model Based on the Competition Between Annealing of the Disorder Zone and Stabilization by the Next Empact

The view taken here is that the time for the next impact to occur in the region $4\pi R_0^2$ around the initial impact is well defined and given (as above) as $\tau = (4B\pi R_0^2)^{-3}$. If this were a random process, then the times for the next impact to occur would be distributed over a range of values with $(4B_{\pi}R_0^2)^{-1}$ is their average. Since we have an ion beam the process is not believed to be fully random, with the rate of next impacts, k_I, being an essentially constant quantity:

$$k_{I} = \frac{1}{\tau} = \frac{4B}{(Bt)_{0}}$$
(12)

The disorder region will, however, anneal by a random process of defect jumps. The rate of jumps will be given by

$$k_{A} = k_{0}e^{-\Delta E'/kT}, \qquad (13)$$

where k_0 is the attempt frequency of the defect and $\Delta E'$ the activation energy for its motion. The probability of n jumps occurring in time interval t will be given by the Poisson distribution law as

$$P_{n}(t) = \frac{e^{-k_{A}t}(k_{A}t)^{n}}{n!}$$

where $P_n(t)$ is the probability of n events occurring in the time interval t. If 1 jump is rate-controlling for the annealing of the disorder region (for small regions this may be the case) then the probability of no annealing is

$$P_{o}(t) = e^{-k}A^{t}$$

The fractional survival of disorder regions during time dt at t then follows as -k + t

$$dF = k_{I}dt \cdot e^{-k_{A}t}$$

$$F = \int_{0}^{\infty} k_{I} e^{-k_{A}t} dt$$

$$= \frac{k_{I}}{k_{A}}$$

whence

If 2 jumps are rate-controlling for annealing then the probability of no annealing is given by

$$P_{o}(t) + P_{1}(t) = e^{-k_{A}t} + e^{-k_{A}t} k_{A}t$$

which gives .

$$F = 2 \frac{k_{I}}{k_{A}}$$

Similarly for n jumps we have

$$F = n \frac{\kappa_{I}}{k_{A}}$$
 (14)

The condition for the formation of an amorphous layer is that the disorder regions that survive should overlap, i.e.

$$(Bt)_{T} \pi R_{0}^{2} F = 1$$
.

This gives with equations (2), (12), (13) and (14)

$$(Bt)_{T} = K e \qquad (15)$$

where $K = \frac{0}{4nB}$ and k is Boltzmann's constant.

Equation (15) is only valid in the high temperature region where

$$k_A > n k_I$$

At low temperatures where $k_A \leq nk_I$ the threshold dose will be (Bt)₀.

Figure 3.6 shows a plot of equation (15) with $K = 12 \times 10^{18}$ and $\Delta E' = 0.56$ eV. The attempt frequency k_0 is thus

$$k_{o} = n(2 \times 10^{7})$$

This value of the frequency factor is still rather low but is much better than that which would have been obtained from Morehead and Crowder's model using the same diffusion time. It is difficult however to know what to compare the frequency factor with since the defects responsible for the annealing are not known. It should also be noted that this model results in a straight line, as was observed by Mazey and Nelson.⁽¹³⁾

Summary and Conclusions

The threshold dose determined by the dissolution of the soluble layer on bombarded Si provides an easy technique for the determination of the dose required to produce this layer. Since the depth of the layer defines a region in the crystal of constant concentration of damage, i.e. the damage required to render the Si soluble, therefore by assuming a damage distribution and knowing the depth of the layer the threshold dose to produce this concentration of damage at the surface and at the maximum of the distribution can be inferred.

The dose to give this damage concentrationat the maximum agrees within a factor of 2 with the dose determined by the number of ions that have come to rest beyond the interface. For room temperature bombardments the dose of ions beyond the interface is $8 \times 10^{12} \text{ ions/cm}^2$. A 10 keV bombardment gives this level of damage at the damage distribution maximum when the dose is $9 \times 10^{12} \text{ ions/cm}^2$ and at the surface when the dose is $3.2 \times 10^{13} \text{ ions/cm}^2$.

It is possible (though not necessarily proven) that the soluble layer formed in the ion bombardment extends further into the crystal than the amorphous layer. Thus observations of the dose required to produce an amorphous layer using the electron microscope, MeV-particle backscattering, or optical reflectivity give a dose which is higher than that determined in the present work. The damage required to render the silicon soluble in HF-H₂O₂ thus appears to be less than that required to produce amorphous silicon. Stein et al.⁽²³⁾ propose that the damage regions are

not amorphous at formation, but rather the regions grow and at a high enough dose the regions become amorphous due to their large size. The threshold dose determined in the present work may indicate this dose, i.e. that for just beginning to form amorphous damage regions. It was determined by Stein et al.⁽²³⁾ to occur at 10^{13} ions/cm² for Sb¹²¹ bombardment of Si as indicated by a decrease in the divacancy concentration.

Whether or not the soluble layer and the amorphous layer coincide, the dose to produce this soluble layer will still be governed by the annealing process of the damage zones. A model proposed by Morehead and Crowder gives an activation energy of 0.31 eV for this annealing. This is very close to that determined by Watkins(27) for single vacancy diffusion though we regard this as a coincidence. However, the diffusion time of 10^{-8} sec required to give a reasonable attempt frequency of 10¹² sec⁻¹ is unreasonable in the spirit of the model. Since the zones are stabilized by overlap of the disorder zones, the diffusion time for a given zone will be the time for another zone to overlap it. With the dose rate used here this will occur in 10⁻¹ sec. A model based on this and the time for annealing to be initiated gives a frequency factor of $2n \times 10^7 \text{ sec}^{-1}$, where n is the number of ratecontrolling jumps required for annealing to be initiated, and an activation energy of 0.56 eV. This frequency factor is still lower than the usually expected value; it is, however, even for $n = 1, 10^2$ higher than would be obtained from Morehead and Crowders equation using the same diffusion time.

Method	of Observation	Criterion for Amorphousness	Incident Ion	Incident Energy (keV)	Threshold Dose (ions/cm ²)	Reference
	Transmission	Diffuse Rings in Diffraction Pattern	Ar ⁴⁰ Si ²⁹	100 40	5x10 ¹⁴ 1x1015	(19) (19)
// *	Reflection Diffraction	Disappearance of Diffraction Spots	Kr ⁸⁴	30	2x10 ¹⁴	(20)
	Electron Chan- neling Patterns of SEM*	Degradation of Pattern	Ne ²⁰ Sb121	80 100	3-7×10 ¹⁴ 4-7×10 ¹³	(16) (16)
MeV-particle Backscattering		Saturation of the area under the damage peak	Ga ⁷⁰ Sb121	40 40	3x10 ¹⁴ 10 ¹⁴	(21) (22)
	Visual Observation	Appearance of milky colour	,31 Ne ²⁰	100 60	10 ¹⁴ 1014	(14) (13)
otical echniques	Optical Reflectivity with Photons 3-6.5 eV	Saturations of the change in reflect- ivity	Sb ¹²¹	40	10 ¹⁴	(24)
	Optical Reflectivity with Photons 1.8-2.2 eV	Saturation of the change in reflect- ivity	Sb ¹²¹	40	4x10 ¹³	(25)
	Infrared	Divacancy concentr- ation = 0	sb ¹²¹	400	10 ¹⁴	(23)
	Absorption of 1.8µ wave- length	Divacancy concentr- ation starts to decrease	Sb ¹²¹	400	10 ¹³	(23)

Table 3-IDose to Create an Amorphous Layer Using Various Meansof Observation

M - electron microscope

M - scanning electron microscope





Fig. 3.2. Dissolution curves for hot implants of Kr^{85} into Si at 10 kev to a dose of 1.87 x 10 ions/cm²(dose rate = 3.12 x 10 ions/cm²-sec). Shown on each curve is the temperature of the implant.



Fig. 3.3 Temperature dependence of the threshold dose as determined by the dose of ions that came to rest below the layer.



Fig. 3.4 Determination of Threshold Dose #2 and #3 for 10 kev Kr^{o} bombardments of Si from the concentration of damage C_{d}^{+} at the soluble-insoluble Si interface. C_{d}^{+} is the critical damage concentration required to render the Si soluble in an $HF-H_{2}O_{2}$ solution







Fig. 3.6. A plot of log $(Bt)_T$ vs 1/T from equations (6) and (15); the values of the parameters are given in the equations shown. The experimental points extend from Threshold Dose # 1 to # 2.

SECTION IV: GAS RELEASE OF Kr⁸⁵ FROM BOMBARDED SILICON

Introductory Comments

The annealing of the disorder zones was investigated in section III. Now we wish to examine the annealing process which occurs when the sample is heated after bombardment at doses which result in the formation of an amorphous layer. More specifically, we want to obtain direct evidence concerning the motion of Kr in the annealing. In such a study the dissolution of the soluble layer is shown to be very useful.

In this section more evidence is given to support the view that the crystallization of the amorphous layer occurs by epitaxial growth of the underlying Si at 650 to 700°C. As this epitaxial growth occurs, some Kr^{85} is shown to be pushed out in front of the interface, some Kr^{85} to be left behind in the crystallized Si. The Kr^{85} in the crystalline Si is shown not to diffuse in the time scale of a few minutes until 900 to 950°C.

INTRODUCTION

Energetic ions incident upon a target will be slowed down by a series of collisions with the target atoms. Once the energy of the incident ion has fallen below the displacement energy the ion will be trapped in the lattice. The ability of this ion to subsequently move around in the lattice will be determined by its surroundings. If the lattice around it is undisturbed then the activation energy and frequency factor governing the migration will simply be the normal diffusional parameters for target and dopant. However the incident ion creates damage as a result of this slowing down. The ion may thus be situated in a damaged lattice, and since the activation energy and frequency factor are determined by the surrounding lattice they will deviate from the normal values. The ion can thus no longer be thought of as being interstitial or substitutional, but rather it may be attached to dislocations, vacancy clusters, or interstitial clusters of incident or target atoms, or it may sit in a lattice that has undergone a phase change. Rather than all the ions experiencing the same lattice environment we may have a series of environments, and thus a series of activation energies. These activation energies may be discrete indicating basically different diffusion processes or may be continuous. A concontinuum of activation energies will result from small changes in the lattice environment from one atom to the next; thus one atom requires an activation energy Q and the other Q + dQ. The incident ion's migration in the lattice will thus reveal information about the defect

environment in which the incident ion finds itself. The diffusion process may however be quite complex as a result of the complexity of the lattice damage.

Gases are often used as the bombarding species so that when the ion reaches the surface it will be removed into the gas phase. The diffusional process can then be followed by the change in the activity of the sample. Since it is the damage which is of interest inert gases are used to avoid any chemical effect between the target and incident ions.

Heating of the bombarded sample will result in diffusion and release of the ions from the sample when the temperature is such that the inert-gas ions can overcome the activition energy for migration and migrate to the surface in the time scale of the experiment (in the order of a few minutes). The isochronal heating of the sample is done either with a continuous increase in temperature or a stepwise increase. With the continuous temperature increase, a flow of gas is passed over the sample during heating and the activity of this gas monitored to give a plot of the rate of gas released with temperature. If the stepwise heating is used, then the activity of the sample is measured after each heating to give the integral release curve. If the temperature increase at each step is small enough the integral curve obtained can be differentiated to give the rate of gas release curve.

A system of stages has been developed⁽¹⁾ to describe the

(1) R. Kelly and Hj. Matzke, J. Nucl. Mat. <u>17</u>, 179 (1965)

release of inert gas in ion-bombardment experiments which follows along the lines of the recovery of electrical resistivity after quenching, cold working, or irradiation. The gas release can be divided into 3 basic stages indicating 3 basic groups of diffusion processes. These stages are denoted by the temperature region in which they occur with respect to the temperature of self diffusion, T_{cd} , of the target. Briefly these stages are:

Stage I T<<T_{sd}

Since it occurs at a temperature that is abnormally low it is thought to result variously from the diffusion of inert-gas atoms located at highly mobile sites such as interstitials, migration of inert gas near the surface, release accompanying a phase change (usually the amorphous to crystalline transition), or diffusion through a damaged layer with a spectrum of activation energies.

Stage II T≃T_{sd}

Stage II occurs at approximately the normal diffusion temperatures of the target material. The release is roughly compatible with conventional diffusion data although it may be subjected to weak trapping.

Stage III T>>Tsd

This stage is associated with the slow diffusion of gas bubbles, which are ordinarily strong traps for the inert gas.

The purpose of the present work is to characterize the release processes in the gas release curves of Kr^{85} bombarded Si. In this work use is made of the soluble layer produced in ion bombardment to produce a marker of fixed depth from the surface. Such a marker

allows the motion of the inert gas to be observed.

EXPERIMENTAL PROCEDURE

Bombardment

The samples were bombarded using a radio frequency ion source as shown in section II. The samples were p-type Si wafers of <III> orientation, and $p=5-10\Omega$ -cm.

Isochronal Heating of Bombarded Samples

The isochronal heating was done in a vacuum furnace specially constructed for this work as shown in fig. 4.1. This furnace allows the activity of the sample to be counted without breaking vacuum. The temperature was increased by steps of 50°C and the samples were held at each temperature for 10 minutes. After each heating the sample is drawn out of the furnace area, allowed to cool, and then drawn further back to beneath a 25.4 μ stainless steel window where its activity is counted using a Geiger-Müller system. The pressure inside the furnace at room temperature is 3-4 x 10⁻⁶ torr, at 600°C $\approx 10^{-5}$ torr, and at 1000°C $\approx 6 \times 10^{-5}$ torr. The maximum temperature attainable is 1100°C. The temperature of the sample is recorded by a thermocouple which touches the bottom of the quartz boat holding the Si sample.

To insure a fast pump down and to minimize contamination of the system the furnace was cooled to room temperature before vacuum was broken and vacuum was always broken using He gas.

For gas-release experiments with Si the vacuum furnace and stepwise heating technique was found to give better results than the continous heating, flow gas technique used by Jech and Kelly⁽²⁾. This is because (a) the technique using a flow of gas requires higher activities, (b) the samples were often found to be covered with a white film after the gas release, (c) some times the sample would touch the thermocouple, alloy with it, and melt, and (d) there was a fair amount of variation from one sample to the next with respect to the temperature at which the release stages occurred. Using the vacuum furnace the sample remained clean and the results were consistent.

Dissolution of Soluble (Amorphous?) Layer

Dissolution of the soluble layer produced in the ion bombardment was done either in a concentrated solution of HF (i.e. 48% HF) or in a 2 pt. 48% HF to 1 pt. 30% H_2O_2 solution.

RESULTS AND DISCUSSION

Effect of Bombarding Dose on the Gas Release

To investigate the effect of dose on the gas release, Si samples were bombarded with 10 kev Kr^{85} to doses of 3.74×10^{14} , 3.74×10^{15} and 3.74×10^{16} ions/cm². The samples were then annealed isochronally with temperature increases of 50°C and heatings of 10 minutes. Figure 4.2 shows the integral gas release curves at the 3 doses. The gas is released in 2 stages, the first having its maximum between 650 and 700°C at least for the two lower doses and the second stage having its maximum between 900 and 950°C. This first stage occuring at 650-700°C agrees with the annealing of the amorphous

(2) C. Jech and R. Kelly, J. Phys. Chem. Solids, <u>30</u>, 465 (1969).

layer as has been observed by MeV-particle backscattering in the temperature region of 550 to 700°C⁽³⁾ and at ~630°C by electron diffraction.⁽⁴⁾ Jech and Kelly⁽²⁾ showed gas release results for 10 kev Kr⁸⁵ bombardment of Si to doses of 2.24 × 10¹⁵ ions/cm² and 3 × 10¹⁴ ions/cm². They used a continuous temperature increase of 25°C/min. (\equiv 1 min.) and counted the activity of a flow gas (N₂). They also observed 2 stages, the first stage occuring at 700 to 750°C essentially as in the present work. However the maximum of the second stage occurred at ~925°C for the 3 × 10¹⁴ ions/cm² dose (which agrees with the present work) but at ~1150 for the 2.24 × 10¹⁵ ions/cm² dose. This release peak at ≈1150°C was also observed in the present work when the continuous temperature increase flow-gas technique was used but was never observed using the vacuum furnace; it may thus be a consequence of contamination.

Increasing the dose from 3.74×10^{14} to 3.74×10^{15} ions/cm² results in an increase in the amount of activity that is lost in the first stage, 50-70% being lost at 3.74×10^{14} ions/cm² and 75-85 being lost at 3.74×10^{15} ions/cm². This result is in agreement with the dose effect shown in the dissolution curves of figures 2.4 and 2.5. As the dose is increased the soluble layer increases in thickness and as a result contains a greater percentage of the activity. We note however that the layer defined by the dissolution experiment

(3) J. W. Mayer, W.Eriksson, S. T. Picraux, and J. A. Davies Can. J. Phys. <u>46</u>, 663 (1968).

(4) D. J. Mazey, R. S. Nelson, and R. S. Barnes, Phil. Mag. <u>17</u>, 1145 (1968)

contains ~98% of the activity for 10 kev bombardment to 3.74×10^{14} ions/cm², whereas the annealing of the amorphous layer releases only 50-70% of the activity. This may be a result either of the soluble layer being thicker than the amorphous layer or activity remaining in the amorphous layer after annealing.

At the very high dose of 3.74×10^{16} ions/cm² little or no distinction can be made between the 2 release peaks since the first peak has shifted to higher temperatures. At such a high dose the crystallization of the amorphous layer may be retarded by the formation of small bubbles.^(4A) In addition Davidson and Booker⁽⁵⁾ have shown the annealing of high-dose bombarded Si **to** result in a semi-polycrystalline structure rather than the single crystal structure observed at lower doses. It is therefore expected that the gas release will be different. Effect of Heating Time on Gas Release

Two Si samples were bombarded at 10 kev to a dose of $1.87 \times 10^{15} \text{ions/cm}^2$. Both samples were heated from 500°C to 950°C in 50°C steps. One sample was however held at each temperature for 15 min. and the other for 1500 min. The results, as shown in figure 4.3, reveal a shift of the high temperature stage from 900-950°C to 750 to 850°C with longer heating time. This is the expected result for a normal diffusional process: As the heating time is increased more activity should be released at each time. The first stage however remains at between 600 and 650°C. From these results it would appear that the amorphous phase is stable below this temperature range

⁽⁴A) M. D. Matthews, Harwell Report (U.K.) AERE-R 6802 (1971).

⁽⁵⁾ S. M. Davidson and G. R. Booker, Radiat. Eff., <u>6</u>, 33(1970).

rather than <u>metastable</u>, though this result is rather unexpected. Also of interest is the decrease in the amount of activity released in the first stage as the time increases. For the 15 minute heating 80-90% of the activity was lost in the first stage whereas only 40-50% was lost for the 1500 min. heatings. This could be a result either of diffusion of more Kr into the underlying crystal with increased time or some sort of rearrangement of the Kr in the amorphous layer that results in less coming out with crystallization. Such a stabilization would however be expected to result in a shift of the release temperature as in fig. 4.2.

Annealing of the Amorphous Layer

If the annealing of the amorphous layer occurs by epitaxial growth of the underlying silicon substrate, then this motion may be observable by the dissolution of the soluble layer after the sample is heated at various temperatures. It is necessary, of course, that epitaxial growth does not remove all the Kr^{85} in the amorphous layer and that the Kr^{85} doesn't diffuse into the underlying silicon. This latter possibility is dealt with later. Si samples were bombarded with 10 kev Kr^{85} to a dose of $3.74 \times 10^{15} \text{ ions/cm}^2$. The samples were then heated for 1 hour at temperatures ranging from 500°C to 800°C. After the anneal the soluble layer is etched in a concentrated HF solution (48% HF). The percentage of <u>original</u>* activity at the knee of the dissolution curve will in principle distinguish between (a) motion of the interface leaving behind the same activity from (b) motion of the Kr^{85} , thence an increase in activity, or

^{*}The dissolution curves are given with respect to the activity of the sample after bombardment and not after the anneal.

motion of the interface with Kr^{85} being left behind. The dissolution curves are shown in figure 4.4* No difference was observed in the dissolution curves until an anneal temperature of greater than 500°C was used. Above this temperature the percentage of original activity in the sample increased. This is the expected result both if the Kr moves and also for epitaxial growth provided some of the Kr⁸⁵ is left behind in the crystalized region. (If the epitaxial crystallization of the amorphous layer swept out all the activity in this layer, the dissolution curves would have remained unchanged.) Note that above 700°C the dissolution rate is slow, thus indicating a lack of solubility after the crystallization of the amorphous layer.

Motion of Kr⁸⁵

We have argued that the results of figure 4.4 could be explained equally well in terms of motion of the Kr^{85} into the crystal region below the soluble layer or in terms of interface motion (with activity left behind). To distinguish between these alternatives Si samples were bombarded at 40 kev with radioactive Kr^{85} to a dose of 1.87×10^{15} ions/cm² and then heated in the vacuum furnace for 10 minutes at temperatures ranging from 600°C to 975°C. After the anneal the samples were rebombarded at the same dose and energy but with non-radioactive Kr^{84} . This rebombardment reforms the soluble layer to

Note that the time scale of Fig. 4.4 is hours compared to minutes for Fig. 2.4 and 2.5 using an $HF-H_2O_2$ solution.

the same depth. Dissolution of this layer will indicate any motion of Kr^{85} into or out of the region below the interface. The dissolution was done in a solution of 2 pts. 48% HF to 1 pt. 30% H₂O₂. The activity below the layer was found to be constant at between 0.2 and 0.7% of the initial activity for anneals up to $\approx 800^{\circ}$ C where it was found to decrease rapidly to $\approx 0.03\%$ at 900 to 950°C, as shown in figure 4.5. This reveals that the Kr⁸⁵ in the crystalline region does not diffuse until the second gas-release stage, and suggests that the first gas release stage involves interface motion.

Another piece of information is provided by the gas sputtering of radioactive Kr^{85} in the rebombardment with non-radioactive Kr^{84} . It is for this reason that the energy of 40 kev was chosen for the bombardments. As shown in figure 2.3 the amount of gas sputtering is quite low for the rebombardment at this energy. However, if the Kr^{85} moves towards the surface the amount sputtered will increase. The results are shown in figure 4.6 where the activity of the sample after heating is shown along with the percentage of this activity lost in the subsequent non-radioactive bombardment. It is noted that the percentage of active gas sputtered is a maximum at the first stage. This indicates an increased concentration of Kr^{85} near the surface and thus confirms the role played by interface motion.

Conclusions

Implanted Kr^{85} in Si in the dose region of $\approx 10^{15}$ is released upon heating of the sample by two processes, one occuring at 650 to 700°C and the other at 900 to 950°C. The first stage is a result of epitaxial recrystallization of the underlying crystal into the amorphous layer

and is therefore Stage I. As the epitaxial growth occurs Kr moves towards the surface, although some Kr is left behind in the crystallized amorphous silicon, the amount being determined by the annealing time. During the first stage (Stage I) the Kr in the underlying crystalline Si does not diffuse. The diffusion of the Kr in the crystalline silicon gives the second stage, and is therefore a Stage II process. It is moreover a typical Stage IIA⁽⁶⁾ process as can be shown by a comparison with Si self-diffusion. The temperature for Si self-diffusion for a time and distance scale as in this work is about 1185°K⁽²⁾ while the second release stage occurs at between 1173 to 1223°K. The migration of Kr⁸⁵ in this process may thus be inferred to occur without gas-damage or gas-gas interactions.

(6) R. Kelly and C. Jech, Proc. Brit. Ceram. Sol., <u>9</u>, 243 (1967).



Fig. 4.1. Gas release vacuum furnace.



Fig. 4.2 Integral gas release curves for 10 kev Kr⁸⁵ bombardments of Si. The insert gives the dose of each bombardment



Temperature (°C)

1 -

Fig. 4.3. Integral gas release curves for 10 kev Kr^{85} bombardments of Si to 1.87 x 10¹⁵ ions/cm². The heating time at each temperature is given in the insert.


Fig. 4.4. Dissolution of the soluble layer for Si samples bombarded and heated for 1 hour at the temperature shown.





4.5. Motion of the ${\rm Kr}^{85}$ in the crystalline Si, as shown by the percentage of initial activity below the original soluble-insoluble interface after a 10 min. anneal at the temperature shown.





Fig. 4.6. Motion of Kr⁸⁵ towards the surface as mevealed by the percentage of activity, after each 10 min. anneal, that is gas sputtered in the non-radioactive rebombardment. The upper graph shows the percentage of initial activity released with each anneal.

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