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# Photoionization of group-III acceptors in silicon*

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A simple model is presented to describe the bound-to-continuum optical absorption process for group-III acceptors in silicon. Hydrogenic continuum states are used and the hydrogenic-ground-state wave function is scaled to account for central-cell corrections. Very good agreement with experiment is obtained along with physical insight into details of the photoionization process.

A number of calculations[1-5] of the photoionization spectra of group-III acceptors in silicon have appeared since the optical-absorption spectra[6,7] were reported in the 1950's. The optical spectra exhibit both bound states and ionization continua, and as one goes through the series boron-aluminum-gallium-indium the spectra change significantly.

A standard against which to compare all of these photoionization spectra is that of the hydrogen atom, since the simplest version of the theory of shallow acceptors makes use of the effective-mass approximation. A salient characteristic of the hydrogen spectrum[8] is that its maximum is at the photoionization threshold and the absorption strength falls off monotonically with increasing photon frequency. The hydrogenic bound-to-continuum spectrum was treated theoretically[8] many years ago and is well understood. Lax[9] first explored the consequences of applying the hydrogenic theory to defect problems.

It is noteworthy that for *none* of the acceptors is the experimental maximum at threshold; rather, there is a rise in absorption followed by a falloff as photon energy is increased. The boron spectrum comes closest to hydrogenic,[6] but by indium there is very little absorption into discrete states and a large continuum with an initial rise in absorption over a large energy range ~0.15 eV.

All of the points mentioned here have been made a number of times and have served as the motivation for calculations which go beyond the hydrogenic model[9] of the acceptor. The first of these was by Lucovsky,[1] who used a model developed for the deuteron in which the ground state is bound within a square well approximated by a $\delta$ function. Shortly thereafter, Bebb and Chapman[2] treated this problem using a quantum-defect method developed for atoms. More recently, Ning and Sah[3] and Rynne *et al.*[4] have reported on various aspects of the theory. In all cases, some degree of agreement with experiment was reported; for example, spectra similar to that observed for indium-doped silicon could be computed. Calculations have also been made of the photoionization of deep impurities.[5]

It is interesting to note that in all of the above calculations except for that of Bebb and Chapman, plane-wave states were used to represent the continuum. In the course of a more general investigation into the bound-to-continuum problem for defects, we realized that this could seldom be justified except possibly for large photon energies, especially in the case of Coulomb centers.[10] For example, plane-wave final states yield extremely poor results for the hydrogen atom, namely, a spectrum which begins at zero absorption and rises for nearly 6 eV before reaching a maximum value.[3,11]

Thus, the major justification for using plane-wave final states in the acceptor problem seems to be one of expediency; the calculations are relatively straightforward, they have some validity for large photon energies, and they do give spectra which agree to some extent with experiment. However, plane-wave final states always yield zero absorption at threshold, while with continuum states which are appropriate to the self-consistent potential of a Coulombic system such behavior seldom occurs[12] and then only by accident. In the experimental group-III acceptor spectra there are no indications that the absorptions at threshold are zero and ample indications that they are finite.[6,7]

We have found a simple approximate way of treating the acceptor bound-to-continuum absorption which exhibits the basic physics of the problem while at the same time giving agreement with experiment of comparable quality to that reported earlier. There are two assumptions made in our approach: (i) the continuum states are those of the hydrogen atom, with appropriate scaling to account for dielectric and effective mass effects; (ii) the ground state is hydrogenic, but its extent is smaller than one would obtain using the scaling of assumption (i).

Assumption (i) is simply an extension of the observations[6] that the *bound* optically excited states of the acceptor are largely independent of which of the group-III impurities one considers; their envelope functions are $p$-like and are very diffuse, hence central-cell corrections have little effect on them. The same assumption is made here for the continuum.

Assumption (ii) is a method for taking account of the central-cell correction to the ground state, where this correction is known to be largest. It is admittedly crude; the acceptor ground states in silicon are much more complicated than a single hydrogenic function,[13,14] but this assumption is a logical first step in testing whether this model is physically reasonable.

Both of these assumptions also imply that we are considering only the hydrogenic envelope functions; the modulating Bloch functions are assumed to have little effect on the problem. This procedure, common to earlier calculations[1-4] as well, is approximately valid as long as one is not trying to describe resonant states associated with subsidiary band edges.

After making these assumptions we have extended the procedure used by Bethe and Salpeter[8] to calculate the electric-dipole matrix element between the ground state and the continuum state, obtaining a closed-form expression for the optical-absorption cross section $\sigma_D$:

$$\sigma_D = \left(\frac{\mathcal{E}_e}{\mathcal{E}_0}\right)^2 \frac{2^9 \pi^2 \alpha \hbar\omega m_2^* (Z_2')^{-4}}{3\hbar^2 \epsilon^{1/2}} \frac{\eta^3(1-2\eta)^2(x+1)}{(x+\eta^2)^6} \times \frac{\exp[-4x^{-1/2}\cot^{-1}(\eta x^{-1/2})]}{1-\exp(-2\pi x^{-1/2})}, \qquad (1)$$

where $\alpha$ is the fine-structure constant $e^2/\hbar c$, and $\hbar\omega$ is the photon energy. $\mathcal{E}_e/\mathcal{E}_0$ is the ratio of the electric field at the defect to the average field in the medium. $Z_2'$ is the ratio of the absolute value of the impurity charge $Z_2$ (+1) to the Bohr radius $a_2$ associated with the hydrogenic Hamiltonian from which the continuum states are obtained:

$$Z_2' = Z_2/a_2 = Z_2 m_2^* e^2/\hbar^2\epsilon, \qquad (2)$$

where $\epsilon$ is the dielectric constant, and $m_2^*$ is the absolute value of the effective mass associated with the continuum states. $x$ is a dimensionless quantity which is proportional to the energy $E$ measured from the threshold of the continuum absorption

$$x = 2m_2^* E/\hbar^2(Z_2')^2, \qquad (3)$$

while $\eta$ is the ratio of the "inner" to the "outer" effective charge

$$\eta = Z_1'/Z_2', \qquad (4)$$

where

$$Z_1' = Z_1 m_1^* e^2/\hbar^2\epsilon, \qquad (5)$$

defined with respect to the hydrogenic Hamiltonian which leads to the ground state.

While the electric dipole form of the absorption cross section is that most often used in calculations,[1-3] it should be remembered that the electric-dipole matrix element is obtained from a gradient matrix element through a relation which is valid only if the initial and final wave functions are eigenstates of the same Hamiltonian.[11] Since this is not the case here, we have also calculated the transition matrix element in the gradient form and have obtained a closed-form expression for the corresponding optical absorption cross section $\sigma_G$:

$$\sigma_G = \left(\frac{\mathcal{E}_e}{\mathcal{E}_0}\right)^2 \frac{2^8 \pi^2 \alpha \hbar^2 m_2^*}{3m_T^2 \hbar\omega \epsilon^{1/2}} \frac{\eta^5(x+1)}{(x+\eta^2)^4} \times \frac{\exp[-4x^{-1/2}\cot^{-1}(\eta x^{-1/2})]}{1-\exp(-2\pi x^{-1/2})}. \qquad (6)$$

$m_T$ is the effective mass used in the transition operator; its value will be discussed below. The other quantities are as defined in Eq. (1). It is easily verified that Eqs. (1) and (6) are identical to each other and to the hydrogenic expression[8,9] when $m_1^* = m_2^* = m_T = m_e$ and $Z_1 = Z_2$.

Equations (1) and (6) are written in terms of the dimensionless energy parameter ($x$) and the ratio of effective charges ($\eta$) to emphasize that each equation defines a family of curves of $\sigma$ vs $x$ for different values of $\eta$. Although the two expressions are somewhat different, it turns out that both yield nearly equal results for the present situation except that the absolute values of $\sigma$ differ.

Substituting Eq. (2) into Eq. (3), we obtain

$$E = (Z_2^2 e^4 m_2^*/2\hbar^2\epsilon^2)x. \qquad (7)$$

Since $Z_2 = 1$ and $\epsilon = 11.7$ for silicon, the only available parameter is $m_2^*$. If as assumed the continuum states have no central-cell corrections, the same value of $m_2^*$ should be used for all 4 impurities. A value $|m_2^*| = 0.135 m_e$ is found to yield good results for all but boron, where a smaller value works better. $\eta$ is allowed to take on a different value for each impurity, yielding finally the results shown in Fig. 1. Table I gives the parameters and some other results.

Detailed agreement between theory and experiment is better than should be expected, given the approximate nature of the theory, and should not be overemphasized. We shall nevertheless point out several features of the results. Perhaps most important, good results are obtained using just one value of $m_2^*$, suggesting that assumption (i) is approximately valid. The ratio of effective charges $\eta$ increases as one goes from boron to indium; this is consistent with a central-cell correction to the ground-state wave function which is smallest for boron and largest for indium, as is generally

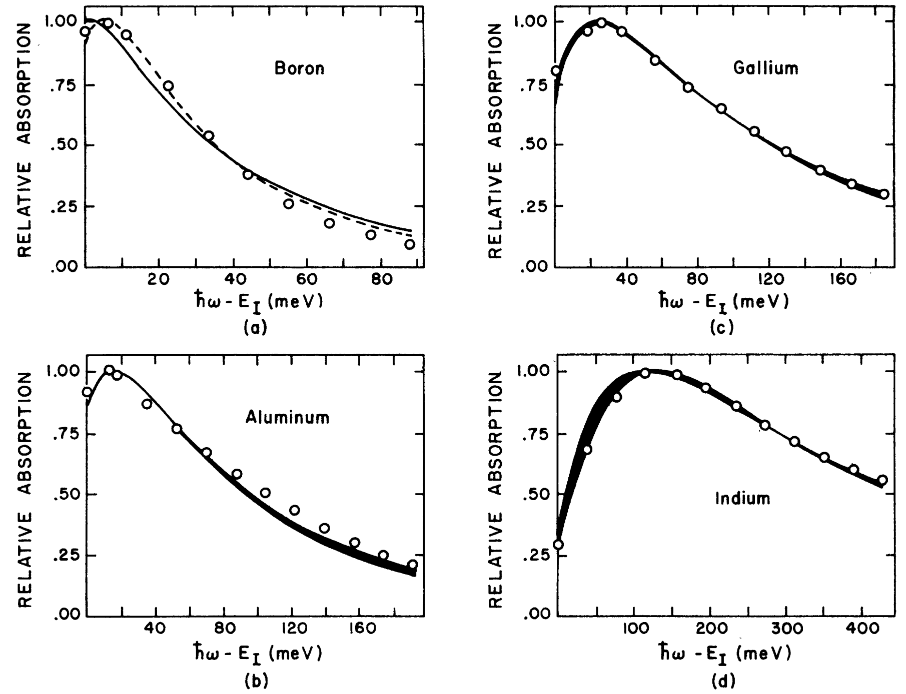

FIG. 1. Theoretical and experimental bound-to-continuum optical absorption vs energy for group-III acceptors in Si. Absorption is on a relative scale, while energy (in meV) is measured from the photoionization threshold $E_I$. $\hbar\omega$ is the photon energy. (a) boron, (b) aluminum, (c) gallium, (d) indium. Solid lines represent theory with $m_2^* = 0.135 m_e$, as does the dashed line for boron with $m_2^* = 0.07\, m_e$ (see text); circles, experiment. The widths of the solid lines represent the differences in results obtained by using Eqs. (1) and (6). Experimental results for boron, aluminum, and gallium were obtained from Burstein *et al.* (Ref. 6); those for indium from Messenger and Blakemore (Ref. 15). Given the uncertainties in the exact location of the onset of bound-to-continuum absorption and the errors introduced in reproducing published figures, the "experimental" points should be considered to have rather large error bars. More recent experiments on boron, aluminum, and gallium reveal structure (Ref. 16) associated with bound states and with phonon absorption superimposed on the continuum. Such effects are not considered here.

believed. The mean ground-state radii computed here are somewhat larger than reported elsewhere,[17] but again scale in the appropriate way.

Ground-state energies obtained with the hydrogenic Hamiltonian are in poor agreement with experiment; for example, we obtain an ionization energy for boron of ~ 20 meV vs 45 meV obtained experimentally.[6] This, however, is not surprising since our bound-state Hamiltonian is hydrogenic and contains no explicit central-cell terms in the potential energy. Inclusion of higher angular momentum components in our ground-state wave function would further lower the energy.[14]

The maximum value of the absorption cross sections for the indium impurity, using the above parameters, was found to be

$$\begin{aligned} \sigma_D(\max) &= (\mathcal{E}_e/\mathcal{E}_0)^2 5 \times 10^{-16}\ \mathrm{cm}^2 , \\ \sigma_G(\max) &= (\mathcal{E}_e/\mathcal{E}_0)^2 (m_T/m_e)^{-2} 2 \times 10^{-17}\ \mathrm{cm}^2 . \end{aligned} \tag{8}$$

These are to be compared with experimental values reported to be $2 \times 10^{-16}$ cm$^2$ by Burstein *et al.*[6] and $3.3 \times 10^{-17}$ by Messenger and Blakemore.[15] There is no firm theoretical guideline as to what mass to use for $m_T$; a value of $0.2 m_e$ would, however, bring both theoretical expressions for $\sigma$ into agreement, and $0.2 m_e$ is within the range of effective masses used in other parts of the calculation. The effective-field ratio would then have to be less than 1 to obtain agreement with experiment: this is another

TABLE I. Results of fitting Eq. (1) (dipole) and Eq. (6) (gradient) as shown in Fig. 1. $\eta$ is defined by Eq. (4), while $\langle r \rangle$ is the expectation value of the radial coordinate in the ground state.

| Acceptor | | B | Al | Ga | In |
|---|---|---|---|---|---|
| $\eta$ | dipole | 2.1 | 2.8 | 3.1 | 5.2 |
| | gradient | 2.2 | 3.3 | 3.7 | 7.1 |
| $\langle r \rangle$ (Å), present calculation | dipole | 34 | 25 | 23 | 13 |
| | gradient | 31 | 21 | 19 | 10 |
| $\langle r \rangle$ (Å), Ref. 17 | | 23 | 15 | 14 | 8 |

indication, we feel, of the highly approximate nature of the theory.

Aside from detailed comparison of experiment and theory, there are some physical aspects of the present results which are noteworthy. First, the physics of the general behavior shown in Fig. 1 is straightforward.[12,18] Speaking in terms of the dipole form [Eq. (1)], the transition probability between the ground state and a continuum state depends on the overlap of the localized ground-state wave function and the oscillatory continuum wave function. For hydrogen this overlap happens to be a maximum at threshold; for higher-energy continuum states the wavelength is smaller, partial cancellation occurs, and the overlap decreases. If the ground-state function is more compact than that of hydrogen, the maximum overlap does not occur at threshold but at some shorter wavelength, hence the optical spectrum first rises as the photon energy increases.

Second, the present theory does not force the theoretical curves to begin at zero absorption, as is the case when plane-wave continuum states are used.

Third, the value of the effective mass $m_2^* = 0.135 m_e$ needed to obtain good agreement at first sight seems small in terms of quoted "average" masses of $\sim 0.45 m_e$. However, the effective mass in the light-hole band[19] *is* $\sim 0.15 m_e$. The $j=\frac{1}{2}$ "split-off" band begins ~ 40 meV higher in energy; its effective mass is $\sim 0.23 m_e$. It thus appears that transitions into the continuum derived from the light-hole band and perhaps the $j=\frac{1}{2}$ band are favored over transitions to the heavy-hole continuum. This in fact seems reasonable; the lighter-hole bands occupy smaller regions of reciprocal space for the energies of interest than does the flatter heavy-hole band, thus leading to larger transition matrix elements with the ground-state wave function which is derived from Bloch states spanning a limited range about $\vec{k}=0$.

Although this model calculation cannot replace more accurate ones,[2] it has the virtue of being both simple and straightforward to understand. It should therefore be considered for a wider range of applications, both to other impurities and to other semiconductors and insulators.

*Note added in proof.* Pantelides and Bernholc[20] have recently published the results of a calculation of defect photoionization. Their calculation involves a detailed treatment of solid-state properties and represents an improvement over much of the earlier work, in that they have taken pains to use a good ground-state wave function and the crystal density of states, as well as Bloch functions for the final states. They obtain good agreement with experiment, although they predict the absorption to be zero at threshold. This threshold behavior, as in the cases mentioned in the present paper for which plane-wave final states were used, presumably comes about because their Bloch functions are not corrected for the presence of the defect.

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