Optical Properties of Heavily Doped Silicon between 1.5 and 4.1 eV

G. E. Jellison, Jr., F. A. Modine, C. W. White, R. F. Wood, and R. T. Young
Solid State Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37830
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The optical constants of heavily doped silicon are determined between 1.5 and 4.1 eV with use of polarization modulation ellipsometry. For photon energies less than 3.4 eV it is found that there is a substantial increase in the optical absorption coefficient for As-doped silicon, but a much smaller increase for B-doped or P-doped silicon. It is believed that this is due to ***d***-electron admixture into the conduction band when the dopant is As.

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The optical properties of silicon have received much attention because of both the technological importance of this material and its interesting characteristics. The indirect gap in Si is 1.1 eV, while the direct gap is 3.4 eV; that is, optical absorption takes place in the pure material via a phonon-assisted transition for photon energies from 1.1 to 3.4 eV, while no phonon is required for photon energies above 3.4 eV. In the early work of Dash and Newman,[1] the optical absorption coefficient (α) of high-purity silicon was measured in the spectral range from 1.1 to 3.1 eV at 77 and 300 K with use of optical transmission. Philipp and Taft[2] used reflectivity data and Kramers-Kronig analysis to determine the index of refraction (n) and extinction coefficient (k) of high-purity Si in the spectral range 1 to 10 eV. Many effects of heavy doping on the optical properties of Si have also been considered. Optical absorption studies of heavily doped Si were performed by Vol'fson and Subashiev[3] in the spectral range from 1.0 to 1.5 eV and by Balkanski, Aziza, and Amzallag[4] in the spectral range from 0.3 to 1.5 eV; at photon energies well below the indirect band gap in Si, free-carrier absorption was found to dominate,[4,5] while for photon energies near the indirect band gap, tailing in α was observed to be a function of doping concentration. Considerable controversy still exists as to the exact nature of the tailing, but this will not be considered here.[6]

Despite the great interest in silicon, heavy-doping effects on the absorption edge near the direct gap have not been studied to date. Such an experiment is difficult with conventional techniques since it is difficult to measure $\alpha > 10^4$ cm^{-1} with use of transmission or $\alpha < 5\times10^5$ cm^{-1} with use of normal-incidence reflectivity. However, with the use of ellipsometry techniques such measurements become possible. Aspnes *et al.*[7] used spectroscopic ellipsometry to examine silicon ion implanted with 10^{16} As/cm^2 at 30 keV as a function of laser annealing power density. This Letter presents data obtained with use of a similar technique [polarization modulation ellipsometry (PME)] as a function of dopant density. In particular, we focus on the absorption coefficient for photon energies below the direct band edge (3.4 eV). It will be shown that α increases dramatically with increased doping in degenerate As-doped Si but that the effect is much less pronounced in degenerate B-doped or P-doped silicon. This effect cannot be explained by present theories of heavy doping; indeed, most theories[6] deal only with photon energies near the indirect gap. To explain the observed data, we will invoke d-electron admixture into the conduction band.

Samples were prepared from single-crystal, nominally p-type (8–12 Ω cm) float-zone–refined, lap-polished silicon. The samples were ion implanted with either 100-keV As, 35-keV B, or 5-keV P ions and laser annealed with ten 1.3 J/cm^2 pulses from a Q-switched ruby laser (pulse width, 20 ns). Several implantation doses were used; the concentrations quoted in this paper will be the volume concentration of the heavily doped surface layer. The resulting impurity concentrations are relatively constant to a depth of 0.3–0.4 μm, where they rapidly go to zero with increasing depth.[8,9] The samples were cleaned and the oxide was removed with a short (30 s) HF treatment, after which the samples were set aside in covered containers for about a week in order that the native oxide thickness stabilizes. The carrier concentrations were determined from Hall-effect measurements. The use of ion implantation followed by laser annealing for sample preparation has several advantages[8,9]: (1) The solubility limit can be exceeded[8,10] to give higher doping densities than have been achieved previously, (2) the resulting near-surface region is free of electrically active defects (down to 10 Å), (3) the surface is optically flat,[7] and (4) the doping con-

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centration profile is more nearly an abrupt junction than that obtained by diffusion.[11]

Rutherford backscattering (RBS) experiments were performed on the two most heavily doped As-implanted, laser-annealed samples (3.2×10^{21} and 4.6×10^{20} As/cm^3). The results indicated that the samples were nearly perfect single crystals (low minimum yields), and that the percent substitutionality was 95.5% for the 3.2×10^{21}-As/cm^3 sample and 99% for the 4.6×10^{20}-As/cm^3 sample. However, it was found that there was an excess of oxygen on the surface of these samples (3.7×10^{16} O/cm^2 for the 3.2×10^{21}-As/cm^3 sample and 1.8×10^{16} O/cm^2 for the 4.6×10^{20}-As/cm^3 sample, compared to $\sim10^{16}$ O/cm^2 for undoped Si).

The ellipsometry spectra were taken with a modified version of the polarization modulation ellipsometer (PME) described by Jasperson and Schnatterly.[12] Such a configuration yields the quantities N and S, which are related to the normal ellipsometry parameters ψ and Δ by the expressions $N=\cos(2\psi)$ and $S=\sin(2\psi)\sin\Delta$.

The transformation of ψ and Δ to n and k (or α) data (recall $\alpha=4\pi k/\lambda$) was performed with the aid of a computer. A two-boundary model was employed (air-oxide-conductor), where the top and bottom media were considered semi-infinite. The solution required numerical solution, which was performed with use of a two-dimensional analog of Newton's method. It was assumed that the oxide had an n of 1.46. The oxide thickness of the pure samples was measured with use of a Gaertner L117 nulling ellipsometer with use of known values[1,2] of n and k at $\lambda=632.8$ nm. This oxide thickness (24 Å) was then used for all calculations and all samples except the two most heavily As-doped samples, where the oxide thickness was taken from the surface oxygen concentration determined by RBS, assuming that the oxide is SiO_2 (84 and 42 Å, respectively). Since it appears that this excess oxide thickness is As related, and since the oxide thickness of the 4.6×10^{20}-As/cm^3 sample was only 18 Å greater than the undoped sample, the other samples *cannot* have had a much larger oxide thickness than 24 Å, since this would lead to a negative k, which is impossible. The resultant calculated spectra of n, k, and α are shown in Figs. 1–3. Clearly this model is appropriate for the undoped samples and the heavily doped samples, provided that the product $\alpha X(0.35\ \mu m)>2$ (i.e., $\alpha>6\times10^4$ cm^{-1}, in which case any light reflected off the heavily-doped-Si–pure-Si boundary will be absorbed before it could be detected). Incorporation of a third boundary (heavily-doped-Si–pure-Si interface) reveals that the two-layer approximation is valid above 2 eV.

The error analysis revealed that n was sensitive to ψ and the angle of incidence, while k (or α) was mainly sensitive to Δ and the oxide thickness. Figure 1 shows representative confidence limits for n and k, respectively. Most of the systematic error results in a monotonic increase or decrease of the n or k curve as a whole; spectral features are real, even if their heights are less than the error estimates.

Figure 1 shows n and k for various concentrations of arsenic. The open circles and filled circles in Figs. 1 and 2 represent the data published for pure Si by Dash and Newman[1] and by Philipp and Taft,[2] respectively. Since n and k are Kramers-Kronig pairs, they are not independent; indeed one would expect to see the peak in n visible in Fig. 1 at the point of maximum dk/dE. Also, the peak height of n decreases with in-

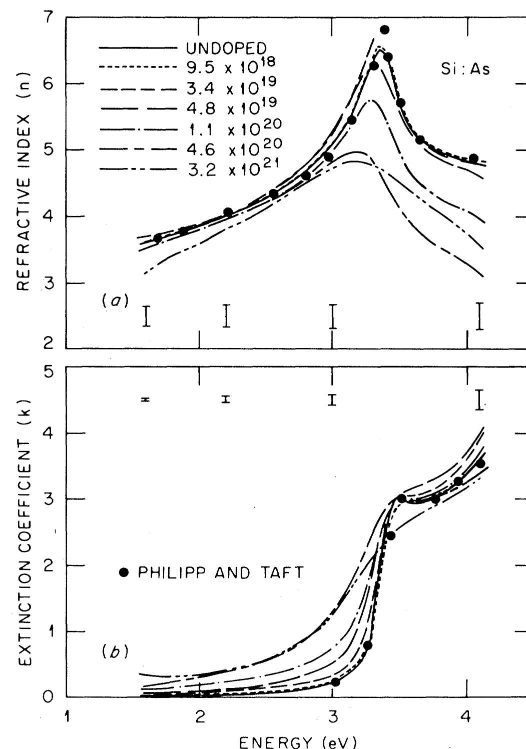

FIG. 1. (a) Index of refraction, n, and (b) extinction coefficient k vs photon energy for several As concentrations (cm^{-3}) in silicon. The error bars show typical confidence limits at the specified energy. Data shown by the filled circles are representative data from Ref. 2.

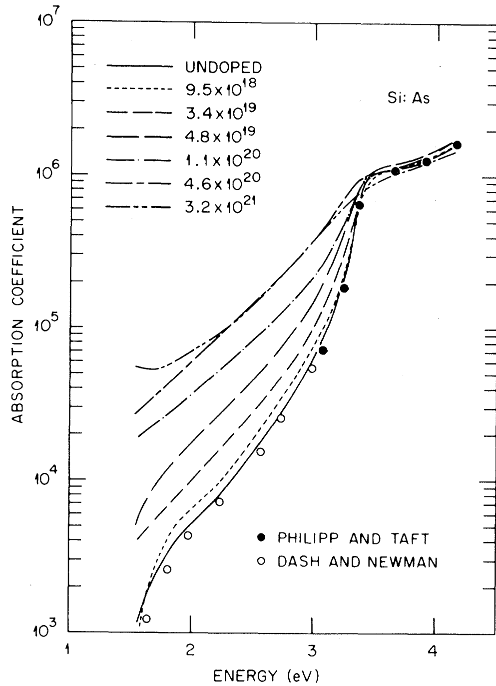

FIG. 2. Absorption coefficient vs photon energy for several As concentrations in silicon. Data shown by the open circles and filled circles are representative data from Refs. 1 and 2, respectively.

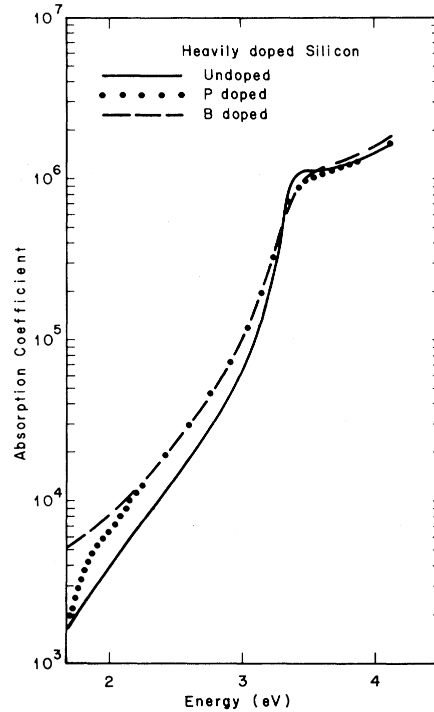

FIG. 3. Absorption coefficient vs photon energy for B-doped silicon (3×10^{20} B/cm), and P-doped silicon (1.2×10^{20} P/cm^3).

creasing dopant concentration, reflecting the decreased maximum of dk/dE. Note that the undoped sample exhibits a small peak in k at 3.4 eV (direct gap). When the degenerate limit is exceeded ($>5\times 10^{18}$ As/cm^3), this peak becomes rounded off. [A heavily doped but nondegenerate sample ($\sim 4\times 10^{16}$ As/cm^3) showed the same structure as the pure sample.] The most pronounced heavy-doping effect in As-doped Si is shown in Fig. 2: For all samples other than the 3.2×10^{21}-As/cm^2 sample, it is empirically found that

$$\alpha(h\nu, N) = \alpha_0(h\nu) + KN\exp[(h\nu - 3.4\text{ eV})/E_0], \quad (1)$$

where $\alpha_0(h\nu)$ is the α of undoped Si, and N is the doping concentration, and where $K = 1.8\times 10^{-15}$ cm^3 and $E_0 = 0.58$ eV. The most heavily doped sample exhibits a rounding of the 3.4-eV shoulder in k and α [Figs. 1(b) and 2] and a broadening of the peak in n [Fig. 1(a)]; this is probably due to the fact that this sample contains 6-at.% As, and can no longer be considered a doped Si crystal but rather an alloy. In contrast to the large effect observed in As-doped Si, the effect is relatively small in B-doped (p-type) or P-doped (n-type) Si, shown in Fig. 3. Quantum efficiency measurements of solar cells fabricated with a heavily doped As emitter show little if any decrease in blue response compared with cells fabricated with P- or B-doped emitters. Also, a piece of pure Si was laser annealed and its ellipsometry spectra were taken; no difference was observed between the ellipsometry spectra of this sample and an undoped sample. Therefore this absorption process must be an electron-hole pair creation process and is not a function of the laser-annealing process.

The correct interpretation of these results is not obvious and will probably require a significant theoretical effort to arrive at a completely satisfactory explanation. However, a few significant observations can be made and a plausible interpretation proposed. Clearly we can eliminate processes which depend upon the type of dopant (n or p), interband processes, and phonon perturbations (since there is no obvious correlation with the mass of the dopants). Moreover, since As has a close lattice match (in terms of covalent radii) with Si we do not expect large lattice

strains to occur for As-doped Si, even at high doping levels. Therefore, we conclude that the large effects observed for As-doped samples are due to the presence of the d electrons in As. The As impurities will introduce either true localized levels or resonance states lying well below the top of the valence band ($\Gamma_{25'}$) at the Brillouin-zone center. Orthogonality and screening effects due to the d electrons may influence the *energy levels* of higher-lying states (in both the valence and conduction bands) but it will probably not alter greatly the joint density of states. It is much more likely that the presence of the d orbitals produces a rapid increase in many matrix elements of the dipole operator which vanish in the perfect crystal; the inclusion of d orbitals in the basis set introduces the possibility that strong $p \to d$ transitions can occur *on the same atom* where $\langle p|r|d\rangle$ is expected to be large. Thus, although the coefficient of the d orbitals may be rather small, the strength of the matrix elements and the fact that there are ten d electrons will lead to a rapid increase in α as the concentration of As increases. In B- and P-doped Si the enhancement of α will not be nearly so great because the outer s and p orbitals of B and P do not differ significantly from their counterparts in the host Si lattice.

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Dynamic Monte Carlo Renormalization Group

Jan Tobochnik
Department of Mathematics, Rutgers University, New Brunswick, New Jersey 08903

and

Sanjoy Sarker and Robert Cordery
Serin Physics Laboratory, Rutgers University, Piscataway, New Jersey 08854

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A novel dynamic Monte Carlo renormalization-group method is devised. Application to the kinetic Ising model in one dimension yields a value of z, the dynamic critical exponent, which is in excellent agreement with the exact result. In two dimensions we find $z = 2.22 \pm 0.13$ with the most probable value $z = 2.17$.

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Recently the Monte Carlo and renormalization-group methods have been combined to analyze a number of problems in critical phenomena.[1-4] In this Letter we extend the procedure used in Refs. 3 and 4 to dynamic critical behavior and apply our method to the computation of the dynamic expo-

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