PHYSICAL REVIEW B **68**, 121201(R) (2003)

Dependence of the ionization energy of shallow donors and acceptors in silicon on the host isotopic mass

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(Received 23 May 2003; published 16 September 2003)

A comparison of the infrared absorption spectra of isotopically pure ^{28}Si and ^{30}Si reveals small shifts in the transition energies for both the shallow donor phosphorus and the shallow acceptor boron. The impurity binding energies for both species are slightly larger in ^{30}Si than in ^{28}Si. A similar effect was earlier observed for the boron acceptor in ^{13}C vs ^{12}C diamond, and later explained as resulting from a change in the ground and excited state binding energies due to the dependence of the hole effective mass on the host isotopic composition. Here we show that the results for both donors and acceptors in Si can be explained by the same mechanism, with the additional inclusion of the isotopic dependence of the dielectric constant.

DOI: 10.1103/PhysRevB.68.121201 PACS number(s): 78.30.−j, 71.55.−i

I. INTRODUCTION

The effects of the isotopic composition of the host material on the optical and electronic properties of semiconductors have received much attention, as summarized in several comprehensive reviews.[1–3] Most of this work has focused on effects which are controlled by the average composition, but more recently the availability[4] of high quality crystals of isotopically pure Si has revealed effects which are controlled not by the average composition, but rather by the randomness of the composition present in crystals having the natural isotopic abundance. First it was shown[5] that the isotopic randomness present in natural Si (hereinafter Si) produces an effective local variation in the band gap energy, which in turn results in an inhomogeneous broadening that is the dominant factor in determining the observed photoluminescence (PL) linewidths of the no-phonon transitions of shallow donor and acceptor bound excitons (BE). Next it was shown[6] that the isotopic randomness present in Si is the origin of the much studied ‘‘residual’’ ground state splitting of shallow acceptor impurities in Si. The surprisingly large size of this effect was explained by detailed modeling using accurate acceptor ground state wave functions, split by the fluctuations of the isotopic composition around individual acceptors via the dependence of the valence band edge energy on isotopic composition.[7] Finally, it has recently been shown[8] that the isotopic randomness present in Si produces a significant inhomogeneous broadening of many of the long-studied ground state to excited state infrared absorption transitions of shallow donors and acceptors. Thus, many of these transitions are much sharper in isotopically pure Si than in natural Si, and many of the homogeneous linewidths are much narrower than had been previously assumed.

Here we consider a different aspect of the infrared absorption spectrum of shallow donors and acceptors in isotopically modified Si that is not dependent on isotopic disorder. We show that the absorption transitions of the shallow acceptor boron (B) and the shallow donor phosphorus (P) have slightly different energies in ^{30}Si as compared to ^{28}Si, consistent with slightly larger impurity binding energies in ^{30}Si. A similar effect of the host isotopic composition was previously reported for the B acceptor in ^{13}C vs ^{12}C diamond.[9] It was later shown[10] that this could be most readily understood as resulting from changes of the ground state and excited state binding energies due to a small dependence of the hole effective mass on the host isotopic composition. We show that the shifts of the transition energies for both B and P between ^{30}Si and ^{28}Si can be explained by the same mechanism, with the inclusion of the dependence of the dielectric constant on the host isotopic composition, which made only a negligible contribution in diamond. In particular, the calculation explains our observation that the host isotope effect is considerably larger for shallow acceptors than for shallow donors, even though the binding energies of B and P are almost equal.

II. EXPERIMENTAL METHOD

The infrared absorption spectra shown here were obtained from ^{28}Si samples enriched to 99.896%, cut from a crystal used previously for photoluminescence[5,6,11] and absorption[8] studies, and from a ^{30}Si sample containing 98.68% ^{30}Si $+0.62\%$ ^{29}Si$+0.70\%$ ^{28}Si, which was also used in previous PL studies.[11] The ^{28}Si sample contained P and B at concentrations of 7×10^{13} cm^{-3} and 7×10^{14} cm^{-3}, respectively, while the ^{30}Si sample is dominated by B at approximately 2×10^{15} cm^{-3}, with roughly ten times less P (the PL method[12] for determining shallow impurity concentrations becomes difficult at these relatively high concentrations). Identical B and P absorption results were also obtained from a second sample, enriched to 99.94% ^{28}Si, and containing slightly lower concentrations of B and P. In addition to its higher dopant concentrations, the ^{30}Si sample is also known[11] to suffer from random internal strain fields, likely due to carbon impurities,[13] which cause a broadening and splitting of the P BE photoluminescence line.

The samples were freely suspended in a sample chamber filled with superfluid He and sealed with polypropylene win-

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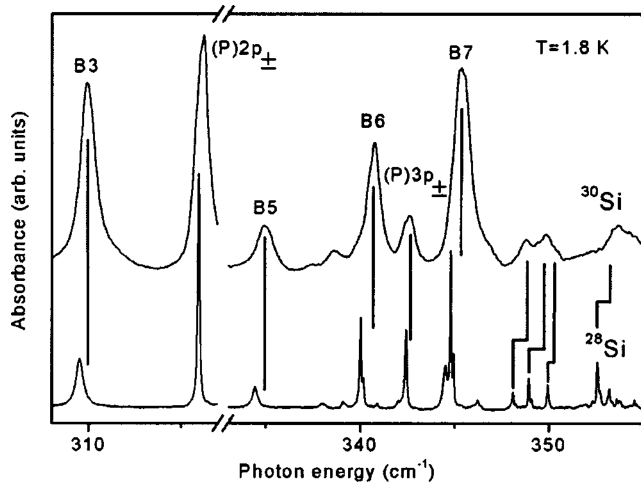

FIG. 1. Several infrared absorption lines of the B acceptor and P donor in ^{28}Si are compared with the same transitions in ^{30}Si. The energy shift of the lines with the host isotopic composition is seen to be larger for B than for P. The vertical lines centered at the ^{30}Si transition energies aid in visualizing these shifts. Some of the stronger transitions in the ^{30}Si crystal were saturated as a result of higher impurity concentrations, and hence are not shown. The reasons for the large broadening of the ^{30}Si transitions are discussed in the text. The B transitions are labeled using the standard[14] line numbering scheme.

dows. Spectra were collected with a Bomem DA8.02 Fourier transform interferometer using a silicon composite bolometer at 1.6 K, and Mylar beamsplitters. The instrumental resolution used for these measurements was 0.02 cm^{-1}. Some of the stronger transitions were saturated in the more heavily doped ^{30}Si sample, but, as only one sample of this rare material was available, producing a thinner sample was not practical.

III. RESULTS AND DISCUSSION

The infrared absorption spectra from the ^{28}Si and ^{30}Si crystals are compared in Fig. 1, with vertical lines drawn to emphasize the small energy shifts between the transitions. The B transitions are labeled with a line numbering scheme used in earlier[14] infrared absorption studies of B in Si. As reported previously,[8] the transitions in the ^{28}Si sample are very sharp, many of them being much narrower than in the best spectra ever reported for Si. Indeed, many of the B transitions in ^{28}Si (lines B6 and B7 in Fig. 1 for example) reveal extra structure not resolvable in Si spectra, which has been explained[8] as resulting from a difference of 0.15 cm^{-1} in the ground state binding energy of the two stable B isotopes, ^{10}B and ^{11}B. Unfortunately, transitions in the ^{30}Si crystal show significant broadening, most likely due to both concentration effects and C contamination. As a result, the uncertainty in determining the impurity line positions in this sample is significant. In addition, some of the stronger transitions were saturated in the ^{30}Si sample. Table I summarizes all of the ^{28}Si to ^{30}Si line shifts for B and P that could be determined from these spectra. Since the splitting between ^{10}B and ^{11}B is much too small to be resolved in the ^{30}Si spectrum, the B results should be considered to apply to the average over the natural B isotopic abundance (for a given transition, the shift between ^{28}Si and ^{30}Si should in any case be essentially identical for ^{10}B and ^{11}B).

As observed for B in diamond,[9] and expected from the model,[10] the isotopic shift in the transition energies increases with the energies of the transitions, or in other words, with decreasing final state binding energy. In order to give an accurate value for the shift in the ground state binding energy, the highest observable lines for each impurity (B7 for the B acceptor and $3p_{\pm}$ for the P donor) were used, together with a simple extrapolation assuming that the size of the isotope shift scales linearly with the binding energy of the state involved, giving shifts of the ground state binding energy of 0.73 ± 0.1 cm^{-1} for the B acceptor and 0.32 ± 0.1 cm^{-1} for the P donor (in both cases the binding energies are larger in ^{30}Si than in ^{28}Si).

IV. THEORY

The basis of our discussion is the usual equation for the ionization energy of shallow (hydrogenic) levels in semiconductors:

$$E_B = Ry \cdot m^* / \varepsilon_0^2, \tag{1}$$

where Ry is the hydrogen Rydberg, ε_0 is the static dielectric constant (~11.4 for Si) and m^* is the appropriate average effective mass (in units of the free electron mass) to be discussed below. While Eq. (1) is too simple to provide accurate values of impurity binding energies, it can be used to estimate the shift in E_B with isotopic composition from the dependence on m^* and ε_0, together with the known value of E_B from natural Si, which we take to be ~ 340 cm^{-1} for both B and P.

The influence of the average isotopic mass M on ε_0 scales donor and acceptor binding energies identically. For acceptors in diamond, the effect due to ε_0 has been shown to be negligible compared with the effect due to m^*.[10] For silicon, however, we show here that both contributions to the E_B shift are important. The difference in ε_0 between ^{30}Si and

TABLE I. Energy shifts (in cm^{-1}) for the P donor and B acceptor transitions between ^{28}Si and ^{30}Si, and the extrapolated difference in ground state binding energy E_B.

Transition	(P) $2p_{\pm}$	(P) $3p_{\pm}$	B3	B5	B6	B7	P E_B	B E_B
Energy in ^{28}Si minus energy in ^{30}Si (cm^{-1})	-0.20 (±0.1)	-0.30 (±0.1)	-0.43 (±0.1)	-0.53 (±0.1)	-0.65 (±0.1)	-0.68 (±0.1)	-0.32 (±0.1)	-0.73 (±0.1)

^{28}Si can be estimated from the zero temperature renormalization of ε_0 by the electron-phonon interaction, which is known to be proportional to $M^{-1/2}$.[15] This renormalization is easily obtained from the temperature dependence of ε_0, which can be written as[15]

$$\Delta\varepsilon_0 = AM^{-1/2}[1+2n_B(\langle\omega\rangle/T)], \tag{2}$$

where A is a constant, n_B is the Bose-Einstein occupation factor and $\langle\omega\rangle$ an average phonon frequency in the same units as the temperature T. Here we take, for silicon, $\langle\omega\rangle = 430$ K,[16] a reasonable value since its maximum phonon frequency is 743 K. Equation (2) allows us to determine the zero-point renormalization of ε_0, $AM^{-1/2}$, and the difference in this renormalization between ^{30}Si and ^{28}Si, which we designate as $\delta\varepsilon_0$, from the normalized slope of ε_0 vs T measured at high T, which is $d\varepsilon_0/\varepsilon_0 dT = 8.6\times10^{-5}$ K^{-1}.[17] We thus find $\Delta\varepsilon_0(T=0)=0.22$ (in reasonable agreement with the *ab initio* calculations of Ref. 18) and $\delta\varepsilon_0/\varepsilon_0 = +6.4\times10^{-4}$ (δ represents the value for $M=28$ minus that for $M=30$). Using Eq. (1) and a typical value of $E_B = 340$ cm^{-1} we calculate the corresponding isotopic change $\delta E_B = -0.43$ cm^{-1} for both B and P, resulting from the isotopic dependence of ε_0.

We now estimate the dependence of m^* on M. This dependence is related to the gap which determines m^* according to $\boldsymbol{k}\cdot\boldsymbol{p}$ perturbation theory.[19] This theory relates m^* to a direct energy gap at the corresponding point of the Brillouin zone and the square of a matrix element of the linear momentum operator. The latter is assumed to be independent of the perturbation under consideration, whereas the former can often be measured by optical spectroscopy techniques.[11,20] It can also be calculated using semiempirical band structures.[21,22] Here we use the extensive calculations of the zero-point band renormalizations given in Ref. 21 for several conduction and valence band extrema of silicon.

We first estimate the effect of the zero-point renormalization on the m^* of donors, i.e., at the conduction band minima which occur, for Si, near the X-point of the Brillouin zone. The transverse mass, $m_t^* = 0.19$, is determined by the smallest direct gap at the Δ_1 extrema which is about 4.3 eV. From Ref. 16 we obtain the zero-point renormalization of this gap to be -20.77 meV (the renormalization is negative; all gaps considered here increase with increasing isotopic mass). This yields an effective mass renormalization of

$$\Delta m_t^*/m_t^* = -20.77\times10^{-3}/4.3 = -4.8\times10^{-3}. \tag{3}$$

The longitudinal mass, $m_l^* = 0.91$, is determined by larger gaps (≈ 10 eV) and by the free electron term, a summand equal to 1 neglected here, for simplicity, for all masses under consideration. Hence, m_l^* can be assumed to be independent of M. This implies that the isotope effect on E_B can be calculated by using in Eq. (1) $(2/3)\delta m_t^*/m_t^*$ instead of $\delta m^*/m^*$. We thus obtain for the donor P a contribution to the change in E_B with isotopic mass equal to -0.038 cm^{-1}. Adding to this value the contribution of the change in ε_0, -0.43 cm^{-1}, we find the total $\delta E_B = -0.47$ cm^{-1}, in acceptable agreement with the experimental result (-0.32 ± 0.1 cm^{-1}).

We calculate next the contribution to δE_B resulting from changes in m^* for acceptors. The calculation is complicated by the degeneracy of the top Γ_8 valence band and the concomitant existence of a light hole and a heavy hole band. In the case of diamond, treated in Ref. 10, it was shown that only the so-called E_0' gap contributes to m^*. For silicon, two of the gaps that determine the hole masses are close in magnitude, the E_0' gap ($=3.3$ eV) and the E_0 gap ($=4.2$ eV). The zero point renormalizations of these gaps can be read from Table 4.I of Ref. 16 to be 75 and 102 meV, respectively. Hence the *relative* changes of both gaps are nearly the same. The relative gap renormalizations will, in both cases, be taken to be 2.3×10^{-2}.

The simplest approximation one can make to calculate the E_B of acceptors in silicon is the so-called one-spherical-band approximation (Eqs. 4.43 and 4.45 of Ref. 19). Within this approximation $m^* = (\gamma_1)^{-1}$, where γ_1 is one of the Luttinger parameters, γ_1, γ_2, and γ_3. Within the assumption of equal relative zero-point renormalizations of the gaps E_0 and E_0', the parameter γ_1 is also renormalized the same way (except for a change in sign). In this case the contribution of m^* to the dependence of E_B on isotopic mass becomes -0.27 cm^{-1} for B. Adding to this value the contribution of ε_0 we find the total result $\delta E_B = -(0.27+0.43) = -0.70$ cm^{-1}, in excellent agreement with the experimental result (-0.73 ± 0.1 cm^{-1}).

In spite of the good agreement between theory and experiment just obtained, one may object that the spherical approximation is not realistic for acceptors in silicon: the light hole and heavy hole masses are far from being equal (0.15 and 0.50, respectively, Ref. 19, p. 75). However, to a first approximation, their difference does not change our estimate of the effect of isotopic mass on E_B. For silicon, it is easy to show that the following equation takes into account rather well the difference between light and heavy hole masses:

$$m^* = \left\langle \frac{1}{2}\left[\left(\frac{1}{\gamma_1(1+\mu)}\right)^{3/2} + \left(\frac{1}{\gamma_1(1-\mu)}\right)^{3/2}\right]\right\rangle^{2/3}, \tag{4}$$

where $\mu = 2(3\gamma_3+2\gamma_2)/5\gamma_1$. Equation (4) represents the average density of states effective mass of the holes which determine the acceptor binding energy within the Koster-Slater model (see Sec. 4.3.2 of Ref. 19). Equation (4) also reproduces fairly well the more exact acceptor binding energy, calculated by solving the appropriate coupled effective mass equations[23] for the spherical approximation ($\mu\neq0$). Since γ_2 and γ_3 change with isotopic mass in the same way as γ_1, the presence of μ in Eq. (4) does not alter the dependence of m^* on isotopic mass.

V. CONCLUSIONS

We have observed shifts in the transition energies obtained from infrared spectra for the shallow acceptor B and the shallow donor P between ^{30}Si and ^{28}Si. From these shifts we have determined the dependence of the ground state

binding energies of these two impurities on the average host isotope mass. These results are well explained by calculations based on the effective mass binding energies, which are altered by the host isotope dependence of the electron and hole effective masses, together with the host isotope dependence of the dielectric constant. The shifts between pure ^{28}Si and pure ^{30}Si are quite small, supporting the earlier assertion that this effect would make only a negligible contribution to the inhomogeneous isotope broadening recently shown to be present in the infrared impurity absorption spectra of natural Si.[8]

ACKNOWLEDGMENTS

This work was supported by NSERC. The authors acknowledge useful conversations with E. E. Haller and H.-J. Pohl. The samples used in this work were acquired from VITCON Projectconsult. M.C. also wishes to acknowledge support from the Fonds der Chemischen Industrie.

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