Photoabsorption Cross Section for Silicon Doped with Indium†

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The photo-ionization cross section for indium as an acceptor in a silicon lattice has been deduced from optical transmission coupled with wide-range Hall-effect measurements. The normalized energy dependence observed in our samples agrees well with results previously reported, but the cross section we report has a maximum value of $\sigma_{max} = 3.3 \times 10^{-17}$ cm^2 at $h\nu = 0.3$ eV. This is several times smaller than has traditionally been believed. The effective field ratio necessary to fit our data with a quantum-defect model agrees well with the local field predicted for a cavity in a dielectric medium. The general form of the energy dependence of the cross section accords with a quantum-defect model, but we do find that the behavior for energies above 0.4 eV is dependent on the doping and degree of compensation in the crystal.

INTRODUCTION

In order to better understand the behavior of deep impurity centers in semiconductors, we have made conductivity, Hall-effect, photoconductivity, optical absorption, and lifetime measurements on crystals of In-doped Si with a wide range of impurity content. We were especially surprised at the seemingly small photo-ionization cross section σ_I obtained from our first measurements, until we discovered[1] that previous optical work[2-6] had relied on room-temperature conductivity measurements for an estimate of the neutral acceptor density $(N_a - N_d)$. This procedure we find underestimates $(N_a - N_d)$, and hence magnifies σ_I.

RESULTS

Figure 1 shows curves of p_0 vs $1000/T$ for three of our Si : In samples, as determined from Hall-effect measurements. For all of our samples we made Hall-effect and conductivity measurements over the temperature range $75 < T < 400$ °K, using a 4000-G field and arbitrarily setting the Hall factor as unity.[7] Thus we assumed that

$$p_0 = 1/eR_H \quad . \tag{1}$$

In Fig. 1, crystal 248 is moderately doped and weakly compensated, crystal 250 is strongly doped and strongly compensated, and crystal 260 is strongly doped and weakly compensated. Note that in each case, $p_0(300\ ^\circ\mathrm{K}) \leq 25\%$ of $(N_a - N_d)$. We find that for any crystal doped strongly enough to produce noticeable absorption, that this same result holds, i. e., $p_0(300\ ^\circ\mathrm{K}) \approx 0.2(N_a - N_d)$.

The solid curves in Figs. 1 and 2 represent computer fits to the mass-action equation

$$\frac{p_0(p_0 + N_d)}{N_a - N_d - p_0} = \frac{N_v}{\beta} e^{-E_a/kT} = 3.6 \times 10^{14} T^{3/2} e^{-E_a/kT} \tag{2}$$

for values of p_0 obtained from Hall measurements. Figure 2 shows the ability of the computer to differentiate between the impurity densities of samples taken from different ends of the same crystal. Sample 261SB was cut from the seed end of the crystal and sample 261T01 was cut from the tail end. Note that even though the measured values of p_0 differ only very slightly, the computer shows the tail end to be more heavily doped. It should be recognized that the high-temperature extrapolation in Figs. 1 and 2 depends on the fidelity of the lower-temperature data to Eq. (2), via our computer least-squares fit. This looks to be a rather large extrapolation, but the reliability of this procedure in connection with the samples of Fig. 2 will be seen in Fig. 4.

Our optical transmission measurements were made at 77 °K on a Perkin Elmer model No. 112 spectrometer in an enclosed environment purged with dry N_2. This temperature, of course, does not give good resolution of excitation lines,[8] but is adequate for observing the shape of the photo-ionization continuum.

An elementary analysis of impurity states in semiconductor crystals treats an impurity as a hydrogenlike center with a ground-state energy and a set of excited states. Such an analysis yields a reasonable approximation to the behavior of acceptor impurities with shallow ground states, but it is well known[5,6] that for silicon the indium impurity with its deep-lying ground state is very poorly represented by the hydrogenic model. Early experimental evidence of this fact was obtained by Burstein *et al.*[3,4] and by Newman.[2] Their results (normalized to our maximum) are shown in Fig. 3, compared with two of our samples. Note that the peak absorption occurs at $h\nu \approx 0.3$ eV $\approx 2E_a$, rather than at E_a as would be ex-

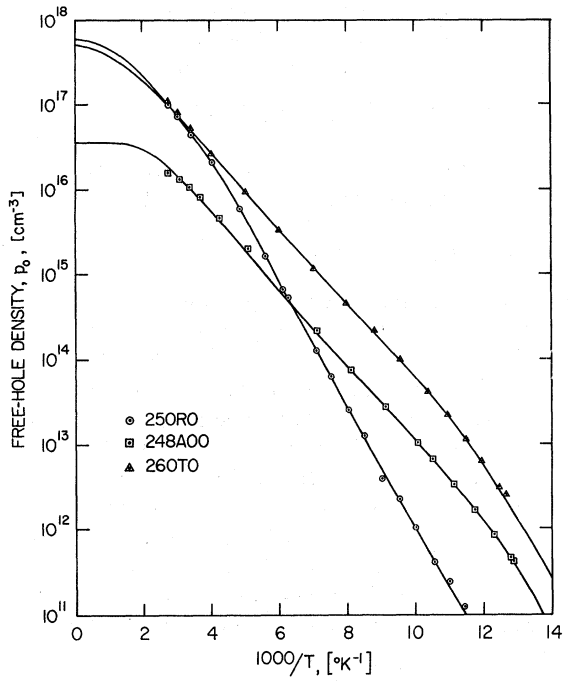

FIG. 1. Free-hole density (deduced from Hall data) vs reciprocal temperature for samples 248A00, 250R0, and 260T0. A computer fit to Eq. (2) requires that $N_a = 3.8\times10^{16}$ cm^{-3} and $N_d = 8\times10^{11}$ cm^{-3} for sample 248A00. For sample 250R0, the corresponding numbers are $N_a = 5.0\times10^{17}$ cm^{-3} and $N_d = 6\times10^{16}$ cm^{-3}; and for sample 260T0, $N_a = 5.8\times10^{17}$ cm^{-3} and $N_d = 9.0\times10^{12}$ cm^{-3}.

pected from the hydrogenic model.[4]

The samples of Fig. 3 represent the maximum and minimum in the rate of high-energy falloff in the data we have taken. We present this data to indicate that the shape of the upper continuum part of the spectrum does not appear to be unique. It is significant to note, however, that both of our curves here share a maximum of $\sigma_{max} \approx 3.3\times10^{-17}$ cm^2, in contrast to the value $\sigma_{max} \approx 2\times10^{-16}$ cm^2 previously accepted.[4–6]

An additional feature of the data for sample 248A00 in Fig. 3 is the structure appearing at lower photon energies. This structure for sample 248A00 is shown on an expanded horizontal scale in the inset, once again with sample 250R0 for comparison. We should note at once that the 140-meV "silicon-oxygen" band is very prominent for sample 248A00, since it was necessary to make this sample very thick (0.5 cm) for absorption purposes to compensate for the small indium density ($< 4\times10^{16}$ cm^{-3}) in this crystal. For the prominent bands at 163 and 180 meV we have no ready explanation, though it is plausible to assume that oxygen or other electrically inactive impurities are involved here. These bands do *not* correspond with transitions from indium in the ground state to excited states associated with the split-off band,[8] and of course our 77 °K observation temperature should not permit us to resolve those transitions. We may note in passing that sample 250R0 shows very weak signs of additional absorption at 163 and 180 meV, and of additional transmissivity at 155 meV.

Figure 4 shows curves of σ_I for samples from the seed and tail ends of crystal 261 compared with the models (which we shall discuss) of Lucovsky[5] and Bebb and Chapman.[6] Note that the measured curves again peak at about $\sigma_{max} \approx 3.3\times10^{-17}$ cm^2. Of the six crystals we have measured, all had values of σ_{max} well within 5% of 3.3×10^{-17} cm^2. This is especially notable since the greatest error-producing factor in determining σ_{max} is the value of $(N_a - N_d)$ obtained from Hall data. In the case of samples 261SB and 261T01, for example, the difference in impurity concentration as indicated by the computer is borne out by absorption results which show the same value of σ_{max} for both samples. The curve of σ_I for sample 260T0 is so close to that for samples 261SB and 261T01 that it has been omitted from Fig. 4 for clarity.

DISCUSSION

Lucovsky[5] arrives at his mathematical model for the photo-ionization of deep impurities in semiconductors by treating the problem as being analogous to the photodissociation of a deuteron, but modified by the properties of the adjoining crystal lattice. For acceptor impurities, this leads to

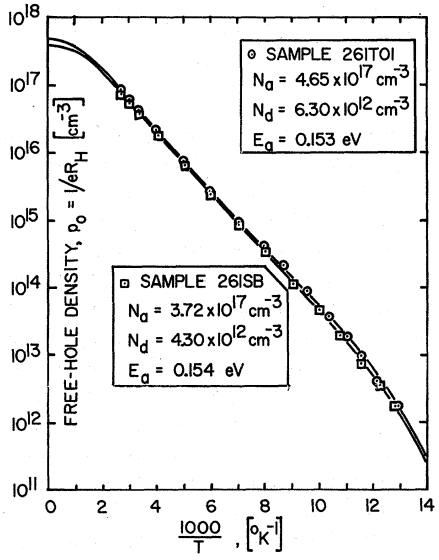

FIG. 2. Free-hole density (from Hall data) vs reciprocal temperature for samples cut from the seed and tail ends of indium-doped silicon crystal 261. The parameters which permit a fit to Eq. (2) are indicated above.

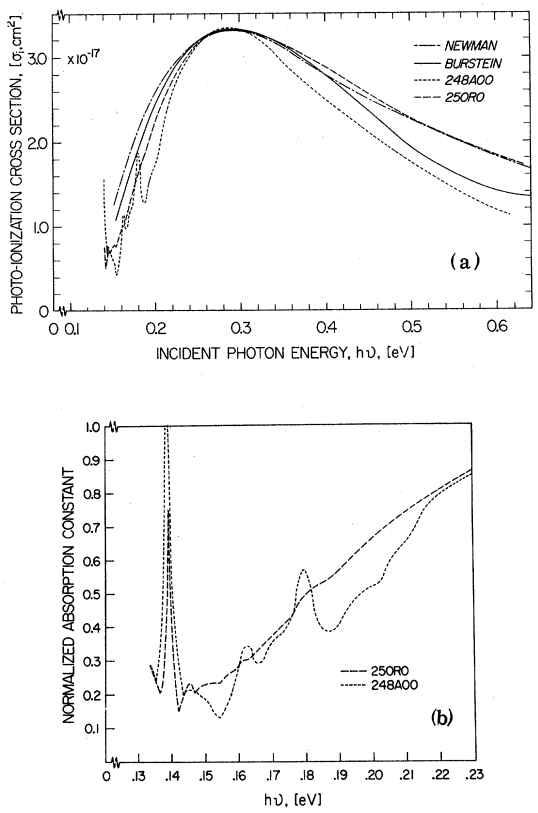

FIG. 3. (a) σ_I vs $h\nu$ for samples 248A00 and 250R0 compared with the results of Burstein *et al.* (Ref. 3) and of Newman (Ref. 2). (The two latter curves normalized to our σ_{max}.) (b) Low-energy data on an expanded scale.

$$\sigma_I(h\nu) = \frac{16\pi e^2\hbar}{3N_0 m^* c}\left(\frac{\epsilon_{eff}}{\epsilon_0}\right)^2 \frac{E_g^{1/2}(h\nu - E_g)^{3/2}}{(h\nu)^3}\ , \tag{3}$$

where N_0 is the refractive index, m^* is the scalar effective mass of valence-band holes, and $\epsilon_{eff}/\epsilon_0$ accounts for the fact that the ϵ field inducing the transition at the impurity site (ϵ_{eff}) differs from the average ϵ field in the bulk crystal (ϵ_0). Since the parameters other than $\epsilon_{eff}/\epsilon_0$ can be determined by other means, this essentially leaves $\epsilon_{eff}/\epsilon_0$ as an adjustable parameter to be used in fitting the data to the theory. The data of Burstein *et al.*[3,4] and Newman[2] have been interpreted as requiring $\epsilon_{eff}/\epsilon_0$ to be significantly different from unity (≈ 3) in order to fit Lucovsky's model[5] and the more detailed quantum-defect model of Bebb and Chapman.[6] Reference to the effective field in the vicinity of a highly localized center as discussed by Dexter[9] has been accepted as plausible justification for a departure of this size.

Although we are not prepared to endorse or discard either of the theoretical models mentioned so far, it is interesting to look at the relationship between the maximum value of σ_I and the effective-field ratio. For Lucovsky's model,

$$\sigma_{max} = 3.8\times10^{-17}\ (\epsilon_{eff}/\epsilon_0)^2\ \text{cm}^2 \tag{4}$$

at $h\nu = 0.30$ eV for In in Si; and for the model of Bebb and Chapman with a quantum defect $\nu = 0.5$,

$$\sigma_{max} = 1.5\times10^{-17}\ (\epsilon_{eff}/\epsilon_0)^2\ \text{cm}^2\ . \tag{5}$$

Recalling that the actual magnitude of the Burstein *et al.* data in Fig. 3 was reported as $\sigma_{max} \simeq 2.0 \times 10^{-16}$ cm^2 yields $\epsilon_{eff}/\epsilon_0 \simeq 2.3$ for Eq. (4) or $\epsilon_{eff}/\epsilon_0 \simeq 3.6$ for Eq. (5). Using the magnitude $\sigma_{max} \simeq 3.3\times10^{-17}$, which we have obtained consistently with the present data, yields $\epsilon_{eff}/\epsilon_0 \simeq 0.93$ for Eq. (4) and $\epsilon_{eff}/\epsilon_0 = 1.48$ for Eq. (5). Values of $\epsilon_{eff}/\epsilon_0$ for shallower acceptor impurities reportedly decrease to a value of $\epsilon_{eff}/\epsilon_0 \simeq 1.4$ for boron according to the Bebb and Chapman model.[6]

The exact nature of deep impurity centers has undergone a reasonable amount of discussion,[10] but the complexity of the problem of overlapping wave-function corrections, dipole-multipole interactions, etc., has made it extremely difficult to predict on a theoretical basis what $\epsilon_{eff}/\epsilon_0$ should be in the case of large departures from unity. As it happens, it has been traditionally accepted that highly localized centers would be subject to extreme departures while diffuse centers should have effective-field ratios much closer to unity.

As a first approximation to a theoretical value of $\epsilon_{eff}/\epsilon_0$, the impurity center can be treated as a spherical cavity in a dielectric medium. If the field applied to the material is uniform, which is a good approximation for transparent material, then the ratio of the (uniform) field within the cavity to the applied field is independent of the radius of the center and is given by[11]

$$\epsilon_{eff}/\epsilon_0 = 3\kappa/(2\kappa+1)\ , \tag{6}$$

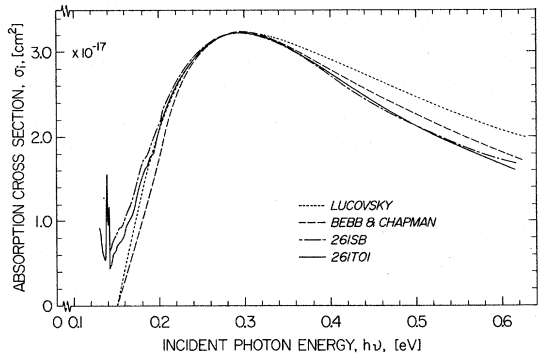

FIG. 4. σ_I vs $h\nu$ for samples 261SB and 261T01 compared with the quantum-defect model and with the δ-function potential model.

where κ is the real part of the relative dielectric constant of the medium. For Si ($\kappa \simeq 11.6$), Eq. (5) thus yields $\epsilon_{eff}/\epsilon_0 = 1.44$. What is being said here is essentially that in order to justify high effective-field ratios in Si, regardless of the size of the center, higher-order correction factors must enter the picture. In the light of the data presented in this paper, however, it appears that large effective-field ratios are not necessary to fit experimental results to theoretical results. In fact, it appears that the depolarizing field description of Eq. (6) seems to describe the departure from unity surprisingly well.

CONCLUSIONS

The observation of a nearly constant σ_{max} in all of our measured crystals suggests that the cross-section is crudely independent of doping (which would be expected for weak impurity concentrations), and it appears that the cross section is constant up to the maximum solubility of indium (as a replacement impurity) in silicon.

The shapes of the absorption cross sections for the various samples are also interesting. We have just commented on the anomalous structure displayed by sample 248A00 at low energies, but must concede that the rate at which σ_I drops off above 0.4 eV appears to depend to some extent on both the indium density and on the degree of compensation. Heavy doping and heavy compensation both seem to encourage σ_I to remain larger at high energies, possibly because of impurity overlap effects.

Finally, we consider it coincidental that the effective-field ratio required to fit our data to the quantum-defect model is essentially the same as the depolarizing effect of a hollow sphere in a silicon crystal. We do, however, feel that it is significant that the effective-field ratio needed to fit our data to either theoretical model[5,6] is essentially the same as that required to fit data for boron-doped silicon to the same models. This suggests that the effective-field ratio does not depend significantly on the "compactness" of the center or the type of center. It is likely that a reevaluation of the impurity concentrations of Al and Ga in earlier measurements would indicate larger values of N_a, which would thus yield lower absorption cross sections and correspondingly lower effective-field ratios.

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