6-1-1984

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Repository Citation

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A simple model for absorption of infrared radiation by impurity atoms in silicon crystals has been developed and applied to electronic excitations of the Group V donors Bi, Sb, As, and P, and the Group III acceptors B, Al, Ga, and In. The model is based on the quantum-defect method for approximating bound donor or acceptor wave functions outside the core region of the impurity. For each donor species, the relative oscillator strengths have been calculated for the transitions from the ground state to the first four excited levels. For each acceptor species, the relative oscillator strengths were calculated for transitions from the $P_{3/2}$ ground state to the first three $P_{1/2}$ excited levels. Comparison with high-resolution absorption spectra show qualitative agreement for the low-lying transitions.

I. INTRODUCTION

The identification of residual impurities as to type and concentration in silicon single crystals is a very important problem. It is well known that small amounts of donors or acceptors can have a marked effect on the electrical properties of the crystal. Infrared absorption spectroscopy is one of the methods used to identify Group III and Group V impurities in the concentration range 10^{14}–10^{18}/cm^3. In principle, an accurate calculation of the absorption cross section $\sigma(\nu)$, or more appropriately the integral of $\sigma(\nu)$ over the width of a given absorption line, would make possible an absolute calibration of that line for use in the determination of the impurity concentration. However, $\sigma(\nu)$ depends on the effective electric field at the impurity, which is difficult to estimate. On the other hand, the ratios of the integrated cross sections for two different lines belonging to the same impurity are independent of this quantity and therefore easier to calculate. Accurate values for these ratios would be useful in calibrating additional lines without the necessity of performing separate measurements for them.

In the present work the relative absorption strengths of certain lines associated with electronic transitions in Group III and Group V dopants in silicon have been calculated. The emphasis was on developing a simple model for calculating the dipole matrix elements which would require only the use of a hand calculator. As described in the next section, the approach was to use the quantum-defect method (QDM) to obtain an analytic expression for the wave functions in the asymptotic region far from the impurity core.

II. THE MODEL

For an isolated impurity undergoing an electronic transition via photon absorption from initial state $|a\rangle$ to final state $|b\rangle$, with energy difference $E_b - E_a$, the oscillator strength is defined by[1]

$$f_{ba} = \frac{1}{3}\left(\frac{2m^*}{h^2}\right)g_b(E_b - E_a)\sum_{j=1}^{3}|\langle b|x_i|a\rangle|_{\text{av}}^2, \qquad (1)$$

where g_b is the degeneracy of the final state and the initial state is assumed nondegenerate. The matrix element $\langle b|x_i|a\rangle$ is essentially that for the ith Cartesian component of the dipole moment operator, and its magnitude squared is averaged over the g_b final states. The effective-mass tensors at the band edge are assumed identical and isotropic, so there is only one effective-mass parameter m^*. The area under an absorption peak is proportional to the integrated cross section, which in turn is proportional to the oscillator strength. For a given impurity, the ratio of the peak areas for transitions $|a\rangle\rightarrow|b\rangle$ and $|a\rangle\rightarrow|c\rangle$ is therefore equal to the ratio of the corresponding oscillator strengths. From Eq. (1),

$$\frac{f_{ca}}{f_{ba}} = \frac{g_c(E_c - E_a)}{g_b(E_b - E_a)}\frac{\sum_{i=1}^{3}|\langle c|x_i|a\rangle|_{\text{av}}^2}{\sum_{i=1}^{3}|\langle b|x_i|a\rangle|_{\text{av}}^2}. \qquad (2)$$

It is this ratio which was calculated and compared to experiment.

The selection rules for electric dipole transitions from an s-like ground state restrict the final state to be p like and therefore to vanish at the impurity core. In this case one might expect the asymptotic region to give the major contribution to the transition matrix elements. Then in the expression

$$\psi(\mathbf{r}) = \sum_{j=1}^{g_d}F_j(\mathbf{r})\phi_j(\mathbf{k},\mathbf{r}) \qquad (3)$$

for the impurity state ψ, only the envelope functions F_j need be considered. The reason for this is that, at large distances from the impurity, F_j varies slowly over a unit cell volume whereas the g_d-fold degenerate Bloch functions ϕ_j at the band edge are orthonormal within this volume.[2] For identical and isotropic effective-mass tensors there is only one envelope function $F(\mathbf{r})$, determined from Schrödinger's equation with a hydrogenic potential:

$$\left(\frac{-h^2}{2m^*}\nabla^2 - \frac{e^2}{4\pi k\epsilon_0 r} - E\right)F(\mathbf{r}) = 0. \qquad (4)$$

The effective-mass theory breaks down near the impurity core, but if Eq. (4) were assumed valid over all distances, $F(\mathbf{r})$ would be a pure hydrogenic orbital and the corresponding energy would be given by a simple Rydberg formula. This is the hydrogenic model of impurity states and is the simplest form of effective-mass theory. A more sophisticated

form would incorporate mass anisotropy and band degeneracy.[2] In the present model one deals only with Eq. (4), but does not assume its validity at small distances; rather, an "effective" principal quantum number ν is determined from the Rydberg formula

$$E = -\frac{1}{\nu^2},\tag{5}$$

using the experimental value for E expressed in units of the "effective" Rydberg $R *$,

$$R * = \frac{e^2}{8\pi k\epsilon_0 a^*},\tag{6}$$

where a^* is the "effective" Bohr radius

$$a^* = \frac{4\pi k\epsilon_0 h^2}{m^* e^2}.\tag{7}$$

In terms of the quantum numbers ν, l, and m, the envelope function is

$$F_{\nu lm}(\mathbf{r}) = R_{\nu l}(r)Y_{lm}(\theta, \phi),\tag{8}$$

where

$$R_{\nu l}(r) = \left(\frac{2}{\nu a^*}\right)^{1/2}\frac{1}{r}P_{\nu l}\left(\frac{2r}{\nu a^*}\right).\tag{9}$$

The asymptotic form of $P_{\nu l}$ is given in the QDM[3] as

$$P_{\nu l}(\rho) \sim N_{\nu l}\rho^\nu e^{-\rho/2}\sum_{t=0}^{t_0}\beta_t\rho^{-t},\tag{10}$$

with $t_0 \leqslant \nu$. The QDM was first applied to this problem by Kohn and Luttinger[4] who used it to calculate corrections to

the effective-mass value of the lowest excited donor levels. Bebb and Chapman[3] later adapted it to the calculation of photoionization cross sections of acceptors in Si and GaAs. Here the method is applied to photoexcitation, and it is necessary first to correct the expressions for $N_{\nu l}$ and β_t given in Ref. 3. The corrected expressions are

$$\beta_0 = \frac{\Gamma(\nu + l + 1)}{\Gamma(\nu - l)};$$

$$\beta_1 = (l + 1) - \nu(\nu - 1);$$

$$\beta_t = \beta_{t-1}[l(l + 1) - (\nu - t + 1)(\nu - t)]/t, \quad t \geqslant 2;$$

$$N_{\nu l} = (-1)^{\nu - l - 1}$$

$$\times\left(\frac{\Gamma(\nu - l)}{2\nu\zeta(\nu)(\nu + l)\Gamma(\nu + l)\Gamma^2(\nu + l + 1)}\right)^{1/2}.$$

$\Gamma(z)$ is the gamma function and the quantity $\zeta(\nu)$ is defined by

$$\zeta(\nu) = 1 + \frac{d\mu}{d\nu},$$

where $\mu = n - \nu$ is the "quantum defect" parameter and n is the nominal principal quantum number of the state.

More recently, Chaudhuri et al.[5] have applied the method to the calculation of field-ionization rates from localized $|s\rangle$ states.

When ν is a positive integer, Eqs. (8)–(10) reduce to the hydrogenic case.

Evaluation of the QDM matrix element is lengthy but straightforward. The result for a transition between the ground state $|\nu s\rangle$ and excited state $|\nu'p\rangle$ is

$$\sum_{i=1}^{3}|\langle \nu'p|x_i|\nu s\rangle|^2_{\mathrm{av}} = \frac{4a^{*'2}}{3\nu\nu'}\left(\frac{a^{*'}}{a^*}\right)^{2\nu+1}\beta_0^2|N_{\nu'l}|^2|N_{\nu0}|^2\left(\frac{2}{\nu}\right)^{2\nu}\left(\frac{2}{\nu'}\right)^{2\nu'}\left[\sum_{t=0}^{t_0'}\beta_t'\left(\frac{\nu'}{2}\right)^t\frac{\Gamma(\nu + \nu' + 2 - t)}{\left[\left(\frac{a^{*'}}{a^*}\right)\frac{1}{\nu} + \frac{1}{\nu'}\right]^{\nu + \nu' + 2 - t}}\right]^2,\tag{11}$$

where primes refer to the excited state. For donors the ground and excited states have the same effective Bohr radius, but for acceptors the $P_{3/2}$ and $P_{1/2}$ states have different effective Bohr radii a^* and $a^{*'}$, respectively. Figure 1 shows schematically the transitions for the two cases.

acceptor $P_{3/2}$ ground state

p' transition

$P_{3/2}$ valence bands

$P_{3/2}$ excited states

conduction band

acceptor $P_{1/2}$ ground state

donor excited states

$P_{1/2}$ excited states

donor ground state

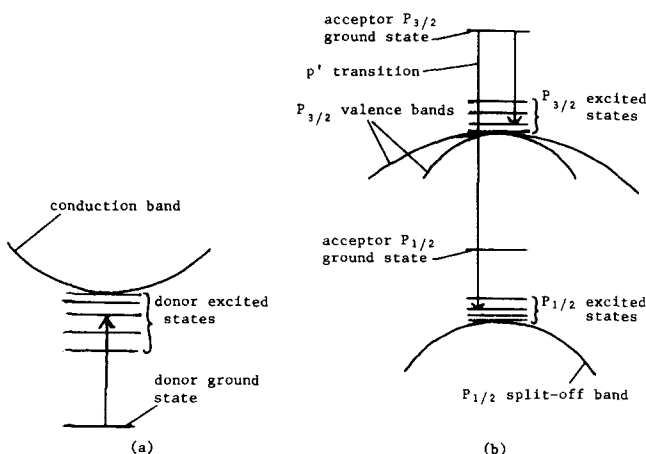$P_{1/2}$ split-off band

(a)   (b)

FIG. 1. Schematic representation of (a) transitions between donor levels and (b) transitions between acceptor $P_{3/2}$ ground state and $P_{1/2}$ excited states, in silicon.

III. NUMERICAL RESULTS

The model presented here requires a choice of the effective Rydberg $R *$ or, equivalently, of the effective mass parameter m^*. For donor electrons the value $R * = 29.2$ meV was used, based on the effective-mass calculation of Kohn and Luttinger.[4] This corresponds to $m^* = 0.294m_0$, where m_0 is the bare electron mass. For the $P_{1/2}$ states of acceptor holes we use $R * = 26.15$ meV, corresponding to

TABLE I. Relative line strengths for Group V donors in Si, normalized to the $|1s\rangle \rightarrow |2p_\pm\rangle$ line for each species. The "normal" principal quantum numbers are used in labeling the states.

Transition	Bi	Sb	As	P	P[a]	P(exp)[b]
$|1s\rangle\rightarrow|2p_0\rangle$	0.604	0.483	0.572	0.540	0.38	0.409
$|1s\rangle\rightarrow|2p_\pm\rangle$	1.000	1.000	1.000	1.000	1.00	1.000
$|1s\rangle\rightarrow|3p_0\rangle$	0.146	0.257	0.211	0.253	0.04	0.121[c]
$|1s\rangle\rightarrow|3p_\pm\rangle$	0.058	0.173	0.112	0.161	0.29	0.432

[a] W. Kohn, Phys. Rev. 98, 1856 (1955).

[b] C. Jagannath, Z. W. Grabowski, and A. K. Ramdas, Phys. Rev. B 23, 2082 (1981).

[c] estimated assuming the same line width as the $|1s\rangle\rightarrow|3p_\pm\rangle$ transition given in (b).

TABLE II. Relative line strengths for the p' series of Group III acceptors in Si, normalized to the $2p'$ line for each species. The symmetry of the final state was taken to be Γ_6 for all three lines.[a]

	Calculated			Observed[b]		
	$2p'$	$3p'$	$4p'$	$2p'$	$3p'$	$4p'$
B	1.000	0.113	0.0037	1.000	0.174	0.044
Al	1.000	0.101	0.0018	1.000	0.231	0.040
Ga	1.000	0.107	0.0023	1.000	0.199	0.024
In	1.000	0.123	0.043	1.000	0.250	0.047

[a] A. Onton, P. Fisher and A. K. Ramdas, Phys. Rev. **163**, 686 (1967).
[b] J. Rome (unpublished data).

$m^* = 0.250m_0$,[6] while for the $P_{3/2}$ states we use $R^* = 36$ meV (Refs. 2,3) $(m^* = 0.362m_0)$. The positions of the Group V donor lines were taken from the tabulation by Kogan and Lifshits[7] and those for the Group III acceptor lines from Onton et al.,[8] Rome et al.,[9] and Rome.[10]

Table I shows the results for the donor line strengths relative to the $|1s\rangle \rightarrow |2p_\pm\rangle$ line. Also shown are the results of an effective-mass calculation by Kohn[11] for Si(P), which takes mass anisotropy into account, and experimental values for Si(P) inferred from the linewidth measurements of Jagannath et al.[12] It is seen that the model overestimates by about a factor of two the $|1s\rangle \rightarrow |3p_0\rangle$ line strength and underestimates by about 60% the $|1s\rangle \rightarrow |3p_\pm\rangle$ strength.

Table II summarizes the results for the acceptors, normalized to the $2p'$ line. The model underestimates the $3p'$ line by about 50% and, except for In, the weak $4p'$ line by a factor of 10. The experimental strengths have not been corrected for instrumental broadening, so are probably an overestimate.

Detailed calculations of line strengths for the transitions to $P_{3/2}$ excited states indicated in Fig. 1(b) have not been included because of the difficulty in describing these states as pure atomiclike orbitals.

IV. CONCLUSIONS

The simple quantum defect method applied here indicates that the ratio of the cross sections for the two most intense photoabsorption lines does not vary much from one species to another for Group V donors in Si, ranging between 48% and 60%. Similarly for Group III acceptors in Si the ratio of the cross sections for the $2p'$ and $3p'$ lines ranges from 10% to 12%. The ratios of the measured $2p'$ and $3p'$ line strengths are approximately twice as large as the calculated values but likewise show no extreme fluctuations. Thus both experiment and our calculations indicate that there is no great variation in the absorption cross section from one

Group III acceptor to another even though the ground states of these acceptors in Si, as opposed to Ge, are relatively far apart in energy. This is significant for the determination of relative acceptor concentrations in Si using photoabsorption or photothermal ionization spectroscopy.

ACKNOWLEDGMENTS

[1] M. Lax, *Proceedings of the Photoconductivity Conference Nov. 4–6, 1954* (Wiley, New York, 1956), pp. 111–145.
[2] D. Schecter, J. Phys. Chem. Solids **23**, 237 (1962).
[3] H. B. Bebb and R. A. Chapman, J. Phys. Chem. Solids **28**, 2087 (1967).
[4] W. Kohn and J. M. Luttinger, Phys. Rev. **98**, 915 (1955).
[5] S. Chaudhuri, D. D. Coon, G. E. Derkits, and J. R. Banavar, Phys. Rev. A **23**, 1657 (1981).
[6] S. Zwerdling, K. J. Button, B. Lax, and L. M. Roth, Phys. Rev. Lett. **4**, 173 (1960).
[7] S. M. Kogan and T. M. Lifshits, Phys. Status Solidi A **39**, 11 (1977).
[8] A. Onton, P. Fisher, and A. K. Ramdas, Phys. Rev. **163**, 686 (1967).
[9] J. J. Rome, R. J. Spry, T. C. Chandler, G. J. Brown, B. C. Covington, and R. J. Harris, Phys. Rev. B **25**, 3615 (1982).
[10] J. Rome (unpublished data).
[11] W. Kohn, Phys. Rev. **98**, 1856 (1955).
[12] C. Jagannath, A. W. Grabowski, and A. K. Ramdas, Phys. Rev. B **23**, 2082 (1981).