Optical absorption in heavily doped silicon

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Optical-absorption measurements at 300 and 4 K on a series of heavily doped Si:As and Si:B samples are reported. The interband contribution is isolated and confronted with the predictions of an electron-gas calculation. Disorder effects are observed and impurity-derived states are found to play a significant role, invalidating the electron-gas model at concentrations lower than 10^{20} cm^{-3}. The gap shrinkage follows a critical behavior, going to zero at the insulator-metal transition and varying approximately linearly with concentration at high doping. The discrepancy between device-based and optical determinations of the gap shrinkage is discussed.

I. INTRODUCTION

The ways in which heavy doping modifies the electronic properties of a semiconductor are commonly described in terms of band tailing and of a reduction of the fundamental energy gap. Band tailing is a result of the random nature of the impurity distribution and the gap shrinkage represents the self-energy of the various interactions of the charge carriers. The theoretical evaluation of the gap shrinkage is still in a controversial stage[1] and a recent review[2] has noted the large discrepancies between the experimental values of the gap shrinkage of heavily doped silicon deduced from optical properties with those obtained from transistor measurements.

In view of its technological importance, heavily doped silicon has been the subject of a surprisingly small number of optical studies. Apparently only two papers[3,4] have dealt with the effects of doping on optical absorption at the fundamental gap, reaching opposite conclusions with regard to the contribution of zero-phonon transitions. This paper presents optical-absorption data for a series of heavily doped silicon samples doped with As and B. The measurements have been carried out at room temperature and at 4 K. In order to extract the gap shrinkage from the absorption spectrum, the interband contribution has been isolated and compared with a model for the density of electronic states. A nearly homogeneous, weakly interacting electron-gas model has been used for this purpose. It has the merit of being widely used and tractable. Heavily doped silicon is often considered to be a good test of electron-gas calculations and such calculations have been described in relation with the metal-insulator transition.[5] The electron-gas model predicts that mass renormalization is small and that heavy doping causes a nearly rigid movement of the majority band into the forbidden gap.

The analysis of the low-temperature interband absorption data yields for the gap shrinkage Σ as a function of the impurity concentration N_I:

$$\Sigma \cong E_0 \left(\frac{N_I - N_C}{N_C} \right)^{\gamma}, \quad N_I \geq N_C \ , \tag{1}$$

where for Si:As $E_0 \cong 14$ meV, $N_C \cong 6\times10^{18}$ cm^{-3} is close to the concentration of the metal-insulator transition, and $\gamma \cong 0.8$. For Si:B, $E_0 \cong 9$ meV, $N_C \cong 5\times10^{18}$ cm^{-3}, and $\gamma \cong 0.8$. At room temperature, the high-doping values of Σ are slightly smaller and the cutoff at N_c is not as sharp.

The form (1) of the doping dependence of the gap shrinkage, symptomatic of a critical phenomenon, is in striking disagreement with self-energy estimations for a weakly interacting electron gas, which is usually dominated by an exchange and/or electron-impurity term of the form

$$\Sigma \propto N_I^{1/3}, \tag{2}$$

It will be shown, furthermore, that the shape of the absorption edge is not accurately described by a simple gas model, mostly because tailing at the minority band edge is neglected. The failure of the electron-gas model in its prediction of both the absorption line shape and the gap shrinkage casts a doubt on the accuracy of Eq. (1). We have checked that the inclusion of disorder effects in the form of band tails results in an absorption line shape in much better agreement with experiment.

II. EXPERIMENTAL

Optical windows of a diameter of 5 mm were milled with diamond pastes into 0.5-mm bulk-doped wafers. The final thickness of the windows ranged from 7 to 400 μm. The thickness was measured mechanically and, whenever possible, was confirmed by measurement of transmission interference fringes.

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To check for damage that might possibly be induced by the milling process, the luminescence of bound multiexciton complexes[6] was measured at 2.4 K on a sample doped with no more that 10^{15} cm^{-3} donors. The luminescence of milled and virgin areas showed no significant differences. The samples were mounted on the cold finger of a helium cryostat and optical transmission was measured by the sample-in, sample-out technique at 300 K and at a temperature close to 4 K with 0.3-m grating monochromator. The lead sulfide detector was mounted 30 mm behind the sample. The absorption coefficent α was obtained from the transmission coefficient T by inverting the relation

$$T=\frac{(1-R)^2\exp(-\alpha d)}{1-R^2\exp(-2\alpha d)}\ , \tag{3}$$

where d is the sample thickness and R is the reflection coefficient of a semi-infinite sample. Measurements of R at room temperature showed only minor variations with doping in the energy range of interband transitions. It was found sufficient to use the reflection coefficient of pure silicon in inverting relation (3). This small dependence of R on doping also justifies the decomposition of α into a sum of independent contributions which will be described below. The net impurity concentration $|N_D-N_A|$ was determined from the room-temperature conductivity using the standard curves of Sze and Irvin.[7]

For As-doped samples, the room-temperature, far-infrared reflectivity could be fitted with a Drude law. A satisfactory fit was obtained below 0.25 eV using values of the free-carrier concentration that agreed well with the impurity concentration deduced from the conductivity measurements. At higher photon energies, inter-conducton-band transitions become important. These are direct transitions between the two conduction bands that cross at the X point of the Brillouin zone. Such transitions are forbidden only on the Γ-X axis. The first experimental observation of these transitions was reported by Spitzer and Fan.[8] They give rise to a broad absorption band peaked around 0.54 eV and extending to the indirect gap at high doping.[4] At low doping, the shape and intensity of this inter-conduction-band feature could be matched accurately on the basis of matrix elements calaculated by Baldereschi.[9]

For B-doped samples, the far-infrared reflectivity cannot be fitted with a Drude law because of the presence of inter-valence-band transitions.[10] The energy of the reflectivity minima agreed well with the results of Lambert.[11]

III. RESULTS

The absorption coefficient of As- and B-doped samples is presented in Figs. 1 and 2. Each curve combines the measurements of several samples cut out of a single wafer. The present results for undoped silicon agree well with the data of MacFarlane *et al.*[12] The three most heavily doped boron samples do not show a smooth relation between doping and free-carrier absorption. The excessive free-carrier absorption in the samples with 70 and 120 × 10^{18} cm^{-3} B

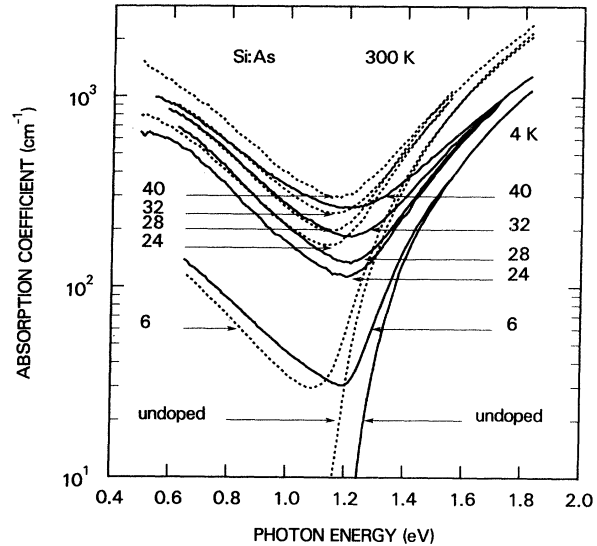

FIG. 1. Optical absorption coefficient vs photon energy for Si:As at 300 and 4 K. The curves are labeled by their net donor concentration divided by 10^{18} cm^{-3}.

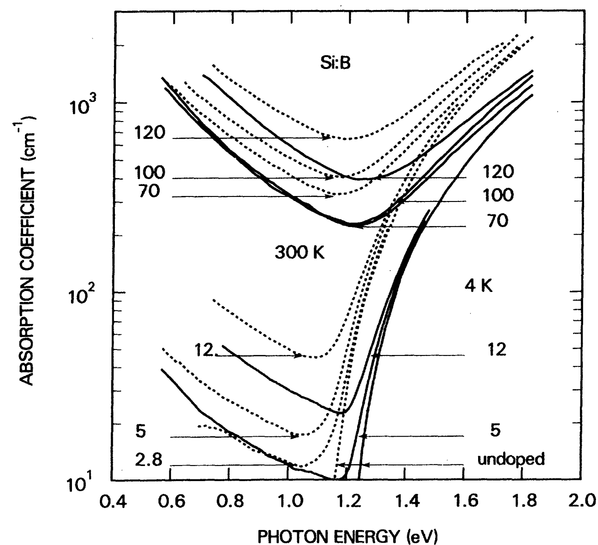

FIG. 2. Optical absorption coefficient vs photon energy for Si:B at 300 and 4 K. The curves are labeled by their net acceptor concentration divided by 10^{18} cm^{-3}.

suggests that these samples are partly compensated. Below 1.0 eV, the absorption curves have been fitted with a power law

$$\alpha = C(\hbar\omega)^{-\delta} \ , \qquad (4)$$

A Drude-like free-carrier absorption implies $\delta = 2$, which indeed provides a good fit for all B samples at 300 K and also at 4 K, except for the three most highly doped samples for which $\delta = 2.4$ was used. For As-doped samples, inter-conduction-band absorption is the dominant process below the indirect gap and its high-energy tail can be fitted with values of δ ranging from 2.4 to 3.1.

Good fits could be obtained over an energy range of at least 0.25 eV. The high-energy extrapolation of these fits was then subtracted from the total absorption coefficient, and the remaining absorption is assumed to reflect valence-to-conduction-band transitions only. In Figs. 3 and 4, the square root of this absorption is plotted as a function of photon energy. It was checked that the result of this subtraction procedure was rather insensitive to the analytic form of the expression chosen for the fit of the low-energy absorption.

Indirect interband transitions normally require phonon participation. When impurities are present, however, zero-phonon transitions are also possible. Previous results[3,4] differ markedly as to the importance of zero-phonon transitions in heavily doped silicon. According to one group of authors,[4] zero-phonon interband absorption is the dominant process in heavily doped P samples, causing a 100% increase in the slope of the absorption coefficient for a donor

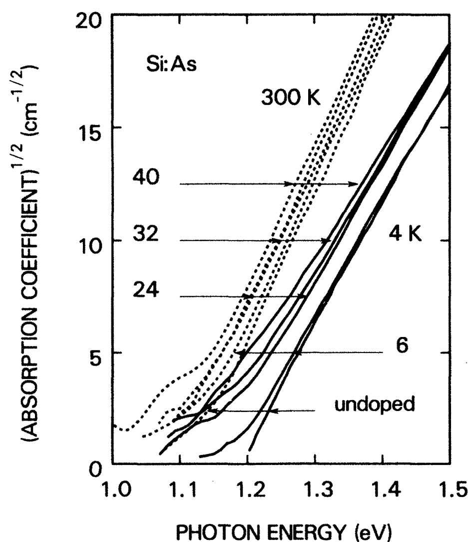

FIG. 3. Square root of the absorption coefficient vs photon energy for valence-to-conduction-band transitions in Si:As. Same samples as in Fig. 1.

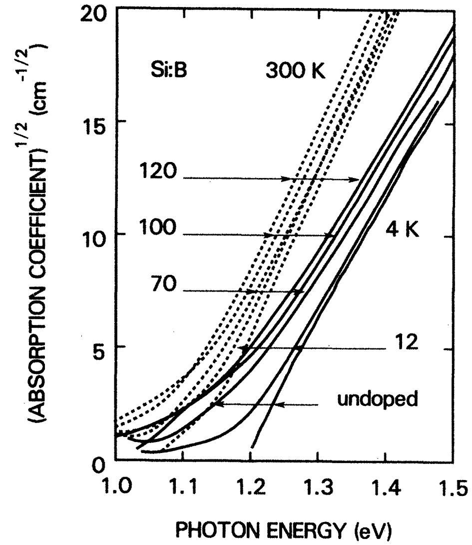

FIG. 4. Square root of the absorption coefficient vs photon energy for valence-to-conduction-band transitions in Si:B. Same samples as in Fig. 2.

concentration of 10^{19} cm^{-3}. From bound-exciton luminescence, it is known[13,14] that the zero-phonon recombination probability is larger for As than for P, and the smallest for B. One would therefore expect zero-phonon absorption to be especially important in As-doped samples. The present results, in agreement with Vol'fson's,[3] show no visible increase of the absorption slope with doping. This is understandable if one considers that the conduction-band states which are most strongly influenced by the impurity potentials are those at the bottom of the band. Since they are also occupied, they should manifest themselves in the luminescence rather than in the absorption spectrum.

The simplest model devised to describe the electronic states of a heavily doped semiconductor is the weakly interacting electron-gas model that corresponds to the high-density limit. In this model, the impurities are assumed to be fully ionized and the impurity charges are smeared into a uniform jellium. Potential fluctuations resulting from the random distribution of impurities are ignored. Mass renormalization of the particles is found to be small[1] and the predominant effect of the interactions is a shift of the majority band of the semiconductor by an amount Σ, the shrinkage of the energy gap. It is then a simple matter to describe how heavy doping affects the absorption edge of a semiconductor: The absorption coefficient of a pure semiconductor for indirect transitions in which a phonon of energy $\hbar\omega_s$ is emitted can be written as[4]

$$\alpha_o = A^2(1+n_s)\,(\hbar\omega - E_g - \hbar\omega_s)^2 \ , \qquad (5)$$

where $\hbar\omega$ is the photon energy, $E_g = E_{g0}$, the indirect gap of the pure semiconductor, n_s is the occupation number for the phonon $\hbar\omega_s$, and $(\hbar\omega - E_g - \hbar\omega_s)$ must be positive. In a doped sample, the absorption edge is modified because of the smaller gap $E_g = E_{g0} - \Sigma$ and because the bottom of the majority band is occupied. The absorption coefficient is given by

$$\alpha = \alpha_0 \frac{8}{\pi} \int_0^1 \frac{x^{1/2}(1-x)^{1/2} dx}{1 + \exp \frac{E_F - x(\hbar\omega - E_g - \hbar\omega_s)}{kT}} , \quad (6)$$

where E_F is the Fermi energy. At 0 K, the absorption edge is shifted by $E_F - \Sigma$, and at all temperatures the absorption slope is higher in a degenerate sample than in an undoped sample.[15] The expected slope increase is not observed in the data of Figs. 3 and 4 because the absorption edge is smeared out by the potential fluctuations associated with the random distribution of impurities.

Casey and Stern,[16] in their analysis of the optical properties of heavily doped GaAs, combined the results of two important theoretical papers[17,18] on disorder effects in semiconductors. In both papers, the electrons interact with the impurities through screened Coulomb potentials and Gaussian statistics are assumed, implying that the screening length is much larger than the mean interimpurity distance r_0 given by

$$\frac{4\pi}{3} r_0^3 N_I = 1 . \quad (7)$$

In uncompensated silicon at or below room temperature, however, both the Debye and the Thomas-Fermi screening lengths turn out to be smaller than r_0. It has been pointed out[1,18] that this is contrary to the assumption of a weakly perturbed electron gas. In order to preserve the convenience of screened Coulomb potentials, Heinrichs's[19] proposal for the screening length λ was adopted:

$$\lambda = r_0 . \quad (8)$$

Then r_0 is also the autocorrelation length of the potentional fluctuations.[18] To evaluate the potential at a point P in the crystal, the contributions from impurities inside and outside a sphere radius r_0 centered at P are treated separately. The fluctuations from impurities outside the sphere can be considered Gaussian. Inside the sphere, the number of impurities follows a Poisson distribution, and their contribution to the potential P was taken to be the value of the screened impurity potentials averaged over the volume of the sphere. The variance σ of this skewed potential fluctuation distribution was found to be

$$\sigma \cong \frac{e^2}{\epsilon r_0} , \quad (9)$$

where e is the electron charge and ϵ the static dielectric constant. σ therefore varies like $N_I^{1/3}$ and reaches 90 meV at a concentration of 10^{20} cm^{-3} impurities. The crystal-averaged densities of states for the valence and conduction bands were obtained by convolution with the potential distribution. Note that most of the tail states, located within about σ of the unperturbed band edge, are not localized. This semiclassical description of disorder effects is not expected to give a true picture of the density of states at the bottom of the majority band to which, however, the interband absorption spectrum is not sensitive.

The joint density of crystal-averaged valence and conduction bands was then substituted in the expression (6) for indirect interband absorption. Equation (6) was further modified to include both emission and absorption of a TO phonon of 58 meV and was evaluated numerically. The gap was shifted in order to provide the best fit with the experimental data between 20 and 300 cm^{-1}. Figure 5 demonstrates that the inclusion of disorder leads to a much better fit of the experimental line shape. It is an indication that the present treatment of potential fluctuations gives a satisfactory account of the tailing of the minority band.

The resulting values of the gap shrinkage are collected in Fig. 6. The same procedure has been applied to the absorption curves given by Vol'fson.[3] The results give values of Σ systematically smaller than Balkanski's[4] for impurity concentrations lower than 5×10^{19} cm^{-3}. No gap shrinkage could be

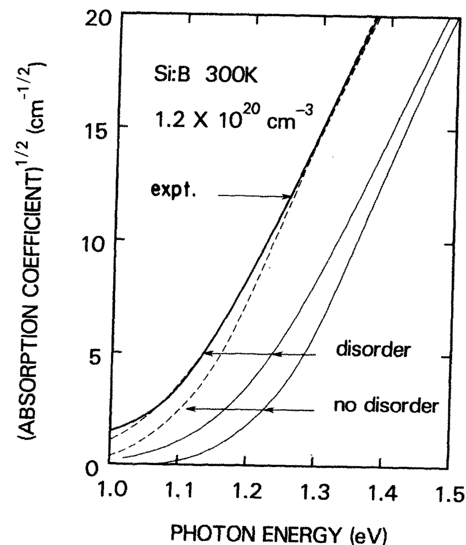

FIG. 5. Example of calculated interband absorption spectra and fitting of the gap shrinkage Σ. The curve calculated without disorder effects is plotted for $\Sigma = 0$ (full curve) and 122 meV (dashed), the curve including disorder is plotted for $\Sigma = 0$ and 102 meV.

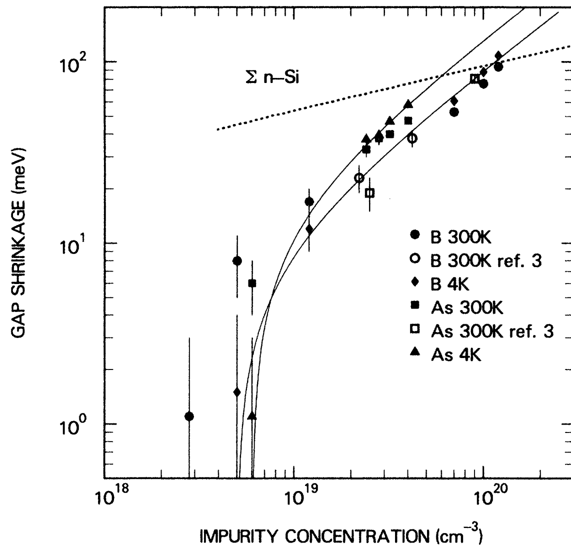

FIG. 6. Gap shrinkage vs doping concentration for Si:As and Si:B. The dashed line is the self-energy from the electron-gas calculation for n–Si described in the text. The solid lines are the plots of Eq. (1).

resolved in samples containing fewer than 3×10^{18}-cm^{-3} impurities. The value of Σ drops sharply as the impurity concentration decreases to about 6×10^{18} cm^{-3} and this is reflected in the proposed doping dependence of Σ given in Eq. (1). It should be noted that the value of the gap shrinkage deduced from absorption measurements depends strongly on the assumed value of the Fermi energy. In the present case, E_F was calculated with density-of-states masses given by Barber,[20] thus taking into account nonparabolicity and/or the complex nature of the majority bands. The results agree quite well with those of Vol'fson.[3] The inclusion of potential fluctuations lowers the calculated Fermi energy by about 10% or, roughly, 10 meV at 1×10^{20}-cm^{-3} impurities.

Because of minority-band tailing, the position of the Fermi level cannot be resolved in the absorption spectra even at low temperatures and therefore the calculated value of E_F cannot be checked. For the samples of Figs. 3 and 4, the Burstein shift of the absorption at $\alpha\cong100$ cm^{-1} amounts to about $E_F/2$ if parabolic bands are assumed. This implies that an error ΔE for E_F results in an error $\Delta E/2$ for the value of Σ. The largest source of error in the evaluation of Σ lies with the extrapolation of a simple high-density model to the low-doping range. Below the insulator-metal transition, impurities are known to extract bound states from the majority-band continuum. There are reasons to believe that this is also true up to a doping concentration of about $10\times N_c$.[21] It could thus be argued that the value of E_F is smaller that calculated and that Σ is smaller than plotted in Fig. 6. In the absence of a satisfactory model for the densities of states in this doping range, such effects cannot, however, be discussed in quantitative terms.

In order to check the validity range of the high-doping model, the result of an electron-gas calculation of Σ for n–Si is also plotted in Fig. 6. First, the total energy was computed, including the exchange energy for six anisotropic valleys,[22] the correlation energy obtained by Rose *et al.*,[23] and the electron-donor interaction calculated as a second-order perturbation with a Lindhard dielectric function.[24] Then the chemical potential μ was derived and Σ was taken as $E_{F0}-\mu$, where E_{F0} is the Fermi energy of the noninteracting gas. This result is typical of electron-gas calculations, and the inclusion of electron-hole terms[1,2] would shift Σ further upwards in Fig. 6. Comparison of the calculated value of Σ with the experimental results leads to the conclusion that the electron-gas model is valid only at impurity concentrations larger than 10^{20} cm^{-3}, beyond the solubility limit of most dopants. To put it in other terms, the electron-gas model seems to be valid in silicon when $\Sigma>2$ Ry, where Ry is the impurity Rydberg. The concentration range covered in Fig. 6 appears to correspond to a transition regime between the high-doping limit of the nearly homogeneous, weakly interacting, electron gas and the low-doping limit in which the charge carriers are strongly coupled to the impurities. One can suspect that disorder effects make an essential contribution to the surprisingly large width of this transition, which is often described as the merging of the impurity band into the majority band. It is not entirely obvious why the gap shrinkage should go to zero at a concentration so close to the metal-impurity transition. This transition is often described as the coalescence of two impurity bands, involving electronic states below the edge of the majority band.[21] The onsent of an optical gap shrinkage at nearly the same concentration signals the simultaneous appearance of many-body effects associated with nearly free effective-mass carriers and tends to support Fritzche's[21] contention that, at the insulator-metal transition, the majority band is starting to mix into the impurity band.

Electronic device measurements, although of a very different nature, provide complementary information on the density of states of heavily doped silicon. For the sake of clarity, n-type silicon will be considered. Typical device measurements[25,26] yield p, the equilibrium minority-carrier concentration. The results are usually presented in the form of the impurity-concentration dependence of the np product, in which the reasonable approximation $n=N_D-N_A$ has been made. Now it is true that a shrinkage of the gap Σ causes an increase of np by a factor of $\exp(\Sigma/kT)$. However, the converse is not true because np is sensitive to changes in the densities of states at the band edges. For example, in a sample

where Boltzmann statistics apply, potential fluctuations of variance σ will increase np by a factor $\exp(\sigma/kT)^2$ (about 2 for 10^{18} cm^{-3} impurities). With the help of an adequate model for the density of states in the tail of the minority band, the measurements of p yields the position of the Fermi level with respect to the unperturbed valence-band edge. The device data indicate that p remains nearly constant throughout the heavy-doping range, or in other words that the Fermi level is clamped at about 1.00 eV above the top of the unperturbed valence band if one assumes a band tail of width σ. The so-called discrepancy between optical and device measurements of the gap shrinkage simply reflects the inadequacy of the model used for the densities of states, and in particular the device measurements confirm the result that the Fermi level is positioned lower in the gap than predicted by the electron-gas model. This result, as well as the critical behavior of the gap shrinkage, are evidence that electron-impurity interactions in heavily doped silicon are strong and beyond the powers of perturbation theory.

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