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Isotopic dependence of the $E'_0$ and $E_1$ direct gaps in the electronic band structure of Si

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(Received 22 July 2005; published 27 October 2005)

The $E'_0$ direct transition of Si between its valence band maximum ($\Gamma'_v$) and conduction band minimum ($\Gamma'_c$) and the $E_1$ direct transition along (111) are studied in isotopically enriched $^{28}$Si, $^{29}$Si, and $^{30}$Si employing photomodulated reflectivity. Their energies ($E_G$) at low temperature are found to increase with increasing isotopic mass ($M$) according to $E_G(M)\propto E'_0 - CM^{-1/2}$, as predicted in the theory for band gap renormalization by zero-point vibrations through electron-phonon interaction and volume changes associated with anharmonicity. Here $E'_0$ is the energy gap of the “infinitely” massive isotope, free of renormalization effects.

DOI: 10.1103/PhysRevB.72.153203

PACS number(s): 78.55.Ap, 63.20.Kr, 78.40.Fy

I. INTRODUCTION

The present knowledge of the electronic band structure of Si stems from experimental observation of electronic transitions in transmission, reflectivity, or cyclotron resonance, on the one hand, and theoretical calculations, e.g., those based on pseudopotential$^1$ or $k \cdot p^2$ methods, on the other. In this manner it has been established that the fundamental, indirect band gap of Si occurs between the $\Gamma'_v$ valence band maximum and the $\Delta_k$ conduction band minima along (100). The fundamental gap has been extensively studied in the past, including its dependence on temperature$^{3,4}$ and pressure.$^5$ Recently, the dependence of the fundamental band gap on the average isotopic mass of Si has been investigated experimentally.$^6$–$^8$

Studied in isotopic effects have provided unique opportunities for comparing experimental results with band structure calculations which implicitly yield electronic energies for a static lattice. We note band gaps measured experimentally are necessarily renormalized by electron-phonon interaction and volume expansion associated with lattice vibrations in combination with the anharmonicity of the interatomic potential. The isotopic investigations allow both the bare band gap of the static lattice and the corresponding band gap renormalization to be determined with high accuracy.$^7$–$^8$ It is in this spirit that the present investigation focuses on the isotopic dependence of the $E'_0$ and $E_1$ direct band gaps of Si.

The variation of the band gap $E_G$ with the average isotopic mass $M$ can be given by

$$
\left( \frac{\partial E_G}{\partial M} \right)_{T,P} = \left( \frac{\partial E_G}{\partial M} \right)_{T,V} + \frac{D}{V} \left( \frac{\partial V}{\partial M} \right)_{T,P},
$$

where $D = -B(\partial E_G/\partial P)_{T,M}$ is the deformation potential for hydrostatic stress and $B$, the bulk modulus. The first term on the right-hand side of Eq. (1) arises from the band gap renormalization by the electron-phonon interaction and the second is due to dependence of the band gap on volume. If $E'_0$ denotes the band gap for the static crystal, the two terms in Eq. (1) describe its phonon-related renormalization to $E_G(M)$ at fixed $T$ and $P$. A theoretical consideration$^8$ yields a simple expression for the band gap renormalization in an elemental semiconductor at absolute zero temperature

$$
E_G(M) - E'_0 = -CM^{-1/2}.
$$

From the above expression, it is seen that $E'_0$ is the bare band gap in a hypothetical crystal made of the infinitely massive isotope, free of phonons and hence renormalization effects.

The $E'_0$ and $E_1$ direct band gaps of Si, separated by only ~100 meV, occur at the $\Gamma$ point and along the $\Lambda$ direction of the Brillouin zone, respectively. Optical transitions across these gaps have been observed in reflectivity,$^9$ ellipsometry$^{10,11}$ and a variety of modulated reflectivity measurements, such as magnetoreflectivity,$^{12}$ thermoreflectivity,$^{13,14}$ electroreflectivity,$^{15,17}$ and wavelength-modulated reflectivity.$^{18,19}$ Recently, Lastras-Martínez et al.$^{20}$ performed ellipsometric measurements on isotopically enriched $^{28}$Si and $^{30}$Si and deduced the isotopic dependence of $E_1$ from the analysis of the data in reciprocal (Fourier-inverse) space. We note, however, that these measurements did not resolve the nearly degenerate $E'_0$ and $E_1$ transitions and the isotopic shift was assigned solely to the stronger $E_1$ transition. In the present Brief Report, we report the direct observation of both $E'_0$ and $E_1$ in photomodulated reflectivity and determine their isotopic shifts.
TABLE I. Isotopic composition and average masses of isotopically enriched Si samples.

<table>
<thead>
<tr>
<th>Sample</th>
<th>%^{28}Si</th>
<th>%^{29}Si</th>
<th>%^{30}Si</th>
<th>M</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample^{28}Si</td>
<td>99.92</td>
<td>0.075</td>
<td>0.005</td>
<td>27.98</td>
</tr>
<tr>
<td>Sample^{29}Si</td>
<td>4.3</td>
<td>91.37</td>
<td>4.3</td>
<td>28.98</td>
</tr>
<tr>
<td>Sample^{30}Si</td>
<td>4.29</td>
<td>7.46</td>
<td>88.25</td>
<td>29.81</td>
</tr>
</tbody>
</table>

II. EXPERIMENT

Table I shows the isotopic composition of the bulk Si samples investigated, as determined by secondary ion mass spectrometry (SIMS); the details of the crystal growth are given in Ref. 21. The samples were Syton-polished and mounted inside an optical cryostat. Radiation from a Xe discharge lamp, spectrally decomposed by a 0.5 m grating spectrometer, was retroreflected from the sample and detected with a Si photodiode. The reflectivity was photomodulated by focusing radiation (λ=635 nm, P=3 mW) from a diode laser onto the sample, the laser beam being mechanically chopped at 200 Hz. The photomodulated signal, measured at 8 K, was recorded using a lock-in amplifier.

III. RESULTS AND DISCUSSION

Figure 1(a) shows photomodulated reflectivity spectrum of ^{28}Si recorded in the range 3.18–3.73 eV at 8 K. The spectrum contains two characteristic signatures, attributed to the excitonic transitions across the E_0’ and E_1 excitonic gaps shown in Fig. 1(b). Note the excitonic signatures do not show the spin-orbit splittings for the valence band at its maximum (ΔSO) or along Λ [expected to be 3/2ΔSO (Ref. 22)].

The data displayed in dots were fitted (lines) with an excitonic line-shape analysis:

\[ \frac{\Delta R}{R}(\omega) = \frac{(W^2 - 1)[\beta_{r}(\omega) + 2A\beta_{l}(\omega)] - 2W[\beta_{r}(\omega) - 2A\beta_{l}(\omega)]}{\Gamma^3(W^2 + 1)^2}, \]

where \( \omega_{ex} \) is the excitonic band gap, \( \Gamma \) a broadening parameter, and \( A \) an asymmetric broadening parameter. Seraphin coefficients \( \beta_{r}(\omega) \) and \( \beta_{l}(\omega) \) of Si for the range of interest are taken from Ref. 10.

The excitonic band gaps \( E_0' = 3.383 \text{ eV} \) and \( E_1 = 3.483 \text{ eV} \) determined from the fits, are in good agreement with previously measured values 3.378 eV,11 3.365 eV,17 and 3.4 eV for \( E_0' \) and 3.46 eV and 3.45 eV for \( E_1 \). In addition, the broadening parameter \( \Gamma \) determined from the fits is 38 meV for \( E_0' \) and 59 meV for \( E_1 \) transition, respectively, in remarkable agreement with values 39.8 and 65.4 meV, obtained from a temperature dependence of the dielectric function of Si.24 Given that \( \Delta SO = 44.1 \text{ meV/amu} \) and the large values for \( \Gamma \), it is perhaps not surprising that the excitonic signatures do not show features associated with spin-orbit splitting.

Isotopic dependence of the \( E_0' \) and \( E_1 \) excitonic band gaps of Si is displayed in Fig. 2, where the photomodulated reflectivity spectra of \(^{28}Si\), \(^{29}Si\), and \(^{30}Si\) are shown for the spectral range corresponding to the shaded area in Fig. 1(a). The \( E_0' \) and \( E_1 \) excitonic band gaps determined from the line-shape analysis are plotted as functions of \( M^{-1/2} \) in Fig. 3. Linear least-squares fits to the data according to Eq. (2) yield the corresponding isotopic dependences \( E_0' = (3.4468 - 0.3378M^{-1/2}) \text{ eV} \) and \( E_1 = (3.6120 - 0.6821M^{-1/2}) \text{ eV} \). Over the small range of available isotopic masses, the isotopic dependences can also be approximated by fits linear in \( M^{-1/2} \). As can be seen in Fig. 1(a), the excitonic line-shape analysis employed in the present study did not reproduce exactly the photomodulated reflectivity spectra observed for photon energies below the peak for \( E_0' \) and beyond that for \( E_1 \); the experimental uncertainties of the isotopic dependences for \( E_0' \) and \( E_1 \) given above could be therefore somewhat underestimated.

Lastras-Martinez et al.20 determined \( (\partial E_1/\partial M)_T \)\( P = (1.9 \pm 0.4) \text{ meV/amu} \) using ellipsometry. We note that the

![Figure 1](image-url)
ellipsometric measurements did not resolve the $E_0'$ and $E_1$ contributions and their result for $E_1$ may be interpreted as a weighted average of the isotopic dependences of $E_0'$ and $E_1$. Our measurements (Fig. 1) indicate that the amplitude of the $E_1$ transition is approximately three times stronger than that of $E_0'$. If we assume that the average isotopic dependence of $E_0'$ and $E_1$ is scaled by the amplitudes of the respective transitions, then our measurements yield the average $\frac{1}{2}[3(\partial E_1/\partial M)_{T,P}+(\partial E_0'/\partial M)_{T,P}]=(1.9 \pm 0.2)$ meV/amu, which agrees with the value of Lastras-Martínez et al.\textsuperscript{20}

In Table II, we show in the fourth column $(D/\sqrt{V})\partial V/\partial M$, i.e., the contribution to $(\partial E_1/\partial M)_{T,P}$ due to the dependence of the molar volume on isotopic mass, calculated using (i) the measured values of the lattice parameter as a function of $M$ and (ii) a theoretical formula of Hu et al.\textsuperscript{26}

$$\frac{1}{V} \frac{\partial V}{\partial M} = - \frac{6B'}{a^{5/2}B^{1/2}M^{5/2}},$$

expressed in terms of macroscopic parameters, where $a$ is the lattice parameter defined by the cubic unit cell of Si and $B'=(\partial B/\partial P)_T$, the third order bulk modulus. We could not make a similar calculation for $E_0'$ because, to the best of our knowledge, the value of the deformation potential for this gap is not reported in the literature. The contribution due to the electron-phonon interaction, $(\partial E_1/\partial M)_{T,Y}$, given in the fifth column, is obtained as a difference of the values in the third and fourth columns according to Eq. (1). The values in the sixth column represent the theoretically calculated contribution $(\partial E_1/\partial M)_{th}$. Dots are data deduced from the excitonic line shape analysis of the photomodulated reflectivity spectra and the lines are linear least-squares fits yielding the isotopic dependences.

For comparison, similar data for the fundamental, indirect excitonic band gap $E_{gs}$ from Ref. 7 are included in Table II. The stronger isotopic dependence of $E_1$ than that of $E_0'$ is noteworthy. We comment that it is consistent with the observed\textsuperscript{24} stronger temperature dependence of $E_1$ than that of $E_0'$. In addition, the close values of $(\partial E_0'/\partial M)_{T,P}$ and $(\partial E_0'/\partial M)_{th}$ imply a substantially weaker effect of molar volume on $E_0'$ than that on $E_1$. Very similar isotopic dependences for $E_{gs}$ and $E_0'$ can be explained by their common valence band maximum ($\Gamma_8$), which experiences significantly stronger interaction with phonons\textsuperscript{27,30} than the respective conduction band minima, $\Gamma_6$ and $\Gamma_6$.

IV. CONCLUSIONS

In the present study, the isotopic mass dependence of the electronic band gaps of Si has been experimentally addressed in the context of direct gaps. The fingerprints for the $E_G(M)$, as revealed in the photomodulated derivative signatures at low temperature for $^{28}$Si, $^{29}$Si, and $^{30}$Si, follow the mass dependence expected for renormalization effects produced

| $E_0'$ (meV) | $1.1 \pm 0.1$ |
| $E_1$ (meV) | $-5148^{28}$ |
| $E_{gs}$ (meV) | $1.01 \pm 0.04$ |

<table>
<thead>
<tr>
<th>$D$ (meV)</th>
<th>$(\partial E_0'/\partial M)_{T,P}$ (meV/amu)</th>
<th>$(\partial E_1/\partial M)_{T,P}$ (meV/amu)</th>
<th>$(\partial E_{gs}/\partial M)_{T,Y}$ (meV/amu)</th>
<th>$(\partial E_{gs}/\partial M)_{th}$ (meV/amu)</th>
<th>$E_G^0-E_G^{28}$ (meV)</th>
<th>$E_G^0$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$E_0'$</td>
<td>1.25 (Ref. 27)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$E_1$</td>
<td>$64 \pm 4^{(28)}$Si</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$E_{gs}$</td>
<td>$59 \pm 1^{(28)}$Si</td>
<td></td>
<td></td>
<td></td>
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</tr>
</tbody>
</table>

FIG. 3. The $E_0'$ and $E_1$ excitonic band gaps plotted vs $M^{-1/2}$. Dots are data deduced from the excitonic line shape analysis of the photomodulated reflectivity spectra and the lines are linear least-squares fits yielding the isotopic dependences.
by zero-point vibrations through electron-phonon interaction and volume changes associated with anharmonicity, i.e., by Eq. (2).

As discussed in Sec. III, the \( E_0' \) and \( E_1 \) signatures in the modulated reflectivity did not show any distinct feature which could be identified with spin-orbit splitting; the large width of \( E_0' \) and \( E_1 \) clearly plays a significant role in this context. In Refs. 7 and 8, the TO-assisted signature for \( E_{g_2} \) was accompanied by that for \( E_{g_3} \), the mass independence of \( \Delta_{SO} \) emerged from that study. On the basis of this evidence it appears that both \( E_0' \) and \( E_0' + \Delta_{SO} \) are characterized by the same isotopic mass dependence. A similar comment applies to \( E_1 \) and \( E_1 + \frac{2}{3} \Delta_{SO} \).

ACKNOWLEDGMENTS

The work at Purdue and UCB received support from the National Science Foundation Grant No. DMR0405082 and Grant No. DMR0405472, respectively. In addition, the U.S. Department of Energy Contract No. DE-AC03-76SF00098 supported the work at LBNL.