Solid State Communications Vol. 3, pp. 299-302, 1965. Pergamon Press Ltd. Printed in Great Britain.

ON THE PHOTOIONIZATION OF DEEP IMPURITY CENTERS IN SEMICONDUCTORS*

G. Lucovsky

Philco Applied Research Laboratory, Blue Bell, Pennsylvania.

(Received 28 July 1965 by E. Burstein)

The wavelength dependence of the photoionization cross section for deep, semiconductor impurity centers, e.g., In doped Si, is calculated using a model in which the ground state wave function is determined solely by a suitable short range ion core potential. Absorption to excited states is explained by a long range, unperturbed coulomb potential.

THE WAVELENGTH dependence of the photoionization cross section is determined by the potential which binds the charged carrier to the atomic system. For shallow semiconductor impurity states, one would expect a calculation based on a coulomb potential to give a good description of the experimental photoionization data. For deep centers, where the hydrogen model is known to be inadequate, significant deviations from the hydrogenic (or coulomb potential) cross section are anticipated. Figure 1 indicates the wavelength dependence of the calculated hydrogen model cross section[1] along with normalized experimental data for B, Al, Ga and In doped Si[2,3]. The curves for shallow (e.g., B) as well as deep (e.g., In) centers show significant deviations from the calculated curves. The experimental data indicate relatively more absorption at higher photon energies, $\hbar\omega/E_i > 2$, where E_i is the measured ionization energy. The maximum value of the cross section does not occur at the ionization limit $\hbar\omega/E_i = 1$, as predicted by the hydrogen model but is displaced to higher photon energies. These differences, which become more pronounced as the ionization energy of the center increases ($E_B = 0.045$ eV, $E_{Al} = 0.057$, $E_{Ga} = 0.065$ eV, $E_{In} = 0.15$ eV), are attributed to large deviations from an exact coulomb potential ($V \sim -1/r$) in the vicinity of the impurity ion core[2].

For a deep center such as In doped Si, it is possible to perform a simple calculation to determine the photoionization cross section. The cross section calculation is based on a model in which the ion core potential rather than the coulomb potential, is responsible for the observed ground state binding energy. Any long range coulomb effects are neglected. To simplify the algebra, the core potential is assumed to be a delta function, the strength of which is determined by the observed binding energy. As has been shown in the calculation of the deuteron photodissociation cross section,[4] the exact form of the short range potential used in the model does not affect the wavelength dependence of the cross section but affects only the magnitude to a small extent. The normalized ground state wave function for the delta function well is given by

$$\psi(r) = \sqrt{\frac{\alpha}{2\pi}} \quad \frac{e^{-\alpha r}}{r} \quad ; \; r > 0 \tag{1}$$

where α is related to the observed binding energy, E_i and the effective mass, m^* by the relationship

$$\alpha = \sqrt{\frac{2m^* E_i}{\hbar^2}} \tag{2}$$

The final state is represented by a superposition of plane wave states corresponding asymptotically to an outgoing plane wave and an incoming spherical wave. The interaction with the photon field may be treated semi-classically.

The expression for the cross section

---

*This work was supported by the Office of Naval Research under contract Nonr - 4848 (00).

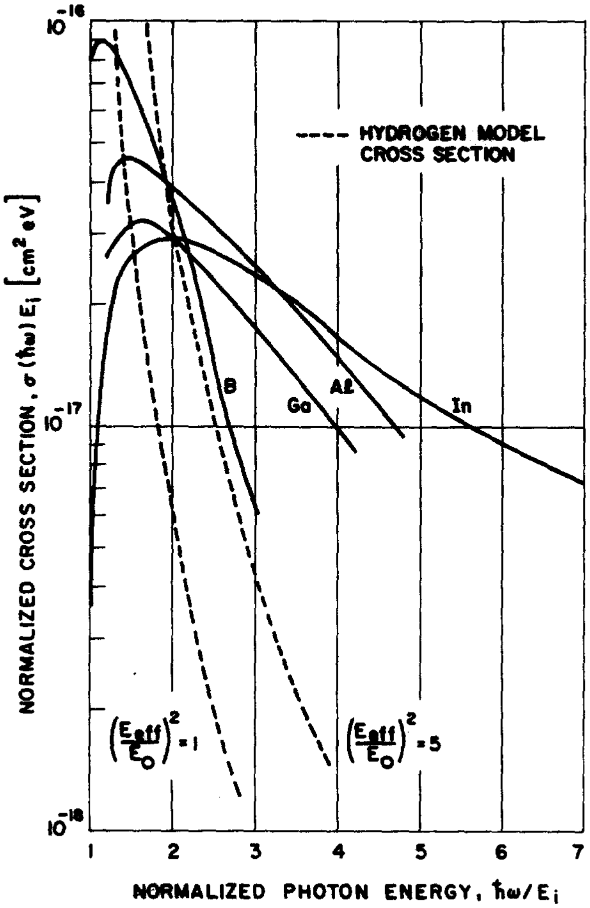

FIG. 1

Plot of hydrogen model photoionization cross section compared with normalized experimental curves for B, Al, Ga and In doped Si.

$\sigma(\hbar\omega)$, derived in the dipole approximation using time dependent perturbation theory,[4] is given by

$$\sigma(\hbar\omega) = \frac{1}{n}\left(\frac{E_{eff}}{E_o}\right)^2 \frac{16\pi e^2 \hbar}{3m^* c} \frac{(E_i)^{\frac{1}{2}}(\hbar\omega - E_i)^{3/2}}{(\hbar\omega)^3} \tag{3}$$

where n is the index of refraction and E_{eff}/E_o is the effective field ratio[5] for the radiation inducing the transition. The function in Equation (3) rises from zero at $\hbar\omega = E_i$, has a maximum at $\hbar\omega = 2E_i$ and falls off approximately as $\hbar\omega^{-3/2}$ for $\hbar\omega \gg E_i$. This is to be contrasted with the hydrogen (coulomb potential) model cross section which has a maximum at $\hbar\omega = E_i$ and falls off approximately as $\hbar\omega^{-3}$ for $\hbar\omega > E_i$. Figure 2 contains a normalized plot of the wavelength de-

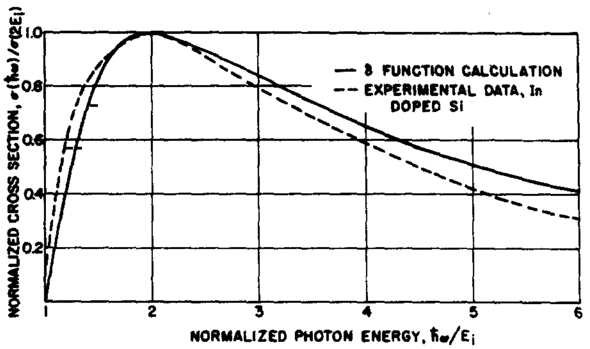

FIG. 2

Plot of δ function model photoionization cross section compared with experimental data for In doped Si.

pendent part of the calculated cross section along with experimental data for In doped Si[3]. The fit has been made assuming an impurity binding energy of 0.15 eV. This is within 7% of the quoted thermal activation energy. The agreement is satisfactory with regard to the magnitude of the cross section as well as the wavelength dependence (Fig. 2). In fitting the magnitude of the cross section, the effective field ratio is found to be of the order of 2.5 which is consistent with the measured index of refraction for Si. It is interesting to note that the relative quantum spectral response of many deep center, extrinsic Ge[6] and Si[7] photoconductors also shows a maximum at a photon energy equal to approximately twice the ionization energy in agreement with the delta function calculation.

The delta function (or zero range model) which neglects long range coulomb effects, does not account for the observed cross sections of B, Al, and Ga doped Si. For these more loosely bound centers, it is necessary to perform a more exacting calculation; e.g., the binding potential may be taken as a short range square well with a long range coulomb tail. The photoionization calculation is inherently difficult due to the orthogonality requirements imposed on the final state free particle wave functions. As is well known from the calculations of the photoionization cross sections of atomic gases[8], this type of potential model, which takes proper account of the ion core, will give a cross section showing increased absorption at higher photon energies and displaying a maximum value at a photon energy between $\hbar\omega = E_i$ and $\hbar\omega = 2E_i$.

Returning to the delta function approximation, it is informative to make some comments concerning the behavior of the oscillator strength. If Equation (3) is rewritten as

$$\sigma(\hbar\omega) = \frac{1}{n}\left(\frac{E_{eff}}{E_0}\right)^2 \frac{2\pi^2 \hbar e^2}{m^* c}\,\Gamma(\hbar\omega) \qquad (4)$$

then, the oscillator strength for the ground state (1s) to continuum transition, $f_{cont;\ 1s}$, is given by the usual expression[9],

$$f_{cont;\ 1s} = \int \Gamma(\hbar\omega)\; d\,(\hbar\omega) \qquad (5)$$

Substitution of (3) and (4) into (5) gives the result that $f_{cont;\ 1s} = 1$. At first this result may seem surprising; however, the delta function approximation admits only one bound state (the ground 1s state) so that in the dipole approximation all of the oscillator strength goes into the 1s to continuum transition. If one considers a more realistic core potential, e.g., an exponential of Gaussian well, then the oscillator strength is reduced by a factor β given by

$$\beta = \frac{1}{1 - \alpha r_0} \quad ; \quad \alpha r_0 < 1 \qquad (6)$$

where r_0 is associated with the effective scattering range of the potential. The oscillator strength removed from the 1s to continuum transition goes into line absorption associated with excitation from the 1s state to higher lying excited states.

Absorption lines associated with transitions from the ground state to excited "p-like" states are observed in B, Al, Ga and In doped Si[2,10]. The energies of these excited states relative to the edge of the valence band are essentially independent of the nature of the dopant. To calculate the oscillator strength for these excitation absorption lines, it is assumed that the excited state wave functions are determined by a long range coulomb potential which is the same for all of the singly charged centers. This approximation is further justified by observing the p-type wave functions (or odd parity wave functions in general) vanish identically at $r = 0$, so that ion core perturbations do not strongly effect their eigenstate energies. We compare the magnitude of the oscillator strengths for 1s → 2p transitions for the idealized coulomb potential and deep (δ-function) potential problems, the difference involving only the nature of the ground state wave function. The ratio of the oscillator strengths is approximately 150. The relative oscillator strengths for the 1s → continuum and 1s → 2p, 3p, etc. transitions in B doped Si agree well with a hydrogen model calculation[9]. We therefore, compare the relative absorption for ground state to excited state transitions for B and In doped Si. The ratio of absorption constants for transitions terminating in the excited states ranges from about 80 to 200[2] in reasonable agreement with the calculation. Moreover, the fraction of the total oscillator strength in the excited state transitions in In doped Si is quite small so that the observed line absorption spectra is not in disagreement with the high oscillator strength of the 1s to continuum transition.

The agreement between the calculated and measured photoionization cross section for deep impurity centers indicates the usefulness of the ion-core (or zero range) potential model. The model is also useful in describing other properties of deep centers which are influenced by the binding potential, e.g., the non-radiative recombination cross section.

References

1. BETHE H., Handbuch der Physik, 24/1, Kap 3, Ziff 47, Julius Springer, Berlin (1933).
2. BURSTEIN E. et al, Photoconductivity Conference, 1954, p. 353, John Wiley, New York (1956), and BURSTEIN E., et al, J. Phys. Chem. Solids, **1**, 65 (1956).
3. NEWMAN R., Phys. Rev. **99**, 465 (1955).
4. BETHE H., and MORRISON P., Elementary Nuclear Physics, 2nd Ed., John Wiley, New York (1956).
5. DEXTER D.L., Solid State Physics, Vol. 6, p. 353, Academic Press, New York (1958).
6. NEWMAN R., and TYLER W.W., Solid State Physics, Vol. 8, p 50, Academic Press, New York (1959).

7. KRUSE P.W., McGLAUCHLIN L.D., and McQUISTAN R.M., Elements of Infrared Technology, John Wiley, New York (1962).

8. SEWELL K.G., Phys. Rev, 138, A418 (1965).

9. LAX M., Photoconductivity Conference, 1954, p. 111, John Wiley, New York (1956).

10. HROSTROWSKI H.J., and KAISER R.H., J. Phys. Chem. Solids, 1, 236 (1958).

Die Abhängigkeit des Photoionisation - querschnittes von der eingestrahlten Wellenlänge, wurde für tiefe Halbleiter Zentren (In dotiertes Si) unter Zugrundelegung eines Modelles berechnet, in dem die Wellenfunktion des Grundzustandes allein durch ein geeignetes Ionen Kern Potential von kurzem Bereich bestimmt ist. Absorbtion zu angeregten Zuständen ist durch ein ungestörtes Coulomb Potential mit weitem Bereich erklärt.