event. The data seem to require that the centers have a radius of gyration of at least some 40 Å and that their shape be nonspherical.

(4) The annealing study indicates that the scattering centers should be thought of as disturbed regions formed by thermal spikes rather than as crystalline inclusions.

(5) Neither the nature of the glass preparation or the impurities in the glass seem to contribute to the observed irradiation effects.

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Optical Reflection Studies of Damage in Ion Implanted Silicon

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Optical (3–6.5 eV) reflection spectra are presented for crystalline Si implanted at room temperature with 40 keV Sb ions to doses of less than $2\times10^{15}/\mathrm{cm}^2$. These spectra, and their deviation from the reflection spectrum of crystalline Si, are discussed in terms of a model based on the average dielectric properties of the implanted region. For samples having a high ion dose ($>10^{15}/\mathrm{cm}^2$) the observed spectra resemble the spectra of sputtered Si films. Anneal characteristics of the reflection spectra are found to be dose dependent. These observations are compared to, and found to substantiate, the results of other experimental techniques for studying lattice damage in Si.

INTRODUCTION

The possible technological importance of doping semiconductors by ion implantation has motivated extensive study into many aspects of implantation processes. Since the incident ions generally induce damage in the target crystal, much effort has been devoted to ascertaining the nature of this damage. Inasmuch as a theoretical treatment of the damage is difficult, most studies have attempted to form a model for the damage based primarily upon experimental observation. Three techniques have been used to examine damage: electron microscopy,[1,2,3] He$^+$ backscattering,[4] and optical spectroscopy.[5,6] Each of these techniques samples the damage in a different manner; consequently, each provides a different kind of information about damage. To put the results of this paper in proper perspective, let us review briefly the relevant results produced by these various techniques.

Detailed transmission electron microscopy studies[1,2,3] have been performed on samples of etch-thinned Ge implanted with O, and Si implanted with Ne, Si, and P. It was found that for small doses (10^{13} 80 keV Ne/cm^2 in Si) black dots corresponding to regions on the order of 50 Å in diameter are observed in transmission electron micrographs of both implanted Si and Ge. The work of Parsons on Ge implanted with 100 keV O indicates that these dots correspond to "amorphous" (heavily disordered) regions. Although detailed studies have not been made of similar regions in Si, it is generally surmised that these regions are also amorphous. In implanted Si samples these amorphous regions disappear upon annealing in the temperature range 400°–500°C. After the anneal many large dislocation loops are observed.

For larger doses ($\sim10^{14}$ 80 keV Ne/cm^2 in Si) the amorphous regions become so numerous that they overlap, resulting in the formation of an amorphous layer. Upon annealing no change is observed in this amorphous layer until approximately 600°C. Above 600°C the previously amorphous layer is observed to have one of two different structures. If the layer is supported by crystalline Si during annealing, the layer becomes crystalline with many large dislocation loops. If not, the layer becomes polycrystalline with many individual crystallites on the order of 1000 Å in size.

Backscattering of He$^+$ ions is another experimental technique which yields information about lattice damage. The backscattered yield of incident ions for certain channeling directions provides a measure of the number of host atoms displaced from lattice sites. Davies *et al.*[4] investigated lattice damage induced in Si implanted with 40 keV Sb ions at room temperature. They concluded that disorder (a measure of the number of displaced Si atoms) increases linearly with dose for doses less than 10^{14} Sb/cm^2; for doses greater than 10^{14} Sb/cm^2, no further increase is observed. Annealing of these samples showed that for doses of approximately 10^{13} Sb/cm^2 (in the range where disorder increases

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[3] S. M. Irving, *Semiconductor Silicon* (The Electrochemical Society, Inc., New York, 1969), p. 433.

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linearly with dose) disorder decreases sharply between 200–300°C. This differs from the anneal temperature range which Nelson *et al.*[2] reported for the disappearance of the black dots. For samples implanted with 5×10^{14} Sb/cm^2 damage does not begin to anneal until 600°–700°C. This agrees with the anneal temperature observed in electron microscopy studies of heavily implanted samples.

By the use of transmission infrared spectroscopy Stein *et al.*,[6] have observed (in oxygen-implanted silicon) the presence of the characteristic divacancy optical absorption band at 1.8 μ. This data is considered to be direct evidence for divacancy formation by ion implantation. Divacancies were produced at a rate of $\sim$5 per incident ion upon implantation at $\sim$50°C with 1.75×10^{14} oxygen ion/cm^2 at 400 keV. The 1.8 μ absorption band was observed to diminish upon anneal between 100° and 250°C. No evidence for oxygen-vacancy center formation was observed. A lower limit of detectability of $\sim3.5\times10^{14}$/cm^2 was established for these centers.

The effect of implantation upon the visual appearance of ion implanted Si was studied by Nelson and Mazey.[2] For light doses, they noted changes in the hue of the implanted layer which they conjecture to result from Rayleigh scattering of incident light (from the localized amorphous regions observed in electron microscopy). For heavy doses, the implanted layer exhibits a "milky" appearance attributed to multiple scattering from a large number of closely spaced, localized amorphous regions. No change was noted in the visible appearance of the implanted region for anneal temperatures less than 600°C.

Recently, we initiated a series of experiments to study the optical reflectivity spectra of ion implanted Si.[5] These preliminary measurements indicated that, considering only ions of mass >39 amu, characteristic changes in the reflectivity of Si due to ion implantation are independent of ion species. We also noted that the reflectivity (particularly at photon energies characteristic of direct transitions in crystalline Si) decreases with increasing ion dose. In the limit of high dose, the reflectivity of ion implanted crystalline Si approaches that of sputtered (amorphous) layers.

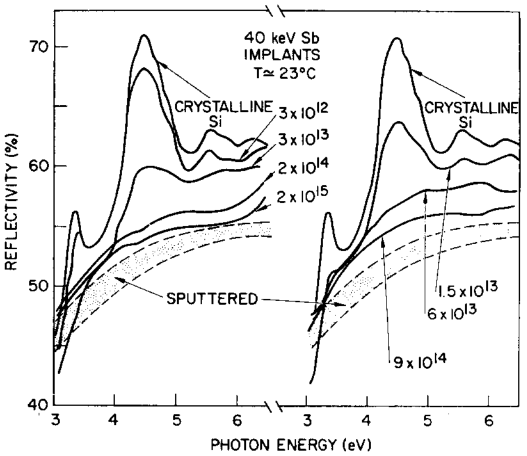

FIG. 1. Reflection spectra of samples of crystalline Si, ion implanted Si and sputtered Si in the 3–6.5 eV energy range. Doses shown are in units of Sb/cm^2.

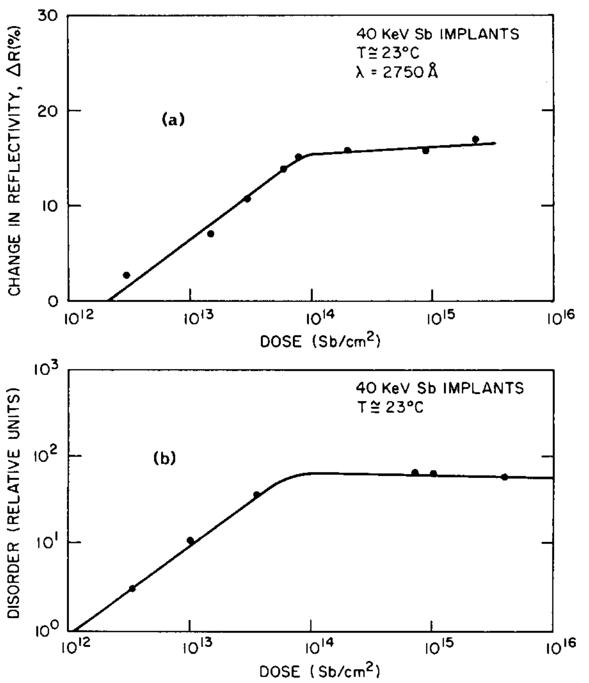

FIG. 2. (a) The difference between the reflectivity (at 4.5 eV) of crystalline Si and that of implanted Si as a function of ion dose. (b) The disorder as a function of dose for implanted Si samples (after Davies *et al.*).[4]

In this paper we report on a more complete set of measurements of the optical reflectivity of Si crystals implanted at room temperature with 40 keV Sb ions with doses in the range 0–2×10^{15} Sb/cm^2. We also report the annealing behavior of samples implanted with 3×10^{13} Sb/cm^2 and 2×10^{15} Sb/cm^2. The dose and anneal behavior of the optically effective damage is found to correlate closely with the damage observed in backscattering experiments. However, in lightly implanted samples the temperature required to anneal the optically effective damage differs from the temperature range reported for the disappearance of the black dots in electron micrographs. In addition, we show that the optical properties of ion implanted materials are best described in terms of a dielectric constant averaged over the lattice damage.

EXPERIMENTAL RESULTS

Figure 1 shows the reflectivity spectra obtained in the 3–6.5 eV photon energy range from Si samples implanted with 40 keV Sb ions for doses up to 2×10^{15} Sb/cm^2. The experimental procedures used here are the same as those described in Ref. 5. Several features are apparent from these spectra. First, no changes in the reflectivity were detectable for doses less than 3×10^{12}

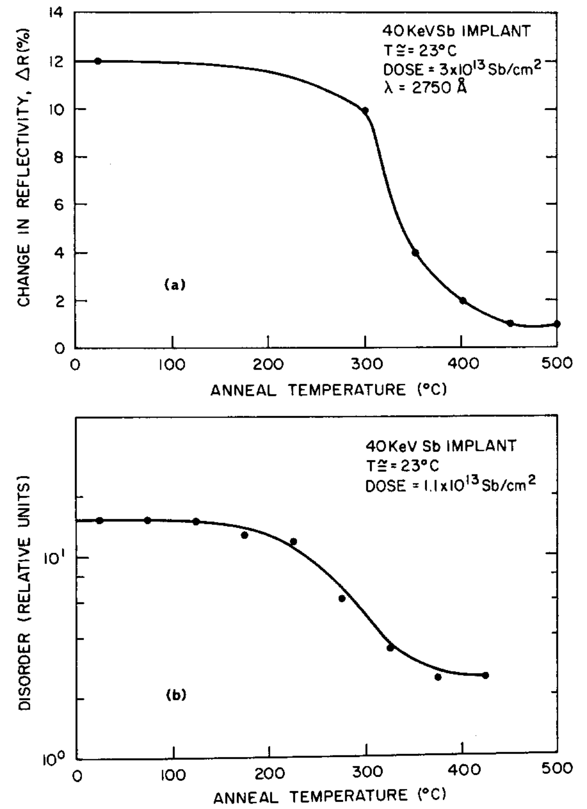

FIG. 3. (a) The difference between the reflectivity at 4.5 eV of crystalline Si and that of a lightly implanted Si sample as a function of anneal temperature. (b) The disorder as a function of anneal temperature for a lightly implanted Si sample (after Davies *et al.*).[4]

Sb/cm^2. Second, for doses from 3×10^{12} to 9×10^{14} Sb/cm^2, the characteristic reflectivity peaks of crystalline Si (dose=0) decrease monotonically with increasing dose. Third, for doses in the range 9×10^{14} to 2×10^{15} Sb/cm^2, little or no additional change in reflectivity occurs. This trend is exhibited more graphically in Fig. 2(a) where the difference between the reflectivity at 4.5 eV of crystalline Si and that of implanted Si is plotted as a function of dose.

In Fig. 2(b), we show a plot of the disorder (defined by Davies *et al.*,[4] for backscattering experiments) versus dose. Comparing Figs. 2(a) and (b), it becomes apparent that changes in both reflectivity and disorder exhibit the same general behavior as a function of dose. For low doses, both quantities increase with increasing dose. For doses greater than 10^{14} Sb/cm^2, both quantities approach saturation and become independent of dose.

In Fig. 1, we have also included the range of reflectivity for "amorphous" samples produced by sputtering high-purity Si onto a room-temperature quartz substrate. Comparison of the reflectivity of the heavily implanted Si sample with that of the amorphous layer indicates that, in the limit of high dose, the reflectivity of an implanted Si sample approaches that of an amorphous Si film.

Both implanted Si samples and amorphous Si layers were checked for surface roughness using a scanning electron microscope. These studies failed to reveal any surface roughness at magnification up to 10 000 diameters. This result suggests that surface scattering is not an important factor in determining the observed reflection spectra.

Diffuse scattering could not be observed. A lightly and a heavily implanted sample were examined with a monochromatic beam throughout the visible spectrum. With the specularly reflected beam blocked from view, no diffusely scattered radiation could be seen with the dark-adapted eye.

To study the difference between the damage induced at room temperature by light implants ($<10^{14}$ 40 keV Sb/cm^2) and by heavy implants ($>10^{14}$ 40 keV Sb/cm^2), we investigated the anneal characteristic for implanted Si samples in these two regions. All anneals were for 10-min periods. In Fig. 3(a), we have plotted the deviation of reflectivity at 4.5 eV of a sample implanted with 3×10^{13} Sb/cm^2 from that of crystalline Si as a function of anneal temperature. This curve indicates that the optically effective damage begins to anneal at ~300°C and that the reflectivity of the layer approaches that of crystalline Si at ~450°C. It should be noted that the onset of annealing at ~300°C for the optically effective damage differs from anneal temperature (400–500°C) reported for the disappearance of the black dots observed with electron microscopy. Davies

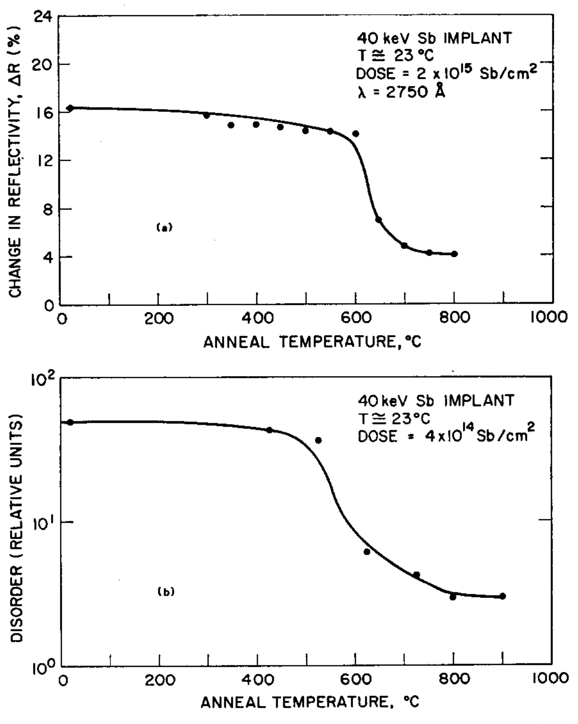

FIG. 4. (a) The difference between the reflectivity at 4.5 eV of crystalline Si and a heavily implanted sample as a function of anneal temperature. (b) The disorder as a function of anneal temperature for a heavily implanted Si sample (after Davies *et al.*).[4]

et al.,[4] using the He$^+$ backscattering technique, measured disorder as a function of anneal temperature for a sample implanted with 1.1×10^{13} Sb/cm^2 [see Fig. 3(b)]. They found that disorder begins to anneal at $\sim$300°C. This temperature is close to that at which damage anneals as shown by the optical reflection technique. The range of temperatures observed by Stein *et al.*,[6] for the annealing of divacancies induced in silicon by a 400 keV oxygen implantation lies somewhat below 300°C.

The annealing behavior of a heavily implanted (2×10^{15} Sb/cm^2) sample was also observed. Figure 4(a) shows the resulting deviation in reflectivity at 4.5 eV from that of crystalline silicon. More than 600°C is required for significant annealing to occur. In Fig. 4(b), we have plotted the anneal characteristic of damage observed by Davies *et al.*,[4] in backscattering experiments for a sample implanted with 2×10^{14} 40 keV Sb/cm^2. On comparing Figs. 4(a) and 4(b), we note that for the two experiments approximately the same temperature is required to anneal the observed damage. This anneal temperature agrees with that measured for the amorphous layers which are observed in electron microscopy studies of heavy-dose implants.

Optical reflection spectra at various stages of annealing are shown in Fig. 5 for a sample implanted with 3×10^{13} Sb/cm^2. This is the same sample discussed with reference to Fig. 3(a), which showed the variation of reflectivity (at 4.5 eV) with anneal temperature. Figure 6 shows similar spectra as a function of annealing for a sample implanted with 2×10^{15} Sb/cm^2 [same sample as in Fig. 4(a)]. In the lighter implant (Fig. 5) a substantial remnant of the 4.5 eV crystalline peak is seen before annealing. This peak returns to essentially the crystalline value after the anneal at 500°C. Although the smaller peak at 3.4 eV is not prominent after implantation, this peak also returns to the crystalline value after the anneal at 500°C. A substantial change in the spectrum is evident between the anneals at 300° and 350°C. The spectrum of the heavier implant (Fig. 6) indicates the amorphous condition of the layer as implanted. There is relatively little change in the spectrum up to the 600°C anneal. A drastic change in the spectrum is noted between the anneals at 600° and 650°C. After the 650°C anneal are seen the first indications of the peaks at 3.4 and 4.5 eV. However, even after the 800°C anneal the peak at 4.5 eV does not return to the crystalline value, and the peak at 3.4 eV shows no growth above its value after the 650°C anneal.

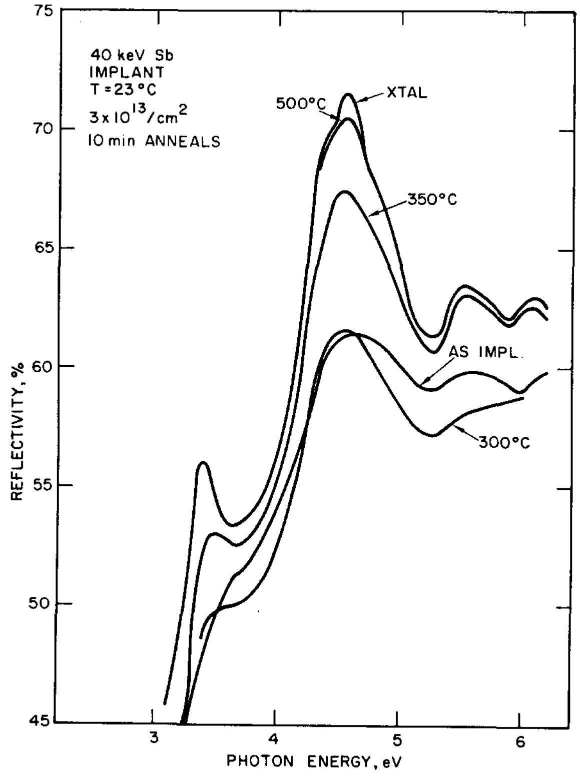

FIG. 5. Reflection spectra in the 3–6.5 eV energy range of a silicon sample implanted at room temperature with 3×10^{13} Sb/cm^2 and subsequently annealed for 10-min intervals at various temperatures up to 500°C.

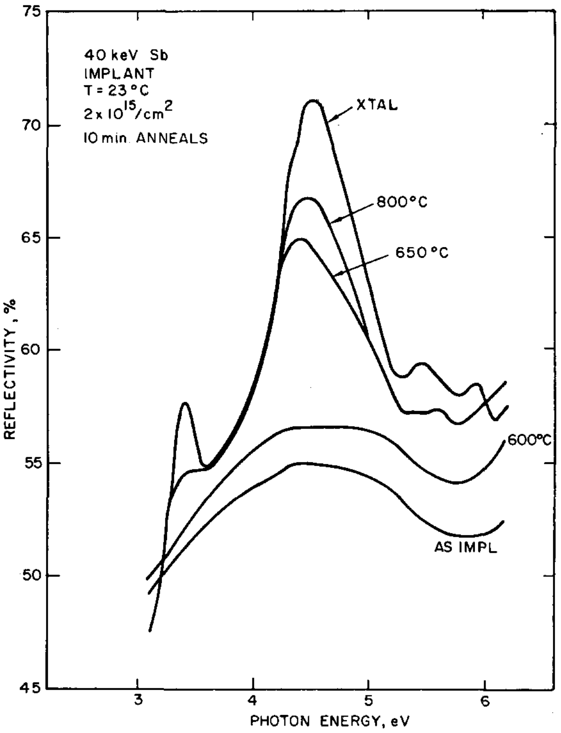

FIG. 6. Reflection spectra in the 3–6.5 eV energy range of a silicon sample implanted at room temperature with 2×10^{15} Sb/cm^2 and subsequently annealed for ten-minute intervals at various temperature up to 800°C.

The material used in this work is specified as follows: 100 Ω-cm, *p*-type, etch polished, float zone, and oriented with the ⟨111⟩ axis of the crystal within about 1° of the sample face.

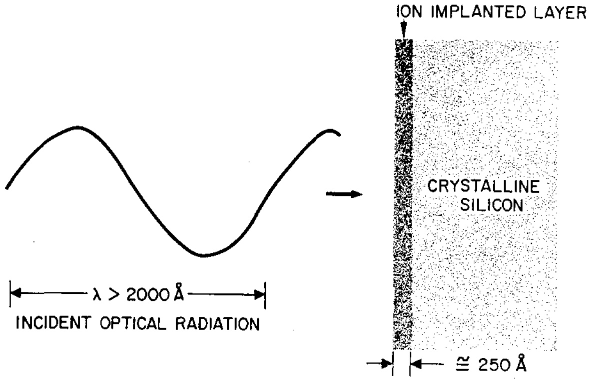

FIG. 7. Schematic representation of an implanted silicon sample as viewed in a plane parallel to the direction of the incident radiation.

DISCUSSION

In examining the extent to which optical reflectivity provides a measure of lattice damage, two questions must be answered. First, what optical characteristics are determined by the reflectivity measurements? Second, what is the relationship between these optical characteristics and the lattice damage induced in crystalline Si by implantation?

To answer the first question, we examine the physical structure of the samples under investigation. Figure 7 illustrates schematically that the samples, as viewed along the incident beam, consist of a damaged layer ~250 Å thick (the range of 40 keV Sb in Si)[7] followed by a substrate of crystalline Si. This geometry (typical for the implantation parameters used here) makes it necessary to consider the effects of light reflected from the underlying crystalline material. If the absorption constant of the damaged layer is greater than 2×10^5 cm^{-1}, we can neglect the light reflected from the underlying crystalline layer since it will be attenuated by more than a factor of *e*. For crystalline Si, this condition is satisfied for photon energies in the 3.2–6.5 eV spectral range.[8] The absorption constant for amorphous Si is not available in this spectral range. However, the data taken by Pulker and Ritter[9] on amorphous Si films in the 1.5–2.5 eV range indicate that the absorption constant of amorphous Si is not very different from the absorption constant of crystalline Si. In addition, the measurements of Phestorf[10] on an Si mirror (probably polycrystalline) in the 2–5 eV range show that the absorption constant for his material was greater than 2×10^5 cm^{-1} for energies between 3.2 and 5 eV (the highest energy for which he reported). These two results support the assumption that the absorption constant is large enough in the 3.2–6.5 eV range to satisfy the condition stated above. Thus, we can neglect the light reflected from the underlying layer and assume that in the 3–6.5 eV spectral range the reflection spectra are characteristic of the damaged layer.

The implanted layer may have many types of disorder (amorphous regions, lattice strain, vacancies, and interstitials), distributed randomly and uniformly throughout the layer. To make the presentation of these ideas more precise, we define a local, but macroscopic, measure of the damage, $D(\mathbf{x})$. For example, $D(\mathbf{x})$ may be taken to be a local structure factor. Although the precise nature of $D(\mathbf{x})$ is unimportant, we can make some general statements about it. The randomness of the damage motivates a description of $D(\mathbf{x})$ in terms of stochastic variables. The correlation length [the statistical property of $D(\mathbf{x})$ which is relevant to a discussion of the optical properties] can be obtained by considering the range of the implanted ions and the corresponding distribution of damage. The range[7] of 40 keV Sb ions in Si is on the order of 250 Å; the range[7] of 15 keV knock-on Si atoms (produced by 40 keV Sb ions) in Si is 180 Å. Thus, the correlation length for $D(\mathbf{x})$ is on the order of 100–200 Å.

The dielectric constant of ion implanted Si differs from that of crystalline Si as a result of lattice disorder. Variations in local density and in crystalline potential lead to modifications of the energy spectrum of allowed electron states and to changes in the form of electronic wavefunctions. Therefore, the dielectric properties of implanted Si are a function of the random variable $D(\mathbf{x})$. The close relationship between the dielectric properties ($\epsilon=\epsilon_1+i\epsilon_2$) and $D(\mathbf{x})$ implies that the fluctuations in ϵ are correlated over distances like the correlation length of the damage (~100–200 Å). This value of the correlation length is smaller than the wavelength of incident optical radiation in Si (>400 Å throughout the 3–6.5 eV spectral range).[11] Thus, optical radiation samples the lattice over distances which are larger than the correlation length. These considerations lead us to postulate that the dielectric properties of the layer are best described by an *average* dielectric constant, $\langle\epsilon(\omega)\rangle$, and that the reflectivity for normal incidence is related to this average dielectric constant by the well-known relation

$$R(\omega)=\left|\frac{1-\langle\epsilon(\omega)\rangle^{1/2}}{1+\langle\epsilon(\omega)\rangle^{1/2}}\right|^2. \tag{1}$$

Detailed calculations performed by Tatarishii and Gerkenshtein[12] and extended by Bassanini *et al.*[13] establish the validity of Eq. (1) in discussing the reflection

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[11] The estimate of the lower bound on the wavelength was made using the value of *n* for crystalline Si obtained by Philipp and Ehrenreich [Phys. Rev. **129**, 1550 (1963)] and the values of *n* reported in Refs. 12 and 13 for more "amorphous-like" materials.

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from the damaged layer. They find that the scalar field in the layer can be separated into two parts: an average field $\bar{\psi}$ satisfying the wave equation

$$\nabla^2\bar{\psi}+(\omega^2/c^2)\epsilon_{\mathrm{eff}}\bar{\psi}=0, \tag{2}$$

and a fluctuating field ϕ satisfying the equation

$$\nabla^2\phi+(\omega^2/c^2)\langle\epsilon\rangle\phi=(\omega^2/c^2)(\langle\epsilon\rangle-\epsilon)\bar{\psi}. \tag{3}$$

In Eq. (2), ϵ_{eff} is the average value of the dielectric constant, renormalized to include the effects of multiple scattering. $\langle\epsilon_{\mathrm{eff}}\rangle$ is given by the expression

$$\bar{\phi}\bar{\phi}^* \cong \frac{4Aa_0{}^3\omega^3\sigma_2{}^2}{r^2\pi c^3\,|\,1+(\epsilon_{\mathrm{eff}})^{1/2}\,|^2\,|\,1+\langle\epsilon\rangle^{1/2}\,|^2\,\mathrm{Im}[(\epsilon_{\mathrm{eff}})^{1/2}+\langle\epsilon\rangle^{1/2}]}, \tag{4}$$

where A is the cross-sectional area of the scattering region, and r is the distance to the observation point from the scattering region. σ_2 is the expectation value of the absolute square of the deviation of the dielectric constant from its average value. In deriving Eq. (5), an incident wave of unit intensity has been assumed. Evaluation of Eq. (5) for $a_0=200$ Å, $\omega/c=2.0\times10^{-3}$ Å, and $\epsilon\sim10$ gives

$$\phi\phi^*\cong10^{-4}(A/r^2)\sigma_2{}^2. \tag{5}$$

For reasonable values of $\sigma_2{}^2$ (e.g., 50) and A/r^2 (e.g., 0.1) the contribution to the total reflected wave due to Rayleigh scattering is small when compared to that due to the specularly reflected wave (e.g., $\phi^*\phi/R<10^{-3}$). Then, we conclude that Eq. (1) gives an accurate representation of the reflectivity of the damaged layer. Consequently, the reflected wave measures the *average* of the dielectric properties over the damaged region with a correction for multiple scattering.

The resolution of the second question is far more complex. A calculation of the optical properties of crystalline Si is difficult. The theory of electronic states of disordered materials is in its infancy; no completely satisfactory theory exists for even the simplest cases. Consequently, it is impossible at the present time to transform any detailed microscopic model of the damaged Si layer into an average dielectric constant and make a detailed comparison with the observed reflectivity. However, it is possible to draw some important conclusions from the experimental data and to analyze their bearing upon the overall model of the lattice damage.

The predominant effect of damage on optical reflectivity is to eliminate the reflectivity peaks associated with the peaks in the joint density of states of crystalline Si. This type of change can result from the relaxation of the direct transition selection rule, a change in the density of states, or a change in the character of the electronic states leading to a variation in the matrix element involved in the transition. (The first and last factors are not independent.) Each of these effects contributes in varying degree to the observed changes.

The variation of the optically effective damage with dose is similar to that of damage observed in He$^+$ backscattering. Both measures of the damage increase with increasing dose until some critical value above which no additional change is observed. With each technique, for lightly implanted samples, noticeable changes in the measure of the damage begin to occur at ~300°C. However, this temperature differs from the temperature range reported by Nelson and Mazey for the disappearance of the black dots observed in electron micrographs. Since Nelson and Mazey[2] do not provide anneal curves for the black dots, we can only speculate as to the meaning of this result. However, we feel this indicates that not all of the damage is associated with the black dots[14] and that additional components of damage (not presently observed in electron microscopy) are observed optically and by He$^+$ backscattering. To settle this point, more complete electron microscopy studies of samples implanted with heavy ions will be necessary.

In the limit of high implanted dose, the optical reflection spectrum of the damaged layer approaches that of a sputtered (amorphous) Si film. The similarity of these reflection spectra suggests that the structure of the heavily damaged layer is similar to that of the amorphous Si film. This observation supports the interpretation of the backscattering and electron microscopy data in terms of the formation of an amorphous layer. The anneal characteristics of the damage observed in the electron microscopy, ion backscattering, and optical reflection spectroscopy are all similar. The onset of annealing occurs at ~625°C.

Optical reflection spectroscopy is a valuable technique to observe a different aspect of damage produced by implantation. Thus, it complements other experimental methods for exploring lattice damage.

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[14] This point is supported by the observation of J. W. Mayer (unpublished manuscript) on the nature of damage in Ge. By comparing ion induced damage with neutron induced damage, he concludes that not all of the damage in low-dose implants is represented by the amorphous regions observed by electron microscopy.