Origin of the Residual Acceptor Ground-State Splitting in Silicon

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The residual ground-state splitting of acceptors in high-quality silicon has been studied intensely by different experimental techniques for several decades. Recently, photoluminescence studies of isotopically pure silicon revealed the ground-state splitting to result from the random distribution of isotopes in natural silicon. Here we present a new model that explains these surprising experimental results, and discuss the implications for acceptor ground-state splittings observed in other isotopically mixed semiconductors, as well as for the acceptor ground state in semiconductor alloys.

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In a recent study [1] of the photoluminescence (PL) spectra of acceptor bound excitons in isotopically pure ^{28}Si, the so-called “residual” or “intrinsic” splitting of the neutral acceptor (A^0) ground state was surprisingly found to vanish. As detailed in [1], these reproducible A^0 splittings had been studied extensively in Si and other semiconductor materials, using a wide variety of experimental techniques, since their discovery by Neubrand in the EPR spectra of A^0 in Si [2,3]. Prior to the discovery [1] of the isotopic origin of these splittings, they were ascribed either to random (but sample-independent) perturbations of unknown origin [3–5], or to a spontaneous lowering of the A^0 symmetry by a Jahn-Teller effect [6–8]. In this Letter we introduce a model for the A^0 splittings observed in natural Si (hereinafter Si) which produces good agreement with the observed splitting distributions for the B, Al, Ga, and In acceptors without requiring any adjustable parameters. The model should also apply to the A^0 ground state in other isotopically mixed semiconductors, and even in semiconductor alloys, where much larger splittings are predicted.

The unperturbed acceptor ground state is a fourfold degenerate state belonging to the Γ_8 representation of the tetrahedral (T_d) group, which can be split by a variety of symmetry-lowering perturbations into a pair of twofold degenerate states. Thus, a random distribution of perturbations, such as strain fields from dislocations and/or impurities, acting on the A^0 ground state breaks the symmetry and produces a distribution of doublet splittings. Given that Si is a mixture of stable isotopes (92.23% ^{28}Si, 4.67% ^{29}Si, and 3.10% ^{30}Si), the isotopic randomness present in Si provides a perturbation which breaks the T_d symmetry at some level, so it is important to consider why isotopic randomness was not in the past suggested as a possible mechanism for providing the random but sample-independent perturbations which were postulated [3–5] as one of the explanations for the residual A^0 splittings.

We believe that the perturbations due to the randomness of isotopic substitutions present in Si were in the past simply assumed to be far too small to account for the observed A^0 splittings. Previous calculations [3–5], which successfully accounted for the larger A^0 splittings due to intentional impurities such as C and O, were based on the long-range strain fields introduced by relatively dilute concentrations of these highly perturbing defects. Using this framework, the A^0 splittings expected from the strain fields resulting from the random isotopic substitution in Si would be orders-of-magnitude too small to account for the observed residual splittings. It is worth considering here the actual size of the effect — the A^0 splitting for the Al acceptor in Si is 0.1 cm^{-1}, a sizable fraction of the *entire* band-gap shift of 0.92 cm^{-1} between Si and ^{28}Si [9,10], even though the splitting arises only from the *statistical fluctuations* in the isotopic composition present in Si, and the A^0 binding energy is less than one-tenth of the band-gap energy.

We adopt here a new approach to this problem, in which we ignore the negligibly small strain effects of isotopic substitution, but consider instead the effect of isotopic composition on the band-gap energy, or more specifically, the energy of the valence-band edge since we are dealing with acceptor states. In Si, the isotopic dependence of the low temperature band-gap energy, and the related shifts in the conduction and valence-band edges, are known to arise predominantly from the renormalization of the energies by the electron-phonon interaction, via the mass dependence of the amplitudes of the zero-point fluctuations [1,10]. On average, this results in a renormalization energy which varies as the inverse square root of the average isotopic mass, M_{av}. However on small length scales, such as the effective Bohr radius of an exciton or impurity, there will be significant statistical fluctuations of the actual isotopic composition around the average value, and the resulting fluctuations in the local band-gap energy have already been shown to be the principal broadening mechanism responsible for bound exciton PL linewidths in Si [9].

Here we treat the ^{29}Si and ^{30}Si present in Si as "isotopic impurities" randomly substituted into the perfect ^{28}Si lattice, and consider the effect of these substitutions on the A^0 ground state by having each ^{29}Si (^{30}Si) impurity introduce a local perturbing potential equal to the energy difference between the valence-band edge in ^{29}Si (^{30}Si) and pure ^{28}Si. We ignore a possible small dependence of the acceptor ground-state binding energy on isotopic composition arising from the isotopic dependence of the hole effective mass and the dielectric constant. This effect has been studied for the B acceptor in ^{12}C vs ^{13}C diamond [11,12], but would make only a negligible correction to the present calculation.

The A^0 ground state in Si is composed of Bloch states from the top of the valence band, which is at the Γ point of the Brillouin zone. The valence-band state at this point is fourfold degenerate and transforms according to the Γ_8^+ representation of the double point group O_h^7 (the cubic O_h^7 symmetry is lowered to T_d at the impurity site). The spin-orbit split-off twofold degenerate Γ_7^+ state lies 44 meV lower. Since the ground-state binding energy of the shallow acceptor in silicon is comparable to or greater than the spin-orbit splitting, it is important to use a Hamiltonian which takes the split-off band into account. In order to include the contributions from both spin-orbit split valence bands, we start with the 6×6 effective-mass Hamiltonian as in Ref. [13].

In the absence of isotopic disorder the neutral acceptor Hamiltonian in the Luttinger effective-mass model is given by

$$H^0 = H^{\mathrm{BL}} - \frac{2}{3}\left(\frac{1}{2} - I \cdot S\right)\frac{\Delta}{\mathcal{R}^*} + V(r) + U(r), \qquad (1)$$

where $\mathcal{R}^* = e^4 m^*/2\hbar^2\epsilon_0^2$ is the effective Rydberg with $m^* = m/\gamma_1$ the effective mass and γ_1 the Luttinger constant. In this model the spherical and cubic contributions, the spin-orbit splitting (proportional to Δ), and the impurity potential $V(r) + U(r)$ have been included. The Hamiltonian H^{BL} is that introduced by Baldereschi and Lipari [14,15], and Δ is the spin-orbit split-off energy. $V(r)$ describes the screened Coulomb contribution of the negatively charged acceptor center and $U(r)$ describes further central cell corrections for nonisocoric impurities as discussed by Lipari, Baldereschi, and Thewalt [16], and Binggeli and Baldereschi [17].

We model the effects of the isotopic impurities on the acceptor ground state by introducing an additional term H^{iso} into the Hamiltonian H of the system, $H = H^0 + H^{\mathrm{iso}}$. H^{iso} acts only at the position of the sites of the silicon crystal that are occupied by ^{29}Si or ^{30}Si isotope atoms. Their effect on the hole energy at each of those sites is assumed to be proportional to the shift of the top of the valence band in pure ^{29}Si and pure ^{30}Si, respectively, relative to its position in pure ^{28}Si.

In the absence of isotopic impurities the fourfold degenerate acceptor ground-state wave functions $\Psi_\sigma^0(\vec{k})$, satisfy the Schrödinger equation

$$H^0\Psi_\sigma^0(r) = E^0\Psi_\sigma^0(r), \qquad \sigma = 1, \ldots, 4. \qquad (2)$$

These eigenstates are evaluated variationally in Ref. [13] and can be written in the form

$$\Psi_\sigma^0(r) = \sum_{l,m,j,j_z} f_{l,m,j,j_z}(r) Y_{l,m}(\vartheta, \varphi)\Phi_{j,j_z}, \qquad (3)$$

where Φ_{j,j_z} are the six Bloch functions at the valence-band extrema, $Y_{l,m}(\vartheta, \varphi)$ the spherical harmonics, and $f_{l,m,j,j_z}(r)$ radial functions [13].

We diagonalize the Hamiltonian H that includes the effects of isotopic disorder in the basis of states $\Psi_\sigma^0(r)$. To do this we discretize the wave functions $\Psi_\sigma^0(r)$ on the atomic sites $r = r_i$ of the silicon crystal, and parametrize the effects of the ^{29}Si and ^{30}Si isotopic impurities in $H^{\mathrm{iso}} = \sum_i H_i^{\mathrm{iso}}$ according to the simple ansatz:

$$\langle \Phi_{j,j_z}(r_i)|H_i^{\mathrm{iso}}|\Phi_{j',j_z'}(r_{i'})\rangle = \delta_{j,j'}\delta_{j_z,j_z'}\delta_{i,i'}W_i, \qquad (4)$$

where W_i is given by

$$W_i = \begin{cases} 0 & \text{for } ^{28}\mathrm{Si}, \\ \Delta E^{29} & \text{for } ^{29}\mathrm{Si}, \\ \Delta E^{30} & \text{for } ^{30}\mathrm{Si}, \end{cases} \qquad (5)$$

and ΔE^{29} (ΔE^{30}) represents the energy shift of the top of the valence band of ^{29}Si (^{30}Si) relative to ^{28}Si. Note that the ansatz simply shifts the energy of each Bloch state Φ_{j,j_z} locally by an amount W_i that depends on which silicon atom occupies site i. However, H^{iso} mixes the unperturbed eigenstates Ψ_σ^0 and therefore results in a splitting of the acceptor ground state for each configuration of the isotopic disorder.

In this way the perturbation lifts the fourfold degeneracy, splitting the ground state into a pair of twofold degenerate states, which is mostly due to the effect of the off-diagonal elements of the interaction Hamiltonian matrix $\langle \Psi_\sigma^0|H^{\mathrm{iso}}|\Psi_\mu^0\rangle$. The size of the splitting between the energy eigenvalues is determined by the amplitudes of the unperturbed acceptor wave functions $\Psi^0(r_i)$ at the sites i of the isotopic impurities and by the isotopes involved. As a result, the isotopic impurities in the immediate vicinity of the acceptor site make the major contribution to the ground-state splitting. Besides splitting the eigenvalues, the perturbation causes also a shift of the center of mass of the split pair, which on average is equal to the difference in the valence-band edge energy between Si and ^{28}Si.

Before proceeding we note that a value for ΔE^{29} (ΔE^{30}), which is the valence-band offset in a heterostructure between pure ^{29}Si (^{30}Si) and ^{28}Si, can be obtained

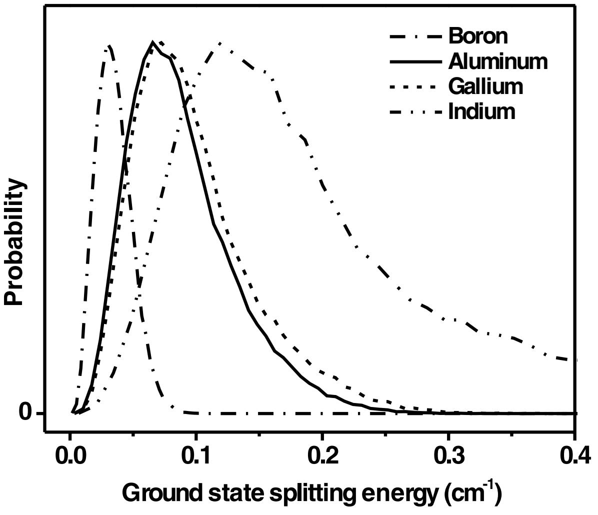

FIG. 1. The calculated statistical distribution of the ground-state splittings for 40 000 configurations of random distributions of the isotopes around the acceptor site. The most frequent values for each acceptor (the most probable value for the ground-state splitting) are listed in Table I.

from calculations of the temperature dependence of electronic band states [18]. The required data are summarized in Fig. 5 of Ref. [18]. In order to obtain band offsets, we must refer the energy of the top of the valence bands of the two constituents to the same zero of energy. This can be achieved by using the work functions which are represented by $-\phi_p$ in that figure. The electron-phonon renormalization of $-\phi_p$ at $T = 0$ K (i.e., the effect of the zero-point vibrations on the corresponding electronic states) is found to be 43 meV for Si, by extrapolating to $T = 0$ the linear part of $-\phi_p$ vs temperature. Since the renormalization energy is proportional to $M^{-1/2}$, we can estimate $\Delta E^{29} \simeq 6.0$ cm^{-1} and $\Delta E^{30} \simeq 11.8$ cm^{-1}. We note that these values are equivalent to stating that 75% of the isotopic dependence of the band-gap energy results from a shift of the valence-band edge, and 25% from an opposite shift of the conduction band edge.

Using this model we compute for the acceptors B, Al, Ga, and In in Si the eigenvalues of the ground state for 40 000 different configurations of random distribution of isotopes around the acceptor site, with an average composition corresponding to Si. At a distance of 50 unit cells from the acceptor site the amplitude of the acceptor wave function Ψ^0 is very small, and as a result, the contribution of the isotopes at larger distances will be insignificant and therefore these have not been included. The difference between the two pairs of Kramers degenerate eigenvalues defines the splitting of the ground state. Each random distribution of the ^{29}Si and ^{30}Si isotopes around the acceptor site leads to a different value of the ground-state splitting, creating a distribution of splittings that peaks at the most probable value, which should correspond to the experimentally observed splitting.

TABLE I. The measured and calculated values of the ground-state splitting (GSS) for B, Al, Ga, and In (listed in order of increasing binding energy).

Acceptor	Experimental GSS in units of cm^{-1}	Theoretical GSS in units of cm^{-1}
Boron	0.043[a]	0.031
Aluminum	0.1[b]	0.07
Gallium	0.1[b]	0.07
Indium	0.15[b] and 0.11–0.16[a]	0.12

[a] Measured by phonon spectroscopy [4,5].
[b] Measured by PL spectroscopy [7,8].

The calculated statistical distribution of the splittings for the B, Al, Ga, and In acceptors in silicon is shown in Fig. 1. The most probable values for the ground-state splitting obtained from these calculated distributions are listed in Table I together with the experimentally observed values. For deeper acceptors the hole is more strongly localized near the impurity core. Therefore $\langle \Psi_\sigma^0 | H^{\rm iso} | \Psi_\mu^0 \rangle$ samples smaller numbers of lattice sites, and is thus more sensitive to local fluctuations. This results in larger ground-state splittings (and broadenings) for deeper acceptors than for shallower acceptors. Comparing our theoretical results with the experimental data, we see that the trend with acceptor binding energy is excellent, and that the model calculation reproduces the observed splittings to within 30%. It should also be noted that the shape of the splitting distributions shown in Fig. 1 is in good agreement with the distributions as determined by phonon absorption spectroscopy [4,5].

The calculated distribution of the ground-state splittings for the In acceptor shows a second (much weaker) maximum, peaking near 0.65 cm^{-1}. We note that the PL and phonon spectroscopy results show no evidence for this secondary, larger splitting. After removing the contribution originating from the four nearest neighbors from H$^{\rm iso}$, the second maximum vanishes. This suggests that a

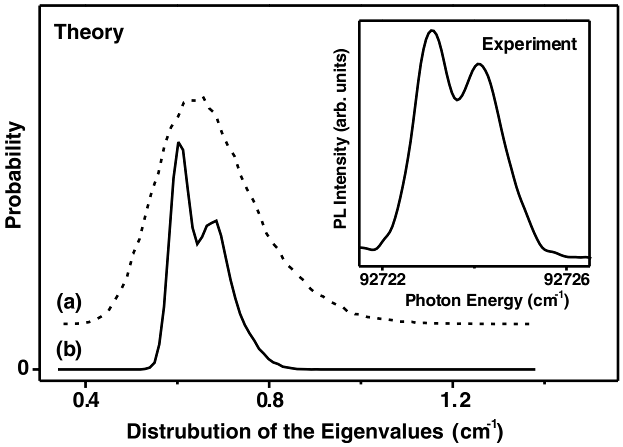

FIG. 2. (a) The statistical distribution of the calculated eigenvalues for Al. (b) After removing 75% of the broadening, the doublet splitting is observable. The inset shows the doublet splitting observed in the PL spectra, on the same energy scale.

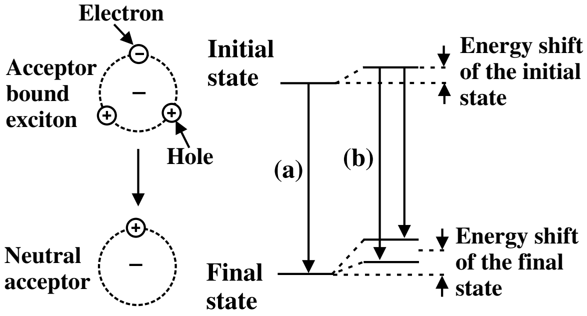

FIG. 3. Schematic of the photoluminescence transition. (Left) The electron and hole in the bound exciton (initial state) recombine leaving behind the neutral acceptor in its ground state (final state). In an isotopically pure crystal the ground state is fourfold degenerate, and as a result, the transitions would be singlets [right (*a*)], while the perturbation caused by the isotopic impurities lifts the degeneracy of the ground state [right (*b*)]. It also causes an energy shift of the ground state, which leads to additional broadening of the transitions. The initial state bound exciton two-hole state is also shifted, but by a smaller amount than the ground state.

six-band description of the unperturbed wave functions Ψ_σ^0 for the deeper acceptor In at such short distances from the acceptor site may not be sufficient [19], or that our model may not be adequate in this regime.

Although isotopic disorder results in a splitting of the acceptor ground state as is seen in Fig. 1, the statistical distribution of calculated eigenvalues shows a single broad peak [see curve (*a*), Fig. 2 for Al]. This is due to the fact that in addition to splitting the acceptor ground state, the isotopic perturbation shifts the center of mass of the split pairs, causing a broadening. By contrast, the corresponding PL spectrum (the inset, Fig. 2) shows a partially resolved doublet. We observe the doublet, and not just a broad single line, in PL because the initial state of the transitions, the bound exciton two-hole state, is shifted by the local isotopic composition in the same direction as the final state, the acceptor ground state. This leads to a partial cancellation of the broadening in the PL spectra. This scenario is shown schematically in Fig. 3. It should also be mentioned here that the initial two-hole state has Γ_1 symmetry, and as a result, the perturbation cannot split this level. Since in the initial state, the two-hole wave function is less localized than the A^0 wave function, the shift induced by the isotopic randomness is expected to be smaller there. By using the shift of the eigenvalue pairs from the center of the distribution as a fit parameter, and by reducing this shift by 75%, we are able to reproduce the observed PL doublet, as shown in Fig. 2(b). We emphasize that the energy splittings are not altered during this fitting procedure.

In conclusion, we have presented a new theoretical model that explains both the magnitude and the distribution of the acceptor ground-state splitting caused by the isotopic disorder present in Si. The variation of the size of the most probable ground-state splitting between different acceptors obtained from the calculated distributions agrees well with the experimentally observed values for all acceptor species, and the size of the splittings are reproduced to within 30%. Exactly the same model could be applied to the effect on the acceptor ground state of the randomness of chemical substitutions in semiconductor alloys, where much larger splittings would be expected due to the much larger size of the valence-band offset obtained by chemical, as opposed to isotopic, substitutions. Finally, in view of these results we feel that it would be highly desirable to repeat in an isotopically pure diamond earlier studies [20] of the splitting of the B acceptor ground state in diamond, which were explained in terms of a Jahn-Teller effect.

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