High-resolution photoluminescence measurement of the isotopic-mass dependence of the lattice parameter of silicon

A. Yang,[1] M. Steger,[1] H. J. Lian,[1] M. L. W. Thewalt,[1] M. Uemura,[2] A. Sagara,[2] K. M. Itoh,[2] E. E. Haller,[3] J. W. Ager III,[3] S. A. Lyon,[4] M. Konuma,[5] and M. Cardona[5]

[1]*Department of Physics, Simon Fraser University, Burnaby, British Columbia, Canada V5A 1S6*

[2]*Keio University and CREST-JST, Yokohama 223-8522, Japan*

[3]*University of California Berkeley and LBNL, Berkeley, California 94720, USA*

[4]*Princeton University, Princeton, New Jersey 08544, USA*

[5]*Max-Planck-Institut für Festkörperforschung, 70569 Stuttgart, Germany*

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We have studied the dependence of the lattice parameter of silicon on isotopic mass, using high-resolution photoluminescence spectroscopy to detect splittings of the shallow donor bound exciton transitions in epitaxial layers of either isotopically enriched ^{28}Si or ^{30}Si grown on silicon substrates of natural isotopic composition. The slight lattice parameter mismatch between the isotopically enriched epitaxial layer and the natural silicon substrate induces a biaxial strain in the epitaxial layer, which results in a splitting of the hole states in the bound exciton. This can be detected with remarkable precision, especially in the highly enriched ^{28}Si epilayers, where the bound exciton lines are extremely sharp.

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I. INTRODUCTION

The effect of isotopic mass on the lattice parameter in single crystals of diamond, silicon, and germanium has been the subject of numerous experimental and theoretical studies. Silicon is of particular interest due to its use for the Avogadro project,[1] in which an accurate determination of the Avogadro constant will be made and will lead to a redefinition of the kilogram. Although there have been several theoretical investigations[2–4] of the isotopic mass dependence of the lattice parameter of silicon, predictions of the strength of the isotopic effect vary significantly. An experimental study was done, in which the temperature dependence of the isotopic effect was determined for Si and Ge for temperatures between 30 and 300 K, and it was shown that the isotopic effect on the lattice parameter increases with decreasing temperature.[5,6] A subsequent study by Wille *et al.*[7] showed that the difference does not increase monotonically as T is lowered, but in fact, there exists a point above 0 K at which the isotopic effect is strongest. That study was done using a sample consisting of epitaxial ^{30}Si grown on natural silicon (^{nat}Si), and the lattice mismatch of order 10^{-5} was measured using Bragg backscattering of highly monochromatic synchrotron radiation.

In the present study, we have employed a different approach for the measurement of the isotopic effect on the lattice parameter of silicon. The lattice mismatches for epitaxial ^{28}Si grown on ^{nat}Si (henceforth ^{28}Si/^{nat}Si) and epitaxial ^{30}Si grown on ^{nat}Si (henceforth ^{30}Si/^{nat}Si) have been measured using high-resolution photoluminescence (PL) spectroscopy of shallow donor bound exciton (BE) transitions.

PL spectroscopy of impurity BE transitions is a topic that has been studied in great detail, but has only recently been applied to the determination of the isotopic mass dependence of the lattice parameter of silicon.[8] This technique has, however, been previously used to measure lattice mismatches of order 10^{-5} for epitaxial layers of undoped GaAs grown on doped GaAs substrates.[9] In this Brief Report, we provide corrected values of the lattice mismatch for the ^{28}Si/^{nat}Si samples, which were subjected to a numerical error in our preliminary study.[8] We also present results for the lattice mismatch of ^{30}Si/^{nat}Si determined using PL spectroscopy, and find it to be consistent with our results for ^{28}Si/^{nat}Si.

Studies of silicon isotope effects on indirect band gap transitions had long been delayed due to the lack of suitable samples. In the first such PL study, Karaiskaj *et al.*[10] observed significantly sharper BE transitions in the no-phonon region in highly enriched ^{28}Si as compared to ^{nat}Si, even though the ^{28}Si sample was of only moderate chemical purity ($[B]\sim 7\times 10^{14}$ cm^{-3} and $[P]\sim 7\times 10^{13}$ cm^{-3}). In ^{nat}Si, the no-phonon phosphorus BE transition has a linewidth of 0.041 cm^{-1} full width at half maximum (FWHM), whereas the observed linewidth of the same transition in the ^{28}Si sample was 0.014 cm^{-1}, essentially identical to the maximum available instrumental resolution of the Fourier transform spectrometer used in the study. The apparent inhomogeneous isotope broadening inherent in ^{nat}Si was attributed to statistical fluctuations of the isotopic composition within the effective radius (~3.5 nm) of the bound exciton. In the same study, it was also noted that there exists a 0.92 cm^{-1} decrease in the indirect band gap energy of highly enriched ^{28}Si as compared to ^{nat}Si. Additionally, shifts of the wave-vector-conserving phonon energies were also observed.

In order to overcome the limitations of the Fourier transform spectrometer, an apparatus for photoluminescence excitation (PLE) spectroscopy based on a tunable single frequency laser source with submegahertz resolution was developed to achieve a significant increase in instrumental resolution. PLE spectra revealed much sharper P BE and B BE transitions—linewidths as narrow as ~0.0012 cm^{-1} FWHM were observed in newer bulk ^{28}Si single crystal samples of improved chemical purity and higher isotopic enrichment.[11,12]

II. EXPERIMENT

Due to the costs and difficulties associated with growing bulk Si crystals of high isotopic enrichment, chemical purity, and crystalline perfection, epitaxial layers are often grown as a way of providing a sample of the material for characterization purposes. Two samples of epitaxial layers of ^{28}Si and one of epitaxial ^{30}Si, grown on ^{nat}Si (92.23% ^{28}Si, 4.67% ^{29}Si, and 3.10% ^{30}Si) substrates, were made available for the present study. The ^{28}Si epitaxial layers (of thickness ~5 μm) were grown from silane enriched to 99.9%, and deposited by chemical vapor deposition on floating-zone grown high purity ^{nat}Si(001) substrate material. The epitaxial ^{30}Si sample, which has an isotopic enrichment of 93.7% (as measured by secondary ion mass spectrometry), consists of an ~16 μm thick layer of ^{30}Si grown by liquid phase epitaxy on a floating-zone grown high purity ^{nat}Si(111) substrate. This is the same sample that was used in the earlier Bragg scattering study.[7]

Samples were loosely mounted (to avoid strain) and immersed in a superfluid liquid helium bath at a temperature of ~1.5 K. Excitation was provided by either the 532 nm line of a frequency-doubled Nd:YVO_4 laser or a 1047 nm diode-pumped Nd:YLF laser for bulk excitation. Spectra were collected with a Bomem DA8 Fourier transform interferometer using a liquid-nitrogen-cooled germanium photoconductive detector. The maximum instrumental resolution used in this study was ~0.005 cm^{-1}.

III. RESULTS AND DISCUSSION

A high-resolution PL spectrum of the no-phonon region for the first epitaxial ^{28}Si sample, which we refer to as ^{28}Si/^{nat}Si–1, is shown in Fig. 1. The P BE transition for the ^{28}Si epilayer is split by 0.149(2) cm^{-1}, with an offset from the bulk ^{28}Si P BE transition energy of 9274.180 cm^{-1} (represented by the dashed line). Fig. 1 also shows the ^{nat}Si P BE transition, which appears 0.92 cm^{-1} above the P BE energy for bulk ^{28}Si due to the difference in band gap energy between the two materials.

In Fig. 2, a high resolution PL spectrum of the no-phonon region for the second epitaxial ^{28}Si sample, which we refer to as ^{28}Si/^{nat}Si–2, reveals a 0.148(4) cm^{-1} splitting of the ^{28}Si P BE transition, which is in good agreement with the splitting measured for ^{28}Si/^{nat}Si–1. In addition to phosphorus, the ^{28}Si/^{nat}Si–2 sample also contained a small amount of the slightly deeper donor arsenic, which also exhibited an ~0.148 cm^{-1} splitting of the As BE transition. The sharpness of the BE transitions in the highly enriched ^{28}Si material makes it possible to measure these small splittings with great precision.

For the ^{30}Si/^{nat}Si sample, a 2.61(6) cm^{-1} splitting of the no-phonon P BE transition in the ^{30}Si epitaxial layer was observed, as shown in Fig. 3. The shift in P BE transition energy between the ^{30}Si epilayer and the ^{nat}Si substrate is consistent with the 16.9 cm^{-1} difference in band gap energy between bulk ^{nat}Si and bulk ^{30}Si.[13] We also note that the induced strain is not completely contained within the epilayer, but, in fact, there is a small amount in the substrate as well, which is evidenced by the 0.18(3) cm^{-1} splitting of the ^{nat}Si P BE transition. The ratio of the splitting for the ^{30}Si epilayer compared to the ^{nat}Si substrate is ~15:1, whereas the ratio of the specified substrate thickness to epilayer thickness is ~31:1. This discrepancy may be due to variations in the thickness of the epilayer. It is also worth noting that the higher energy ^{30}Si P BE component is not symmetric, with a

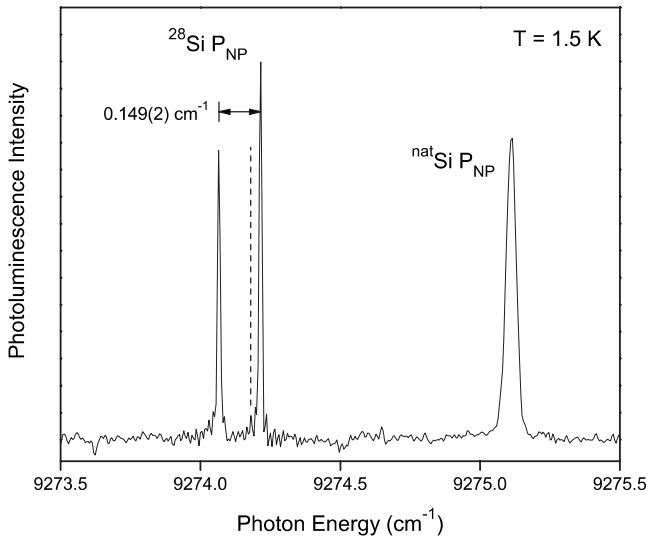

FIG. 1. This high-resolution (0.015 cm^{-1}) photoluminescence spectrum of the no-phonon region for the sample ^{28}Si/^{nat}Si–1, collected at 1.5 K, shows a 0.149(2) cm^{-1} splitting of the no-phonon P BE (P_{NP}) transition in the ^{28}Si epilayer. The energy of this transition for bulk ^{28}Si is represented by the dashed line at 9274.180 cm^{-1}. Also shown is the no-phonon P BE transition in the ^{nat}Si substrate, which appears 0.92 cm^{-1} above the bulk ^{28}Si transition.

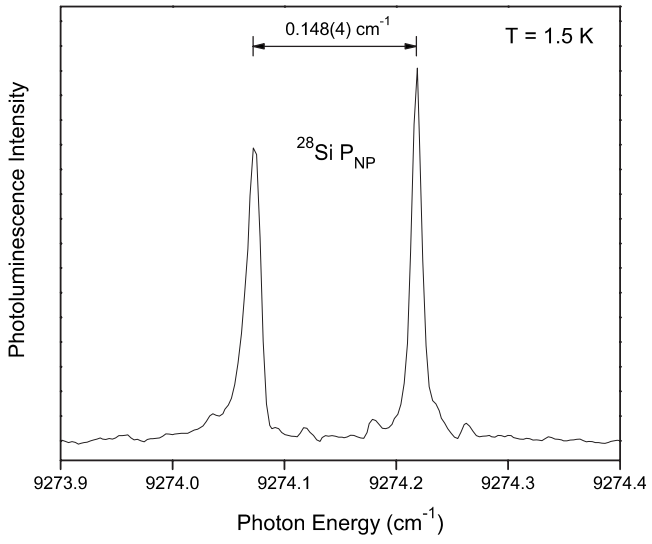

FIG. 2. The 0.148(4) cm^{-1} splitting of the ^{28}Si no-phonon P BE transition for the sample ^{28}Si/^{nat}Si–2 is shown in this photoluminescence spectrum, collected at 1.5 K with an instrumental resolution of 0.005 cm^{-1}.

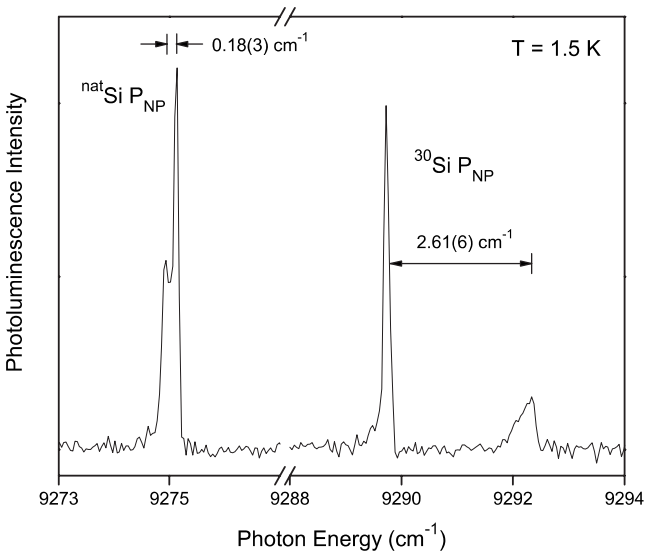

FIG. 3. The 2.61(6) cm^{-1} splitting of the ^{30}Si P BE no-phonon transition for the $^{30}Si/^{nat}Si$ sample is shown in this photoluminescence spectrum, collected at 1.5 K with an instrumental resolution of 0.06 cm^{-1}. The 0.18(3) cm^{-1} splitting of the ^{nat}Si P BE no-phonon transition in the substrate is also shown.

possible reason for the asymmetry being the existence of partially relaxed regions in the ^{30}Si epitaxial layer, which is consistent with the observed distribution being biased toward lower energy, as this would correspond to a smaller splitting associated with partial relaxation. We assume that the peak of this line corresponds to the unrelaxed condition; therefore, the peak position is used to determine the splitting.

The hydrostatic component of the biaxial strain causes a shift of the band gap energy, while the shear component lifts the degeneracy of the light and heavy hole bands at the valence band maximum. This results in a twofold splitting of the donor BE ground state, corresponding to the two observed transitions. For the previous paper,[8] the splitting of the hole states in the BE was taken to be equal to the free hole splitting, while here we use deformation potentials measured for the hole states of the P BE.

The lattice mismatch $\frac{\Delta a}{a}=\frac{a_{e0}-a_{s0}}{a_{s0}}$ (where a_{e0} is the lattice parameter of the relaxed epilayer and a_{s0} is the lattice parameter of the substrate) is related to the difference in the growth-direction lattice parameter $\frac{\Delta a_\perp}{a}=\frac{a_e-a_{s0}}{a_{s0}}$ (where a_e is the out-of-plane lattice parameter of the strained epilayer) by the second order elastic constants of silicon. The extrapolated values of the elastic constants at $T=0$ K are[14] $C_{11}=1.6772\times10^{11}$ Pa, $C_{12}=0.6498\times10^{11}$ Pa, and $C_{44}=0.8036\times10^{11}$ Pa. For an epitaxial layer of ^{28}Si grown on a ^{nat}Si substrate with (001) surface orientation, the lattice mismatch is given by[15]

$$\frac{\Delta a}{a}=\frac{C_{11}}{C_{11}+2C_{12}}\frac{\Delta a_\perp}{a}. \tag{1}$$

The biaxial strain causes the hole states to split by an amount[16]

$$\Delta_{001}=2\left|b\frac{\Delta a_\perp}{a}\right|=2\left|b\frac{C_{11}+2C_{12}}{C_{11}}\frac{\Delta a}{a}\right|, \tag{2}$$

where $b=-1.72(5)$ eV is the hole deformation potential for the P BE for [001] strain.[17] Thus, we find that the lattice mismatch between ^{28}Si and ^{nat}Si at $T\sim0$ K is $3.03(10)\times10^{-6}$ for $^{28}Si/^{nat}Si$–1 and $3.01(12)\times10^{-6}$ for $^{28}Si/^{nat}Si$–2. This corresponds to a change in the low temperature lattice parameter of silicon, referenced to a change of isotopic mass of 1 amu, of $2.77(9)\times10^{-5}$ for $^{28}Si/^{nat}Si$–1 and $2.76(11)\times10^{-5}$ for $^{28}Si/^{nat}Si$–2.

For an epitaxial layer of ^{30}Si grown on a ^{nat}Si substrate with (111) surface orientation, the lattice mismatch is given by[15]

$$\frac{\Delta a}{a}=\frac{C_{11}+2C_{12}+4C_{44}}{3(C_{11}+2C_{12})}\frac{\Delta a_\perp}{a}, \tag{3}$$

and the biaxial strain causes a valence band splitting of[16]

$$\Delta_{111}=\frac{2}{\sqrt{3}}\left|d\frac{\Delta a_\perp}{a}\right|, \tag{4}$$

where $d=-4.53(10)$ eV is the hole deformation potential for the P BE for [111] strain.[17] Together with the observed 2.61(6) cm^{-1} splitting of the no-phonon P BE transition, this yields a lattice mismatch of $4.29(14)\times10^{-5}$, which is significantly lower than the value of $5.60(5)\times10^{-5}$ found by Wille *et al.*[7] for the same sample. This lattice mismatch for the $^{30}Si/^{nat}Si$ sample corresponds to a change in lattice parameter of $2.42(8)\times10^{-5}$ for a change in isotopic mass of 1 amu. However, since the no-phonon P BE transition in the ^{nat}Si substrate was observed to split by 0.18(3) cm^{-1}, indicating a sharing of the strain between the epilayer and the substrate due to the finite thickness of the substrate, it may be more correct to take the effective epilayer splitting to be the sum of the two splittings. This would result in a lattice mismatch of $4.58(18)\times10^{-5}$ for the $^{30}Si/^{nat}Si$ sample, but is still significantly lower than the value obtained by Wille *et al.*[7] Referenced to a change of 1 amu, the low temperature change in lattice parameter would then be $2.59(10)\times10^{-5}$, which is in agreement with the values found for the $^{28}Si/^{nat}Si$ samples.

IV. CONCLUSIONS

Using high-resolution PL, we have measured the splitting of the no-phonon P BE transition in samples of epitaxial ^{28}Si and ^{30}Si, grown on ^{nat}Si substrates, resulting from lattice mismatches as low as $3.01(12)\times10^{-6}$. Values of the lattice mismatch were corrected for the two previously studied[8] $^{28}Si/^{nat}Si$ samples, and results for $^{30}Si/^{nat}Si$ were presented. The change in lattice parameter referenced to a change of isotopic mass of 1 amu was found to be consistent between the $^{28}Si/^{nat}Si$ and $^{30}Si/^{nat}Si$ samples when the splitting of the P BE transition in the ^{nat}Si substrate for the $^{30}Si/^{nat}Si$ sample was taken into account. A discrepancy was found in the lattice parameter variation with isotopic mass between our results and the previous result of Wille *et al.*[7] for the same

$^{30}Si/^{nat}Si$ sample. The origin of this discrepancy is not known at this time, although the x-ray diffraction result of Wille *et al.* is more direct.

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