Photoluminescence of Isotopically Purified Silicon: How Sharp are Bound Exciton Transitions?

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We report the first high resolution photoluminescence studies of isotopically pure Si (99.896% ^{28}Si). New information is obtained on isotopic effects on the indirect band gap energy, phonon energies, and phonon broadenings, which is in good agreement with calculations and previous results obtained in Ge and diamond. Remarkably, the linewidths of the no-phonon boron and phosphorus bound exciton transitions in the ^{28}Si sample are much narrower than in natural Si and are not well resolved at our maximum instrumental resolution of $\sim$0.014 cm^{-1}. The removal of the dominant broadening resulting from isotopic randomness in natural Si reveals new fine structure in the boron bound exciton luminescence.

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The effects of isotopic composition and disorder on the properties of semiconductors have been the subject of numerous recent studies, as detailed in several reviews [1–5]. Isotopically purified Ge and C (diamond) were the first such semiconductors to become available in the form of bulk single crystals of reasonable purity, allowing for the investigation of isotope effects on thermal conductivity, phonon energies and broadenings, and direct and indirect electronic band gaps [1–18]. Previous studies on isotopic effects in Si have been limited to Raman scattering [19–21], thermal conductivity [22,23], and the direct gap [24] due to a lack of bulk samples of sufficient purity for a study of the indirect band gap via photoluminescence (PL) until the recent growth of the samples for the aforementioned thermal conductivity studies. In this Letter we report on the differences between the PL spectra of high purity natural Si (92.23% ^{28}Si + 4.67% ^{29}Si + 3.10% ^{30}Si) and one of these high purity bulk samples of Si enriched to 99.896% ^{28}Si, obtaining new experimental data on the isotope effect on the indirect band gap of Si, together with new information on changes in phonon energies and lifetimes. Remarkably, the no-phonon (NP) bound exciton (BE) PL lines, which have already [25] been shown to be extremely sharp in natural Si (hereinafter referred to as Si), are much narrower in the ^{28}Si sample and are, in fact, not well resolved at our maximum instrumental resolution of $\sim$0.014 cm^{-1}. Thus, the limiting broadening mechanism for no-phonon BE PL in high purity Si is found to be the local band gap fluctuations resulting from isotopic randomness. The removal of this broadening in fact reveals new fine structure in the boron (B) BE. At present we can only set an upper bound of 0.005 cm^{-1} on the full width at half maximum (FWHM) of the no-phonon phosphorus (P) BE transition. The sharpness of this transition is remarkable—this is not a well-shielded atomiclike transition such as for rare earth ions, but the sum of the extended bound exciton transitions throughout the sample, which are fully sensitive to band gap fluctuations, random strains and electric fields, phonon scattering, etc.

The dependence of the band gap energies on isotopic composition has already been observed for the lowest (indirect) gap of diamond (C) [6] and Ge [8–11] and for the Ge [11] and Si [25] direct gaps. It has been shown to result primarily from the effect of the average isotopic mass on the electron-phonon interaction, with a smaller contribution from the change in lattice constant. This simplest approximation, in which crystals of mixed isotopic composition are treated as crystals of identical atoms having the average isotopic mass, is referred to as the virtual crystal approximation (VCA). Going beyond the VCA, in isotopically mixed crystals one would also expect local fluctuations in the band gap energy from statistical fluctuations in local isotopic composition within some effective volume, such as that of an exciton, but prior to our work this had not been observed for any of the more common semiconductor materials (such effects had been seen in LiH-LiD mixed crystals, where isotopic effects are much larger [4]). The VCA also accounts for

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the dominant effects on the phonon spectrum, namely, the change in the harmonic phonon frequency which goes as the inverse square root of the average isotopic mass, and related changes in anharmonic lifetimes which depend on the phonon frequencies, but there are also many observations of isotopic effects on the phonon spectrum which arise from the randomness of the isotopic composition, leading, for example, to scattering. This requires treatment beyond the VCA, and the effects of isotopic randomness on phonon energies and lifetimes have been successfully calculated within the coherent potential approximation (CPA) [2,3,7,12–17,19–21]. These effects occur not only for the Raman phonons but also for phonons away from the center of the Brillouin zone, which cannot be studied using normal single-phonon optical Raman scattering, but instead require the use of multiphonon Raman [12,19–21], IR [16], or x-ray Raman spectroscopy [5], or neutron scattering [12]. The clear observation of the effects of isotopic randomness on the wave-vector-conserving phonons (wcp) involved in phonon-assisted PL transitions reported here thus provides a useful new method of studying such effects in Si.

PL spectra were collected from samples mounted in a strain-free manner and immersed in liquid He at a bath temperature of either 4.2 or 1.3 K, with excitation provided either by the 514.5 nm line of an Ar^+ laser or, for bulk excitation, 1020 nm from a Ti-sapphire laser (with line narrowing provided by an intracavity etalon for precision measurement of the Raman line). The Si sample used for comparison was a float-zone crystal selected to have approximately the same B and P concentration as the ^{28}Si sample (enriched to 99.896% ^{28}Si), which was cut from the SI283 crystal used previously [22,23] for thermal conductivity studies. Spectra were collected with a Bomem DA8 Fourier transform interferometer using a cooled Ge detector (North Coast), as described in previous studies of ultrahigh resolution Si PL spectroscopy [25–29]. The maximum instrumental resolution achieved in this study is estimated to be $\sim$0.014 cm^{-1} as discussed later.

In Fig. 1 we compare the PL spectra of the two samples in the TO phonon-assisted spectral region at 4.2 K with high level Ar^+ excitation and moderate spectral resolution. The spectra are dominated by the well known [25,30] BE (B^1) and bound multiexciton complex (BMEC) lines (B^2, B^3) of the dominant B impurity, with a weaker P BE line (α^1), together with the weak TO and LO replicas of the free exciton (FE) luminescence. Using the method introduced by Tajima [30], we can estimate the impurity concentrations in the ^{28}Si sample to be $[B] = 7 \times 10^{14}$ cm^{-3} and $[P] = 7 \times 10^{13}$ cm^{-3}, in good agreement with the previous [22] Hall determination of a room temperature hole concentration of 6.6×10^{14} cm^{-3} for this crystal. No other shallow impurities were observed at the detection limit of the PL spectra. It is obvious from Fig. 1 that there is an energy shift between the Si and ^{28}Si spectra, but this shift is a combination of a change in band gap energy and a change in the TO wcp energy. The band gap shift can be

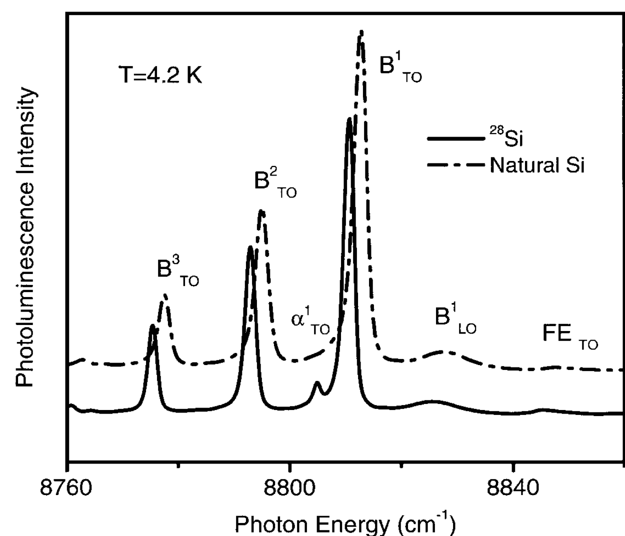

FIG. 1. Photoluminescence spectra of natural Si and ^{28}Si in the TO phonon replica region are superimposed. Both spectra are dominated by the boron BE (B^1) and BMEC (B^2, B^3) lines, with a weaker phosphorus BE line (α^1). Also shown is the broad LO phonon replica of the B^1 line, together with the weak TO replica of the free exciton (FE).

measured directly from the no-phonon spectra, which are shown in Fig. 2 at a spectral resolution of $\sim$0.014 cm^{-1}, with the ^{28}Si spectrum shifted up in energy by 0.92 cm^{-1} so as to align the features in both spectra (the complex fine structure of the B^1 line will be discussed later).

If we assume this 0.92(1) cm^{-1} reduction in the band gap of ^{28}Si relative to that of Si arises solely from the electron-phonon interaction, we obtain a value of 58 meV for the zero-point electron-phonon renormalization of the indirect band gap energy in Si, using the values of the average atomic masses for the two samples given previously [22]. While it appears that no numerical value has yet been published for this parameter, this value is consistent with previous [18] results for similar materials, with the result for the Si direct gap [24], and with theoretical estimates [31]. We estimate that the additional band gap shift arising from the change in lattice constant, which has been shown to be small in Ge [8,11] and will be smaller still in Si due to the smaller dependence of the indirect band gap energy on volume, would contribute only $\sim$0.07 cm^{-1} to the observed shift.

Subtracting this band gap shift from the observed shifts of the phonon replica spectra provides values for the energy shifts of the wcp between Si and ^{28}Si. In the VCA, one would expect the energy of any given phonon in ^{28}Si to be 0.194% higher than that in Si. The observed shift of the TO phonon replica shown in Fig. 1 is 2.06(5) cm^{-1}, resulting in an upshift of the TO wcp energy of 0.24(1)% in ^{28}Si. This rather large deviation from the VCA prediction is expected from CPA calculations which show appreciable disorder-induced effects for phonon energies where the density of states is large [12–17,21]. The observed shift of the TA wcp replica of 1.20(5) cm^{-1}, on the other hand,

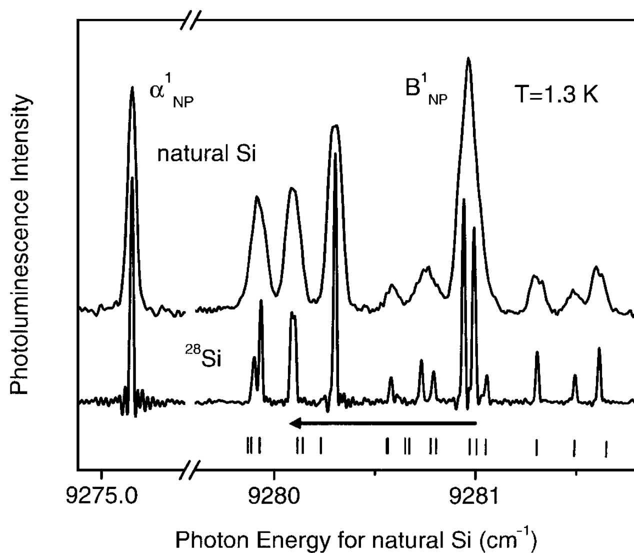

FIG. 2. A high resolution spectrum in the no-phonon region is shown for the natural Si sample, together with the same spectrum obtained from the ^{28}Si sample shifted up in energy by 0.92 cm^{-1} so as to align the transitions (the actual energies of the ^{28}Si transitions can be obtained by downshifting them by the 0.92 cm^{-1} length of the horizontal arrow). The phosphorus BE (α^1) line is seen to consist of a single component, while the boron BE (B^1) line has considerable fine structure. The vertical tick marks below the B BE show the predicted locations of the fine structure components obtained from a theoretical fit to the behavior of the spectrum under uniaxial stress [27]. An identical instrumental resolution of ~0.014 cm^{-1} FWHM was used for both spectra. The oscillations on either side of the P BE line are not noise, but rather the typical $\sin(x)/x$ line shape resulting from transforming an interferogram using boxcar apodization when there is still strong modulation at the maximum optical path difference of 50 cm.

results in an increase of 0.19(3)% in the TA wcp energy, in agreement with the VCA result. Because of the large width of the LO wcp replicas of the impurity-related lines, and the weakness of the FE transitions, we were unable to determine the shift in the LO wcp energy between ^{28}Si and Si.

We were able to obtain accurate values of the zone-center optical phonon energies in the two samples since the Stokes-Raman line of the 1020 nm pump laser falls within the transparency region of Si and is in the same spectral region over which the PL spectra were collected. The Raman phonon energy in ^{28}Si was found to be 0.154(10)% larger than in Si, a shift significantly smaller than that predicted by the VCA, and in good agreement with earlier studies of the Raman phonon in epitaxial Si samples [19–21]. We found no change in the 1.29(1) cm^{-1} FWHM of the O^Γ line between ^{28}Si and Si within experimental error, although an additional broadening has been observed in epitaxial samples with a higher degree of isotopic disorder [21].

In contrast to this, a closer examination of Fig. 1 reveals that the TO wcp replicas of Si are noticeably broader than those of ^{28}Si, indicating that in natural Si the TO wcp has a substantial lifetime broadening arising from isotopic randomness. Extracting this additional broadening parameter is complicated by the fact that the electronic BE transitions are themselves not delta functions (see, for example, the structure of the B BE revealed in Fig. 2), and the impurity-related wcp replicas have an additional broadening which arises from the uncertainty in the center-of-mass wave vector of the recombining electron-hole pair, due to the localization on the impurity, which causes a broadening via the energy dispersion of the particular wcp involved [32]. While the detailed analysis of this broadening will be the subject of a future study, one can get a feeling for the surprisingly large difference between Si and ^{28}Si by noting that for the TO wcp and FWHM of the B^3 line in the former is 2.6 cm^{-1} and in the latter only 2.1 cm^{-1}. It would be interesting to obtain a much more disordered sample, such as $^{28}Si_{0.5}{}^{30}Si_{0.5}$ where one would expect very broad TO wcp replicas. No differences in line shape were discernible in the TA wcp replicas of the two samples, and, as mentioned previously, the LO wcp replicas of the impurity-related PL transitions are so broadened by the localization-dispersion effect [32] that it is not meaningful to compare the LO line shapes (although if higher purity samples with stronger FE PL could be obtained a comparison of LO wcp phonon broadening could be made, since the FE transitions do not suffer from this phonon dispersion broadening).

We have put off until now a discussion of the most remarkable difference in the PL spectra of the ^{28}Si and Si samples seen in Fig. 2, namely, the much sharper no-phonon BE lines seen in the isotopically pure sample, and the resulting extra fine structure revealed in the B BE transition. It must be remembered that the no-phonon BE and BMEC transitions are already very narrow in natural Si, and the detailed study of their linewidths and fine structure became practical only with the advent of ultrahigh resolution Fourier transform PL spectroscopy using Michelson interferometers [25]. Consider first the P BE (α^1) transition, which has no electronic substructure, and in the Si sample was found to have a FWHM of 0.041 cm^{-1}, in agreement with previous [25] measurements. The observed FWHM in the ^{28}Si sample is only 0.014 cm^{-1}, much less than that observed in the best natural Si samples, even though the ^{28}Si sample is of only moderate chemical purity. It must also be stressed that the observed FWHM of 0.014 cm^{-1} is dominated by the instrumental resolution, which at our maximum optical path length difference of 50 cm, and using boxcar apodization and ignoring resolution degradation from the finite size of the collimating aperture, would give a FWHM of 0.012 cm^{-1}. At present we can thus set only an upper limit of 0.005 cm^{-1} on the true linewidth of the P BE no-phonon transition in ^{28}Si. The broadening seen in Si is consistent with a simple calculation combining the isotopic dependence of the band gap energy determined here with statistical fluctuations of the isotopic composition in an "effective" excitonic volume having a radius of ~3.5 nm [4].

A similar reduction in the no-phonon linewidths is seen in Fig. 2 for the components of the B BE line, which had been found [25] to have nine resolved components in natural Si, explained in terms of a threefold splitting of the electron levels of the BE due to the valley-orbit effect, coupled with a threefold splitting of the hole states due to hole-hole coupling. More detailed studies of the B BE followed, involving both uniaxial stress [26] and Zeeman [27] perturbations, revealing that a complete description required the inclusion of additional terms, such as the coupling of the hole angular momentum with the electron spin, and the valley anisotropy. The linewidths of the components of the B BE are again much narrower in the ^{28}Si sample than in Si, with the narrowest components having an observed FWHM of 0.017 cm^{-1}, slightly larger than that of the P BE. As a result, the B BE spectrum in the ^{28}Si sample now reveals 13 resolved components and one partially resolved doublet. This new fine structure is well accounted for by the earlier investigations of the effects of uniaxial stress and magnetic fields on the B BE [26,27]. The vertical tick marks along the bottom of the B BE spectrum, which are seen to be in quite good agreement with the newly observed fine structure, are the predicted zero-stress energies of the various components obtained from a theoretical fit to the observed energies of the many stress-split components as a function of the applied uniaxial stress [26].

While it would clearly be desirable to extend the present studies to even higher spectral resolution, so as to completely resolve the widths and structure of the no-phonon transitions, there are other possibilities that should be pursued. One of the unexpected discoveries resulting from the previous applications of ultrahigh resolution spectroscopic techniques to the PL spectra of natural Si was the observation of a small but reproducible splitting of the ground state of the Al acceptor in Si which was attributed to a Jahn-Teller effect [28]. Similar splittings were soon observed using the same technique for the other relatively shallow acceptors in Si, namely, Ga and In (it is thought that the splitting for the shallowest acceptor in Si, B, is too small to be observable) [29]. This rather unexpected and controversial observation has recently been supported by the observation via electronic Raman scattering of a similar intrinsic ground state splitting of the B acceptor in diamond, which was also attributed to a Jahn-Teller effect [33].

It would be of great interest to study the BE spectra of the acceptors showing split ground states, such as Al, in a ^{28}Si sample, in which the broadening arising from isotopic randomness is absent. We also hope to investigate the PL spectra of samples having a higher degree of isotopic disorder, so that the effects of isotopic randomness can be maximized, as well as to investigate relatively pure samples of ^{29}Si and ^{30}Si when these become available.

In conclusion, we have reported PL measurements of isotopically purified ^{28}Si and compare these to the same transitions in natural Si. The relatively small change in isotopic composition leads to readily observable changes in the energy of the indirect band gap, and in the energies of the wcp and the Raman phonon. Large deviations in some of the phonon energies from the values predicted within the VCA, together with a substantial broadening of the TO wcp in natural Si as compared to ^{28}Si, provide evidence of the importance of isotopic randomness on the phonon energies and lifetimes. Finally, the linewidths of the no-phonon BE transitions in ^{28}Si were found to be much narrower than those of natural Si, revealing new fine structure in the spectrum of the B BE, and suggesting a number of interesting possibilities for further studies.

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