Spin–orbit splitting of acceptor states in Si and C

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Abstract

We report calculations of the Γ_8–Γ_7 spin–orbit splittings of substitutional acceptor levels in silicon and diamond and corresponding Raman measurements for Si:X (X = B, Al, Ga, In). The calculations were performed using a Green's function method based on a full-zone 30×30 $\boldsymbol{k} \cdot \boldsymbol{p}$ Hamiltonian together with a Slater–Koster ansatz for the acceptor potential. The results are in reasonable agreement with experimental data. © 1999 Elsevier Science B.V. All rights reserved.

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1. Introduction

In the last 30 years a lot of effort has been devoted to the study of impurity levels in semiconductors, partly because of their interest for doping applications. The knowledge of acceptor levels allows one to evaluate the effects of different dopant atoms on the carrier concentration. This is of crucial importance in the development of devices, such as transistors or diodes, which are widely employed in electronic systems. Despite the intensive study of these acceptor levels, especially by means of optical spectroscopies, there are some details of the observed spectra which are not completely understood. In the case of Si, a splitting, Δ_0^a, has been observed for B, In, Be^-, Zn^- substitutional impurities. This splitting varies from 23.7 to 0.3 meV depending on acceptor [1–4].[3] Its tentative assignment to spin–orbit interaction requires

an enormous reduction of the corresponding spin–orbit splitting of the $\Gamma_{25'}^{+v}$ valence band states, $\Delta_0 \simeq 44$ meV [5]. In the case of diamond, the reported splitting is 6 meV [6],[4] while for the boron acceptor this splitting is reduced to 2 meV [7–11].

Baldereschi and Lipari showed in Ref. [12] that for silicon doped with boron, $\Delta_0^a \simeq \Delta_0/2$ if the acceptor binding energy, E_b^a, is close to Δ_0. For this purpose they used an effective mass approximation (EMA) involving a Kohn–Luttinger 6×6 Hamiltonian. Although they found a good agreement with the spin–orbit splitting of the ground state of the boron acceptor, their formalism cannot be applied for larger values of E_b^a, for which a large range of $\boldsymbol{k}$-space must be taken into account in describing the acceptor wave functions, leading to non-parabolicity effects, which cause the EMA to break down.

In this work we report calculations for the spin–orbit-induced splitting of substitutional acceptors in silicon and diamond. A Green's function method is used to estimate the splitting of Γ_8 and Γ_7 ground state levels for different impurities, using as input parameter only the experimentally determined value of E_b^a for the acceptor

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[3] The splitting of 4.2 meV in the luminescence peaks of Si:In was attributed by Sauer et al. to vibronic structure. However, it is likely to correspond to the Δ_0^a discussed by us.

[4] No justification for the assignment to Δ_0 of structure seen in ir-induced cyclotron resonance is given in this work.

under consideration. In order to calculate the Green function, the full-zone $k \cdot p$ Hamiltonian is used with a Slater–Koster ansatz for the impurity potential (this ansatz is equivalent to assuming that the hole interacts with the acceptor only if both are in the same primitive cell). The results are compared with previous experiments and with Raman data for Si : X, X being B, Al, Ga and In. Good agreement with the observed reduction of Δ_0^a with increasing E_b^a, as well as qualitative agreement with the absolute values of Δ_0^a, is obtained.

2. Theory: silicon

The electronic levels of acceptors in diamond- and zinc-blende-type semiconductors are usually described using a 4×4 Kohn–Luttinger effective mass Hamiltonian [13] which neglects the Γ_7^+ spin–orbit-split band. Baldereschi and Lipari [12] calculated for Si : B a spin–orbit splitting of $\Delta_0^a \simeq 23.8$ meV using a 6×6 Kohn–Luttinger-Hamiltonian, in which the Γ_7^+ spin–orbit-split bands were treated by perturbation theory. This treatment implies the assumption of parabolic bands which does not hold if E_b^a is larger than Δ_0. This scheme, therefore, does not allow one to explain the smaller splittings observed in Si for In (4.2 meV [3,4]), Be^- (0.6 meV [2]) and Zn^- ($\simeq 0.3$ meV [3]) acceptors. It is thus necessary to take into account the full details of the band structure in the calculation. In this work we used a Slater–Koster potential to represent the acceptor–hole interaction, i.e. we consider this interaction constant if both particles are in the same primitive cell and zero otherwise. This allows us to obtain the binding energy of an acceptor level Γ, $E_b^a(\Gamma)$, by using the equation

$$\frac{1}{V_0} \simeq G_r^\Gamma(E_b(\Gamma)), \tag{1}$$

where V_0 represents approximately the average of the potential over the primitive cell, and G_r^Γ is the real part of the Γ-projected Green function. G_r^Γ is obtained from the imaginary part of the Green function, G_i^Γ, by using a Hilbert transform. G_i^Γ is related to the Γ-projected density of states through

$$G_i^\Gamma(E) = -\pi N^\Gamma(E). \tag{2}$$

$N^\Gamma(E)$ is calculated from the 30×30 full-zone $k \cdot p$ Hamiltonian [14] using the tetrahedron method [15] with a grid of $\simeq 3 \times 10^5$ tetrahedra which was shown to yield adequately converged final results. The total valence density of states is plotted in Fig. 1 together with that calculated by means of ab initio pseudopotentials within the LDA-approximation, using the parametrization in Ref. [16] for the exchange-correlation potential. The agreement is shown to be remarkably good. The parameters used for the $k \cdot p$ Hamiltonian were adjusted from those
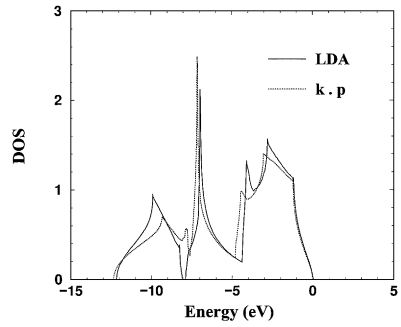

Fig. 1. Total density of valence states calculated for silicon with the 30×30 $k \cdot p$ Hamiltonian, and the LDA-pseudopotential technique, using a Troullier–Martins pseudopotential [23] and a plane-wave expansion with a cutoff energy of 40 Rydbergs and a grid of $20 \times 20 \times 20$ in reciprocal space.

Table 1
Parameters of the full-zone $k \cdot p$ Hamiltonian used for the calculation of the Green function of silicon, taken from Ref. [14] unless otherwise specified

	(eV)		(a.u.)
$E_{\Gamma_1^{+v}}$	-12.36[a]	P	0.600
$E_{\Gamma_{25'}^+}$	0.00	Q	0.525
$E_{\Gamma_{15}^-}$	3.40	R	0.415
$E_{\Gamma_{2'}^-}$	4.185[a]	P'	-0.045
$E_{\Gamma_{12'}^-}$	9.66	P''	0.050
$E_{\Gamma_1^{+c}}$	7.075	P'''	0.660
$E_{\Gamma_{2'u}^-}$	13.47	Q'	-0.4035
$E_{\Gamma_{25'}^+}$	12.79	R'	0.605
Δ_0	0.044	T	0.103
Δ_0'	0.040	T'	0.540

[a] Modified from those in Ref. [14], so as to reproduce the experimental data given in Ref. [22].

in Ref. [14] to reproduce the LMTO band structure corrected for the "gap problem" [17]; they are shown in Table 1. The density of states is projected via Γ_8^+ and Γ_7^+ admixture coefficients interpolated for each tetrahedron. Finally, we made the plausible assumption of equal values of V_0 for Γ_8^+ and Γ_7^+. The $\Gamma_8 - \Gamma_7$ acceptor splitting Δ_0^a is then found by solving Eq. (1) for $E_b^a(\Gamma_7)$ after having determined V_0 using also Eq. (1) and the experimental value of $E_b^a(\Gamma_8)$. This procedure is illustrated by the horizontal line in the inset of Fig. 2. The values of Δ_0^a obtained for silicon by this procedure versus E_b^a are displayed in Fig. 3.

3. Experimental results: silicon

Together with the calculations presented above we performed Raman measurements in Si : X samples, X
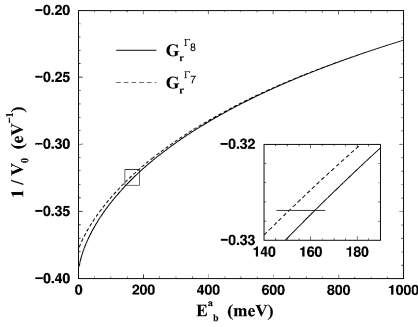
Fig. 2. Real part of the Green funtion of the valence band of silicon (labeled $1/V_0$ in the spirit of Eq. (1)) versus E_b^a. The inset represents a blowup of the rectangle drawn around the binding energy of the In acceptor. It allows one to see $G_r(\Gamma_8)$ and $G_r(\Gamma_7)$ separately and to determine Δ_0^a as illustrated by the horizontal line (see also Fig. 3).
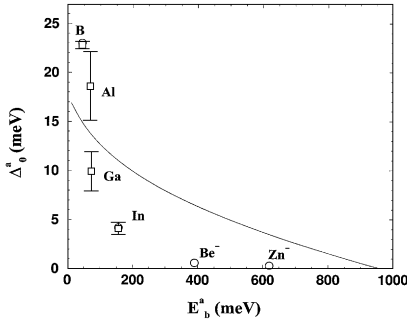

Fig. 4. Raman spectra of Si:X samples [X being B, Al, Ga and In]. The peaks can be assigned to the Γ_8–Γ_7 spin–orbit splitting of the corresponding substitutional acceptor. In the case of Ga doped samples two structures can be observed. The nature of these peaks is not understood.

Fig. 3. Spin–orbit splitting Δ_0^a of a substitutional acceptor in silicon versus binding energy, E_b^a. The circles represent EDSR data from Ref. [3], while the squares correspond to Raman measurements (see Fig. 4).

being B, Al, Ga and In. Most samples were cut from bulk material but we also used epitaxial layers. The carrier concentrations were in the 10^{16}–10^{18} cm^{-3} range. The 7993 Å krypton laser line was used for excitation in backscattering configuration with low power densities. A cold finger cryostat was used to hold the samples at 11 K. A Dilor XY multichannel spectrometer and a charge-coupled device detector were used to record the spectra. The spectral resolution was 1.5 cm^{-1}.

In Fig. 4 we show typical Raman spectra in the range of 4–30 meV, displaying structure that can be attributed to Δ_0^a, the Γ_8–Γ_7 spin–orbit splitting of the corresponding acceptor ground state levels. The peak positions were determined by subtracting a linear background, and taking the centroid of the resulting curves. The observed values of 22.8 (B) and 4.1 meV (In) are in good agreement with those previously reported, namely 22.7 [18] and 4.2 meV [3], from Raman and EDSR experiments, respec-
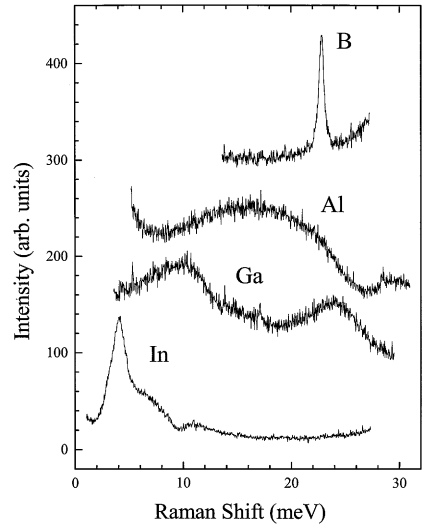
tively. However, a strong broad structure was obtained for Si:Al. This increases the error for the determination of the splitting, although the energy at the maximum is in reasonable agreement with what would be expected from the calculations, as can be seen in Fig. 3. In the case of Si:Ga, two peaks occur in the range of interest, we thus cannot unambiguously assign one of them to Δ_0^a; on the basis of the general systematics (see Fig. 3) we assign the lower one (10 meV) to Δ_0^a. More work should be done to clarify the origin of these features which appeared in all samples investigated (epi-layers and bulk). Tentatively, however, we assign the additional peaks observed for Ga to disorder activated TA phonons (DATA). The shoulder in the Si:In spectrum at 8 meV is likely to be due to vibronic structure (dynamic Jahn–Teller effect) [19]. Our experimental data are compared with the calculation in Fig. 3 where we also show some results of electric-dipole spin resonance (EDSR) measurements [2,3]. The open circles represent the EDSR data, while the open squares stand for the Raman results. The theoretical curve describes the trend of the experimental data, namely a reduction of Δ_0^a with increasing E_b^a, although considerable differences exist between the magnitudes of experimental and calculated splittings. These differences are less conspicuous if we look at the data in terms of the quenching of the Γ_8^+–Γ_7^+ band splitting which amounts to 44 meV for the experimental value in the case of the Zn$^-$ acceptor and 41 meV for the calculated one.

4. Diamond

Similar calculations have been performed for acceptor states in diamond [20]. While lending support to the value of $\Delta_0 = 13$ meV calculated ab initio with the relativistic LMTO method [21] they lead to a calculated value of $\Delta_0^a = 3.9$ meV, in reasonable agreement with the 2 meV observed experimentally for substitutional boron, the only clearly identified acceptor. Because of the value Δ_0^{exc} reported for the splitting of the edge (indirect) excitons in diamond, we also performed a calculation of this splitting with a method similar to that used for acceptor levels, modified so as to take into account the indirect nature of the edge exciton. We obtained the value $\Delta_0^{exc} = 8.6$ meV and rather good agreement with the experimental one ($\simeq 7$ meV).

5. Conclusions

We have presented a calculation for the Γ_8–Γ_7 spin–orbit splitting of substitutional acceptor levels in silicon and diamond, using a Green's function formalism with a full-zone $\boldsymbol{k} \cdot \boldsymbol{p}$ Hamiltonian, and a Slater–Koster ansatz to describe the acceptor–hole interaction. We have also reported Raman measurements for the spin–orbit splitting of acceptor states in Si : X samples (X = B, Al, Ga, In) which reproduce the previously known splittings in the case of B and In. Two structures are observed in the case of Si : Ga which are not completely understood yet. For In, structure of possible Jahn–Teller origin has been also observed. Our calculation shows a reasonable agreement with the experimental quenching from the free band Γ_8^+–Γ_7^+ splitting of that of the acceptors in the case of silicon, although this simple model does not yield a quantitative description. In the case of diamond the observed quenching of 11 meV for boron, i.e. from 13 to 2 meV, can be also understood with our theory, which yields a quenching of 9 meV. A similar procedure has been applied for the free indirect exciton [20].

Acknowledgements

References

[1] G.B. Wright, A. Mooradian, Phys. Rev. Lett. 18 (1967) 608.
[2] H. Schroth et al., Phys. Stat. Sol. B 210 (1998) 747.
[3] H. Schroth, Doctoral Dissertation, University of Stuttgart, 1999, unpublished.
[4] R. Sauer, W. Schmid, J. Weber, Solid State Commun. 27 (1979) 705.
[5] S. Zwerdling, K.J. Button, B. Lax, L.M. Roth, Phys. Rev. Lett. 4 (1960) 173.
[6] C.J. Rauch, in: A.C. Stickland (Ed.), Proceedings of the International Conference on the Physics of Semiconductors, Exeter, 1962 (The Institute of Physics and the Physical Society, London, 1962), p. 276.
[7] E.C. Lightowlers, A.T. Collins, J. Phys. D 9 (1976) 951.
[8] P.A. Crowther, P.J. Dean, W.F. Sherman, Phys. Rev. 154 (1967) 772.
[9] D.M.S. Bagguley, G. Vella-Coleiro, Proceedings of the International Conference on the Physics of Semiconductors, Kyoto, 1966 (J. Phys. Soc. Japan 21 (Suppl.) (1966) 244).
[10] H. Sternschulte, T.R. Anthony et al., Mat. Sci. Forum 258–263 (1997) 757.
[11] H. Kim et al., Phys. Rev. B 57 (1998) 15 315.
[12] N.O. Lipari, A. Baldereschi, Solid State Commun. 25 (1978) 665.
[13] W. Kohn, in: F. Seitz, D. Turnbull (Eds.), Solid State Physics, Vol. 5, Academic, New York, 1957, p. 257.
[14] M. Cardona, F.H. Pollak, Phys. Rev. B 142 (1966) 530.
[15] G. Lehmann, M. Taut, Phys. Stat. Sol. B 54 (1972) 469.
[16] D.M. Ceperly, B.J. Alder, Phys. Rev. Lett. 45 (1980) 566.
[17] U. Schmid, N.E. Christensen, M. Cardona, Phys. Rev. B 41 (1990) 5919.
[18] J.M. Cherlow, R.L. Aggarwal, B. Lax, Phys. Rev. B 7 (1973) 4547.
[19] J. Maier, E. Sigmund, Phys. Rev. B 34 (1986) 5562.
[20] J. Serrano, M. Cardona, T. Ruf, to be published.
[21] M. Willatzen, M. Cardona, N.E. Christensen, Phys. Rev. B 50 (1994) 18 054.
[22] O. Madelung, M. Schulz, H. Weiss (Eds.), Landolt-Börnstein, New Series III, Vol. 22a, Springer, Berlin, Heidelberg, 1987, p. 14.
[23] N. Troullier, J.L. Martins, Phys. Rev. B 43 (1991) 1993.