

Isotopic mass dependence of the lattice parameter in silicon determined by measurement of strain-induced splitting of impurity bound exciton transitions

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Abstract

The strain-induced splitting of the impurity bound exciton (BE) transitions in epitaxial layers of isotopically enriched ^{28}Si grown on silicon substrates of natural isotopic composition has been studied using high-resolution photoluminescence (PL) spectroscopy. The slight difference in lattice parameter between the ^{28}Si epitaxial layer and the natural silicon substrate induces a biaxial strain in the epitaxial layer, which can be detected with remarkable sensitivity using low-temperature PL. Measurement of the splitting of the BE transitions in these epitaxial layers of ^{28}Si provides us a method for determining the isotopic mass dependence of the lattice parameter in silicon with unprecedented precision. The level of precision achieved is attributed to the fact that the BE no-phonon transitions in isotopically enriched silicon are much sharper than in natural silicon. We find that scaled to an isotopic mass difference (ΔM) of 1 amu, the relative difference in lattice parameter ($|\Delta a/a|$) for silicon is 3.3×10^{-5} .

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Photoluminescence (PL) spectroscopy of impurity-bound exciton (BE) transitions is a subject that has been studied in great detail and documented in several reviews. It has, however, never been applied to the determination of the isotopic mass dependence of the lattice parameter in silicon. The use of PL spectroscopy in measuring lattice parameter differences between epitaxial layers and substrates is not unprecedented in semiconductor spectroscopy. For example, Hu et al. [1] measured lattice mismatches in the 10^{-5} range for epitaxial layers of undoped GaAs grown on a variety of GaAs substrates.

In the present study, the effects of isotopic composition on the properties of silicon contribute to the precision and sensitivity with which the lattice parameter variation with isotopic mass can be measured. Studies of these effects on

indirect band gap transitions in silicon had long been delayed due to the lack of suitable samples. In the first such PL study, Karaiskaj et al. [2] observed a 0.92 cm^{-1} decrease in the indirect band gap energy of highly enriched ^{28}Si compared to natural silicon ($^{\text{nat}}\text{Si}$). Shifts in the wavevector-conserving phonon energies were also observed. The band gap shift was explained as being due to mainly to the electron–phonon renormalization, with a negligible contribution from the dependence of the sample volume on isotopic mass. In the same study, it was also noted that the BE no-phonon (NP) transitions were much sharper in the highly enriched ^{28}Si samples than in $^{\text{nat}}\text{Si}$, even though the ^{28}Si sample was of only moderate chemical purity, with a boron concentration of $7 \times 10^{14} \text{ cm}^{-3}$ and a phosphorus concentration of $7 \times 10^{13} \text{ cm}^{-3}$. In natural silicon, the P BE NP transition has a linewidth of 0.041 cm^{-1} full-width and half-maximum (FWHM). The observed linewidth of the same transition in the ^{28}Si sample was 0.014 cm^{-1} ,

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essentially identical to the maximum available instrumental resolution of the Fourier transform spectrometer used in the study. The inhomogeneous isotope broadening inherent in ^{nat}Si was interpreted as resulting from statistical fluctuations of the isotopic composition within the effective radius (~ 3.5 nm) of the BE.

Following the observation of decreased linewidths in the ^{28}Si PL spectrum, it was also discovered that many of the infrared absorption transitions of donors and acceptors were much sharper in ^{28}Si than in ^{nat}Si [3]. These transitions in ^{nat}Si were dominated by the same inhomogeneous isotope broadening that was seen in PL. The broadening of the infrared absorption transitions was interpreted as resulting from local shifts in the impurity ground state binding energy due to fluctuations within the fairly compact ground state wavefunction, rather than the dependence of the ground-state binding energy on isotopic mass. This dependence was found to be small between highly enriched ^{28}Si , ^{29}Si , and ^{30}Si [4].

As mentioned previously, the linewidths of the BE transitions in ^{28}Si were limited by the available instrumental resolution. In order to overcome this limitation, a photoluminescence excitation (PLE) method was adopted to allow for a great increase in the spectral resolution. Indeed, PLE spectra revealed much sharper P BE NP and B BE NP transitions. Linewidths as narrow as 0.0025 cm^{-1} FWHM were observed. However, it is believed that the fundamental limit for BE linewidths in isotopically enriched silicon has still not been reached, as residual splittings have been observed in some of the BE transitions. These splittings are possibly due to the presence of unintentional carbon impurities, which causes random internal strain fields [5]. It would appear that at the present time, the PLE spectroscopy of ^{28}Si is limited by the lack of samples of higher chemical purity. This led the authors to consider alternatives to bulk ^{28}Si for BE spectroscopy.

Due to the cost and difficulty involved with growing a bulk ^{28}Si crystal of high chemical purity, isotopic enrichment, and crystalline perfection, epitaxial layers of ^{28}Si are often grown as a way of providing a sample of the material for characterization purposes. Two samples of epitaxial layers of ^{28}Si grown on ^{nat}Si substrates were made available for the present study. The ^{28}Si was grown from silane enriched to 99.9%.

PL spectra of the $^{28}\text{Si}/^{nat}\text{Si}$ samples collected at moderate resolution (0.5 cm^{-1}) revealed two lines in the P BE NP region: one resulting from the P BE transition in the ^{nat}Si substrate, and the other resulting from P BE transition in the ^{28}Si epitaxial layer. As expected [2], the P BE transition in the ^{28}Si epilayer was shifted down from that in the ^{nat}Si substrate by the 0.92 cm^{-1} difference in band gap energy between ^{28}Si and ^{nat}Si . However, when the PL spectra were collected at high resolution, a splitting of the P BE transition in the ^{28}Si epitaxial layer was observed. This splitting was found to be consistent between the two samples: 0.146 cm^{-1} for the first sample ($^{28}\text{Si}/^{nat}\text{Si}$ #1) and 0.149 cm^{-1} for the second sample ($^{28}\text{Si}/^{nat}\text{Si}$ #2), as shown

in Figs. 1 and 2, respectively. The linewidths of the observed P BE transitions in the ^{28}Si epilayer are essentially equal to the $\sim 0.014\text{ cm}^{-1}$ instrumental resolution of the Fourier transform spectrometer used in the study.

There was also a small amount of the slightly deeper donor As present in the second sample ($^{28}\text{Si}/^{nat}\text{Si}$ #2). The As BE NP transition was also split by 0.149 cm^{-1} , equal to the splitting measured for the P BE NP transition in the same sample.

The observation of such well-resolved splittings of the donor BE transitions in the ^{28}Si epitaxial layer was rather surprising since ^{28}Si and ^{nat}Si have nearly the same isotopic composition. Natural silicon is nearly monoisotopic, containing 92.2% ^{28}Si . The lattice mismatch between the epitaxial layer and the substrate is thus very small.

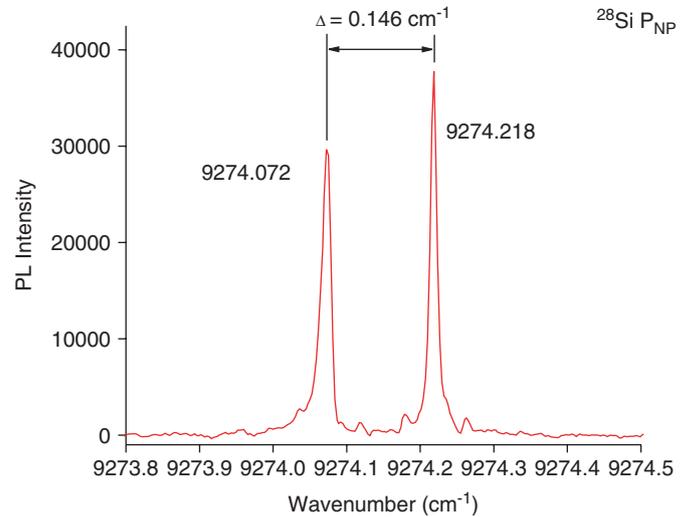


Fig. 1. PL spectrum showing the well-resolved splitting of the P BE NP transition in the ^{28}Si epilayer in sample $^{28}\text{Si}/^{nat}\text{Si}$ #1.

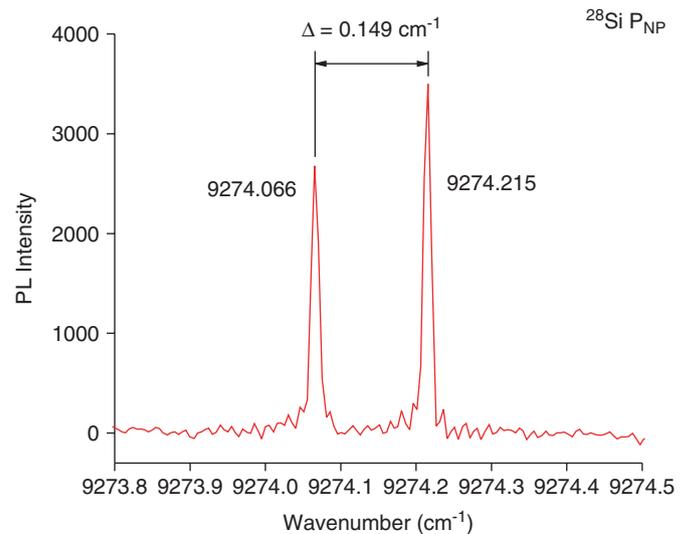


Fig. 2. PL spectrum showing the well-resolved splitting of the P BE NP transition in the ^{28}Si epilayer in sample $^{28}\text{Si}/^{nat}\text{Si}$ #2.

The hydrostatic part of the biaxial strain causes a shift in the band gap, while the shear component splits the valence band, lifting the degeneracy of the heavy and light hole bands at the valence band maximum. The valence band splitting results in a two-fold degeneracy of the donor BE ground state, accounting for the two observed transitions. For an epitaxial layer of ^{28}Si grown on a $^{\text{nat}}\text{Si}$ substrate in the [001] direction, the in-plane strain component in the epitaxial layer is

$$e_{\parallel} = (a_{\text{nat}} - a_{28})/a_{28} \cong (a_{\text{nat}} - a_{28})/a_{\text{nat}} \equiv \Delta a/a, \quad (1)$$

where a_{28} is the lattice parameter of ^{28}Si , a_{nat} is the lattice parameter of $^{\text{nat}}\text{Si}$, and $\Delta a/a$ is the fractional lattice parameter difference. Since only small strains are present in the epilayers, the approximation $a_{28} \cong a_{\text{nat}}$ is used in the denominator.

The out-of-plane strain component is

$$e_{\perp} = -2(C_{12}/C_{11})e_{\parallel} = -2(C_{12}/C_{11})(\Delta a/a), \quad (2)$$

where C_{11} and C_{12} are elastic compliance constants of silicon [6].

The biaxial strain causes the valence band to split by an amount [7]

$$\Delta = 2b(e_{\perp} - e_{\parallel}) = -2b[(C_{11} + 2C_{12})/C_{11}](|\Delta a/a|), \quad (3)$$

where $b = -1.85 \text{ eV}$ is the valence band deformation potential for Si [8].

We thus find that the lattice parameter difference between the ^{28}Si epilayer and the $^{\text{nat}}\text{Si}$ substrate is 2.76×10^{-6} in the first sample and 2.81×10^{-6} in the second sample. Referenced to a change of isotopic mass of 1 amu, the change in lattice parameter in silicon with isotopic mass is 3.2×10^{-5} in the first sample and

Table 1

Values of P BE NP splittings in ^{28}Si epilayer for samples $^{28}\text{Si}/^{\text{nat}}\text{Si}$ #1 and $^{28}\text{Si}/^{\text{nat}}\text{Si}$ #2 with corresponding lattice parameter differences

	$^{28}\text{Si}/^{\text{nat}}\text{Si}$ #1	$^{28}\text{Si}/^{\text{nat}}\text{Si}$ #2
Δ	$0.146 \pm 0.003 \text{ cm}^{-1}$	$0.149 \pm 0.002 \text{ cm}^{-1}$
$ \Delta a/a $	$(2.76 \pm 0.05) \times 10^{-6}$	$(2.81 \pm 0.04) \times 10^{-6}$
$ \Delta a/a _{\Delta M=1}$	$(3.2 \pm 0.1) \times 10^{-5}$	$(3.3 \pm 0.1) \times 10^{-5}$

3.3×10^{-5} in the second sample. The results for the two samples are summarized in Table 1.

Our results agree with those from an X-ray diffraction study of ^{30}Si epitaxial layers grown on $^{\text{nat}}\text{Si}$ substrates, in which the lattice parameter variation with isotopic mass was found to be 2.9×10^{-5} [9]. However, the reliability of this value is questionable since the isotopic purity the ^{30}Si material used is unknown. It is also likely that the ^{30}Si used in that study may not have been of high chemical purity.

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