Impurity Absorption Spectroscopy in ^{28}Si: The Importance of Inhomogeneous Isotope Broadening

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We report high-resolution infrared absorption spectra of the neutral donors phosphorus and lithium, and the neutral acceptor boron, in isotopically pure ^{28}Si crystals. Surprisingly, many of the transitions are much sharper than previously reported in natural Si. In particular, the $2p_0$ line of phosphorus in ^{28}Si has a full width at half maximum of only 4.2 μeV, about 5 times less than the narrowest $2p_0$ line previously reported for natural Si, making it the narrowest shallow impurity transition yet observed. The widely held assumptions that the impurity transitions previously reported in high quality samples of natural Si revealed the true, homogeneous linewidths, are thus shown to be incorrect. The sharper transitions in ^{28}Si also reveal new substructures in the boron and lithium spectra.

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The shallow donors and acceptors in silicon are among the most thoroughly studied and best-understood impurity centers in solid state physics. The electronic structure of their ground and excited states has been investigated using a wide range of experimental techniques, coupled with increasingly detailed theoretical treatments based on effective mass theory, including extensions to accommodate the effects of the impurity short-range potential. The low temperature infrared absorption spectra of their ground state to bound-excited-state transitions were observed very early in the development of semiconductor physics, marking a major step forward for the field [1]. While the experimental and theoretical techniques developed in these studies continue to be widely applied in related areas, such as the absorption transitions of "deep" impurities, of excitonic systems, and of impurities in other semiconductors, there has been relatively little published on these shallow impurity transitions in Si, or other well-studied semiconductors such as Ge, over the past 20 years. This reflects a widely held opinion that these transitions are understood in minute detail—an assumption which we show here to be incorrect in a number of ways.

Numerous authors have addressed the problem of understanding the linewidths and line shapes of transitions between shallow impurity states in Si and Ge. Lax and Burstein [2] first suggested that the then-observed ~1 meV linewidths for phosphorus in Si resulted from the simultaneous participation of acoustic phonons during the absorption process. It was pointed out by Kane [3] that the linewidths reported in these early studies might be entirely instrumental, and that due to the weakness of the electron-phonon interaction in Si, the transitions should themselves be of purely electronic, no-phonon character. Kane also proposed that there could still be a lifetime broadening of the excited states, due to transitions to other nearby excited states resulting from the emission (or at elevated temperature, absorption) of acoustic phonons. Soon thereafter, detailed calculations by Barrie and Nishikawa (BN) [4,5] confirmed that, for a weak electron-phonon interaction, the ultimate linewidths should arise from this "lifetime effect" and that the process discussed by Lax and Burstein contributes only a broad, weak background on which the no-phonon absorption transition is superimposed.

The linewidths predicted by BN were much narrower than what was experimentally observed at that time, but there followed a rapid progress both in spectroscopic resolution and in the perfection of semiconductor crystal growth technology. This resulted in the study, and the effective elimination, of inhomogeneous broadening resulting from the following: (i) electric field effects (Stark effects) resulting from the random electric fields due to ionized impurities, (ii) residual strains resulting from the random strain fields due to impurities and/or dislocations, and (iii) concentration broadening resulting from the overlap of the excited state wave function with those of nearby impurities [6–11]. While some doubts remained [7], the widely accepted consensus after these studies [8,9,11] was that all of the inhomogeneous broadenings had been reduced to insignificance, and that the observed linewidths represented the true, homogeneous, lifetime-broadened widths. These were in reasonable agreement with the predictions of BN [4,5] (however, these predictions were in some cases given only as upper limits). As a result, it has since become widely assumed that if the inhomogeneous broadening mechanisms listed above are minimized, the observed impurity transition linewidths must be the homogeneous linewidths.

All of the foregoing ignores another potentially important, but until now unrecognized, inhomogeneous broadening mechanism in Si (as well as Ge, GaAs, etc.), namely, the broadening which can result from the random placement of the stable isotopes of Si on the lattice points surrounding a given impurity atom. Here we show that for boron (B), phosphorus (P), and lithium (Li) in Si, many of the narrowest linewidths reported in the past, and interpreted as being the true, homogeneous, linewidths, are, in fact, dominated by this broadening mechanism. The same transitions observed in a ^{28}Si sample of only moderate chemical purity are much narrower than those previously reported for the best samples composed of natural Si (hereafter Si). Thus the true, homogeneous linewidths of these transitions are considerably less than had been previously thought. As a result of this reduction in linewidth, new fine structure is observed in the absorption spectra of boron acceptors and lithium donors in ^{28}Si.

We have recently reported ultrahigh resolution photoluminescence studies of boron and phosphorus bound exciton (BE) transitions in isotopically pure ^{28}Si, which revealed a remarkable sharpening of the no-phonon BE transitions [12]. This could be understood as resulting from the statistical randomness of the isotopic composition within the BE wave function in Si, leading to local shifts in the band gap energy, and thus to an inhomogeneous broadening [12]. These results do not, however, directly presage the sharpening of the midinfrared impurity absorption transitions reported here for ^{28}Si. First, the BE transitions are inherently sharper in Si (and in ^{28}Si) than are the impurity absorption transitions studied here, making small inhomogeneous broadenings more apparent. Second, the energy scale to which the broadenings must be compared is essentially the band gap energy for the BE transitions, while for the impurity absorption transitions the relevant energy scale is the much smaller impurity ionization energy. Thus, our observation of substantial inhomogeneous broadenings due to Si isotopic randomness for many of these impurity absorption transitions is initially quite surprising. However, we will show that the size of the broadenings can, in fact, be explained by a relatively simple model, which is based on what has been learned from the BE spectroscopy of isotopically modified Si [12–14].

The high-resolution absorption spectra shown here were obtained from ^{28}Si samples enriched to 99.896%, cut from a crystal used previously for photoluminescence studies [12,13]. This ^{28}Si crystal originally contained only P and B as native impurities, at concentrations of 7×10^{13} cm^{-3} and 7×10^{14} cm^{-3}, respectively. Lithium (Li) was inadvertently introduced into some of these ^{28}Si samples at an approximate bulk concentration of 1×10^{14} cm^{-3} during the furnace annealing process following implantations with Al, Ga, and In ions in a study of BE associated with those acceptor impurities [13]. While the Li absorption lines could be observed only in these annealed samples, we note that the details of the B and P spectra were identical in the annealed and the untreated samples. 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. The samples were freely suspended in a superfluid He-filled sample chamber sealed with polypropylene windows. Spectra were collected with a Bomem DA8.02 Fourier transform interferometer using a silicon composite bolometer cooled at 1.8 K, and Mylar beam splitters. The internal quartz-halogen source of the interferometer provided not only the needed midinfrared radiation, but also sufficient near infrared radiation to give efficient photoneutralization of the compensating impurities, thus reducing the broadening from random electric fields. The (unapodized) instrumental resolution of 0.014 cm^{-1} used for these measurements was verified by measuring the widths of the weak absorption lines resulting from residual water vapor in the evacuated beam path.

We begin by considering the transitions of P, the prototypical substitutional shallow donor impurity in Si. In Fig. 1(a) the $2p_0$ absorption line of P in ^{28}Si is shown to have a full width at half maximum (FWHM) of only 0.034 cm^{-1} (4.2 μeV), or 5 times less than the narrowest P $2p_0$ width previously observed for natural Si [6–8]. This is in spite of the fact that our present ^{28}Si sample is of considerably lower chemical purity than the samples used in those previous studies. It is therefore clear that the dominant broadening mechanism for the P $2p_0$ transition in Si is not the lifetime broadening, as has been widely accepted, but rather the inhomogeneous broadening resulting from the isotopic randomness present in natural Si. The P $2p_0$ line is also considerably sharper than the narrowest absorption transitions previously reported for a semiconductor impurity [11]. This previous record

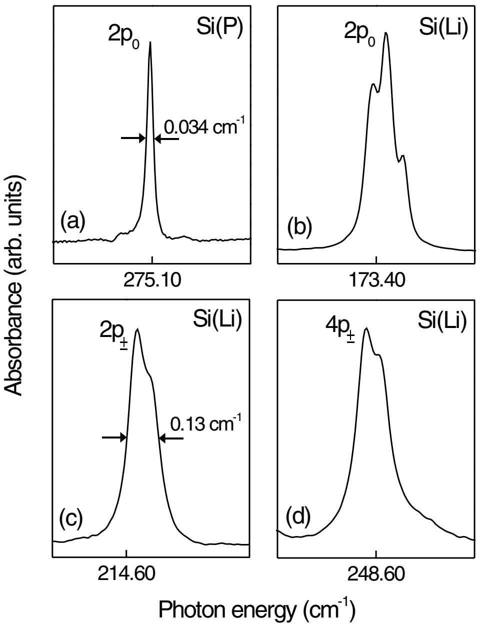

FIG. 1. Four representative donor absorption lines observed in ^{28}Si at a sample temperature of 1.8 K are shown. (a) The transition from the ground state of the P donor to the $2p_0$ excited state, with an observed FWHM of 0.034 cm^{-1}. (b)–(d) Absorption transitions from the Li donor ground state to the $2p_0$, $2p_\pm$, and $4p_\pm$ excited states, respectively. (a)–(d) All have an identical energy width of 0.8 cm^{-1}. The spectra were collected at an instrumental resolution of 0.014 cm^{-1} FWHM.

width of 6.4 μeV was obtained from a shallower defect in Ge, specially selected because its transitions were insensitive to stress, and hence to broadenings from random strain fields [11].

Some of the higher energy P absorption lines were also found to be narrower in ^{28}Si than previously reported in Si—in our ^{28}Si sample the widths of the $2p_{\pm}$ and $3p_{\pm}$ lines were 0.067 cm^{-1} (8.3 μeV), which can be compared to the narrowest previous results for natural Si of 27 and 28 μeV, respectively, [8] or (after correction for instrumental resolution) 18 μeV for both lines [7]. The narrowing of the P $2p_{\pm}$ and $3p_{\pm}$ transitions in ^{28}Si is thus less dramatic than that for $2p_0$, indicating that for these transitions the lifetime broadening is more significant. It should also be pointed out that due to the relatively heavy doping and compensation of the presently available ^{28}Si, concentration broadening effects are expected to become increasingly significant for the higher-lying excited states.

Next we consider the absorption transitions of the shallow Li donor, which occupies the tetrahedral interstitial lattice site in Si. Three representative transitions are shown in Fig. 1(b)–1(d), namely, $2p_0$, $2p_{\pm}$, and $4p_{\pm}$. The partially resolved doublet structure apparent for the $2p_{\pm}$ and $4p_{\pm}$ transitions was also observed for the $3p_{\pm}$, $5p_{\pm}$, and $4f_{\pm}$ transitions, while the $2p_0$ structure is seen to be more complicated. None of this structure has been reported in previous studies of Li, presumably because of the inhomogeneous isotope broadening present in natural Si samples. While the Li $2p_0$ line in ^{28}Si does not lend itself to characterization by a FWHM, our width for the $2p_{\pm}$ line, 0.13 cm^{-1} (16 μeV), is considerably less than the 25 μeV width previously reported for Li in natural Si [8]. Let us consider briefly the new structure observed in the Li absorption transitions in ^{28}Si. Since all transitions show an unresolved doublet splitting of ~0.06 cm^{-1} (the $2p_0$ line shape is consistent with this splitting plus an additional excited state splitting), the most reasonable explanation is a splitting of the Li ground state. In fact, unlike the substitutional donors, which have the $1s\ \Gamma_1$ valley-orbit ground state lying well below the $1s\ \Gamma_3$ and Γ_5 states, Li has in the past been thought to have a degenerate $1s\ \Gamma_3 + \Gamma_5$ ground state [9]. It is therefore tempting to assign the ~0.06 cm^{-1} doublet structure to the $1s\ \Gamma_3$ to $1s\ \Gamma_5$ splitting. It should be noted that, while this ground state splitting has not been observed in previous optical absorption studies, an earlier detailed EPR study [15] of Li in Si did observe a complicated ground state splitting of this magnitude. A different possible explanation of the doublet structure is that it arises from a difference of the ionization energies of ^{6}Li and ^{7}Li donors, but the relative intensities of the doublet components do not agree with the relative abundances of the stable Li isotopes. The additional structure observed for the Li $2p_0$ line may arise from a valley-orbit splitting of the $2p_0$ state. While such valley-orbit splittings have never been observed for the odd-parity excited states of shallow substitutional donors, this need not be the case for interstitial donors. Such a valley-orbit splitting has been reported for the $2p_{\pm}$ state of the interstitial Mg double donor in Si [16].

Next we consider B, the prototypical shallow acceptor impurity in Si. Three previously identified B absorption transitions are compared between natural Si and ^{28}Si in Fig. 2. The line numbering scheme is the same as has been used previously [8,9]. Many of the B lines, including 1, 2, 3, and line 4B shown in Fig. 2, are quite broad and Lorentzian in Si, and do not show any substantial reduction in width in ^{28}Si. Excited state phonon lifetime effects, as described by BN dominate these linewidths. On the other hand, lines 4 and 6 shown in Fig. 2 are substantially sharper in ^{28}Si than in the best spectra in natural Si revealing a new, identical doublet splitting of 0.15 cm^{-1}. This substantial sharpening into identical doublets is observed for a total of seven B lines in the present ^{28}Si spectra.

The question of the origin of the identical 0.15 cm^{-1} splittings of all the sharp B transitions revealed in the ^{28}Si spectrum remains. The simplest explanation would be that it arises from a splitting of the B ground state, but the properties of the B ground state are well known, and do not admit such a large splitting [13,14]. The most likely explanation is that the splitting results from the difference in binding energy between ^{10}B and ^{11}B acceptors, since the doublet intensity ratio accurately reflects the ^{10}B/^{11}B natural abundance ratio of ~20/80. The splitting

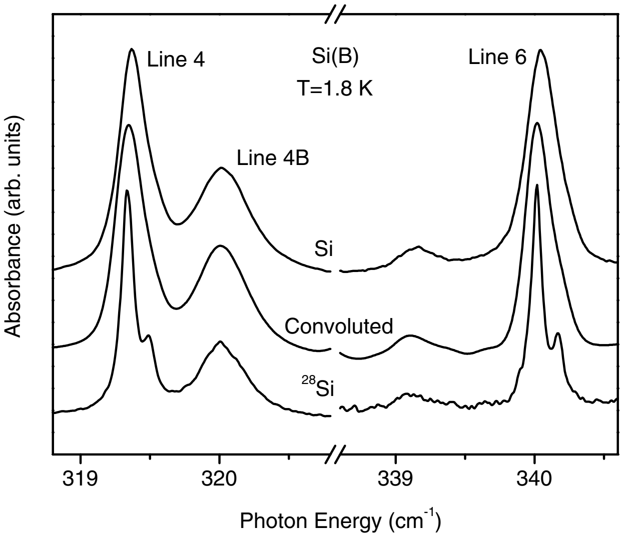

FIG. 2. Absorption lines 4, 4B, and 6 of the B acceptor are compared between Si (top) and ^{28}Si (bottom). Lines 4 and 6 are significantly narrower in ^{28}Si, revealing a new, identical doublet structure, with a splitting of 0.15 cm^{-1}. The 4B transition is broad in both spectra, indicating the dominance of excited state lifetime broadening for this state, even in natural Si. The middle spectra show the excellent agreement between the ^{28}Si spectra, convoluted with the previously calculated [14] isotopic broadening of the B ground state, and the natural Si results.

also has the expected [17,18] sign, with a larger binding energy for the lighter isotope. On the other hand, the $0.15\ \mathrm{cm}^{-1}$ splitting is large for such a shallow impurity, and we cannot at present account quantitatively for its magnitude. It may be related to the unusual feature of B in Si — a large negative chemical shift, or central cell correction, as compared to the predicted effective mass binding energy, which agrees well with the measured binding energy of the isocoric Al impurity in Si.

We consider now the mechanism by which the isotopic composition of natural Si causes these inhomogeneous broadenings. One possibility would be related to the change in impurity binding energy between ^{28}Si, ^{29}Si, and ^{30}Si. Changes in the absorption spectrum of the B acceptor between ^{12}C and ^{13}C diamond have been reported by Kim *et al.* [19], and explained by Cardona [20] in terms of a change in the binding energy resulting from the (small) isotopic dependence of the hole effective mass. Our preliminary measurements and calculations of such effects for shallow donors and acceptors in Si, including contributions from the isotopic dependence of the dielectric constant, indicate that such shifts in binding energy will be much too small to explain the broadenings observed in natural Si. Instead, we follow the approach introduced recently [14] to explain the surprising discovery [13] that the long-studied "residual" acceptor ground state splittings resulted from the isotopic randomness present in Si.

The ground state wave functions of the impurities are fairly compact, and sample a relatively small volume surrounding the impurity ion, and hence in natural Si are subject to relatively large fluctuations of the actual isotopic composition within this effective volume. These fluctuations in turn induce shifts (and for acceptors, splittings) of the ground state energies, which can be related to the known shifts of the valence band (for acceptor impurities) and conduction band (for donor impurities) energies with average isotopic composition. The excited state wave functions, on the other hand, are much more extended, and therefore sample isotopic compositions much closer to the average composition than does the ground state. The difference in the isotopic composition sampled by the ground state and the excited state leads to an inhomogeneous broadening, which is expected to become larger for deeper, and thus more compact, ground states. Since the valence band edge shifts more with isotopic composition than does the conduction band edge [14], the larger broadening for B as compared to P is readily understood. In fact, we can quantitatively explain the B broadening. Our earlier calculation [14] of the acceptor ground state splitting in natural Si provides us with a distribution of B ground state energy shifts [Fig. 2(a) of Ref. [14] explicitly showed the ground state distribution for Al in Si]. In Fig. 2 (middle) we show the result of convoluting the observed ^{28}Si spectrum with the previously calculated [14] B ground state distribution. The result is seen to be in excellent agreement with the spectrum observed in Si.

In conclusion, we have shown that previous assumptions that all important inhomogeneous broadening mechanisms had been minimized in the study of shallow donor and acceptor transitions in Si are incorrect, and that inhomogeneous isotope broadening played an important, but unrecognized role in previous studies. As a result of the improved linewidths obtained in ^{28}Si, we have observed new structure in the Li and B spectra, and offered tentative explanations. Given the expected increase of this broadening for deeper impurities, comparisons with deep impurity spectra in ^{28}Si are needed. Studies of ^{28}Si selectively doped with $^{10}\mathrm{B}/^{11}\mathrm{B}$ would also be interesting. Finally, it would be desirable to search for similar inhomogeneous broadening effects in the many other semiconductors that consist of mixtures of stable isotopes, but are now becoming available in isotopically pure form.

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