Semicond. Sci. Technol. 7 (1992) 1271–1273. Printed in the UK

LETTER TO THE EDITOR

Isotope dependence of the indirect energy gap of germanium

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Received 17 August 1992, accepted for publication 19 August 1992

Abstract. No-phonon luminescence from excitons bound to shallow donors and acceptors in crystalline germanium is found to move to higher energy with increasing mass number A of the germanium at the rate $dE/dA = 0.35 \pm 0.02$ meV. We show that it is possible to predict this shift, to a good approximation, from the temperature dependence of the energy gap and the effect on the lattice parameter of the different isotopes.

With five stable isotopes, germanium is an ideal material for studying the effects of changing the host lattice isotopes on the vibrational and electronic properties of a semiconductor. Data have been presented for the isotope dependence of the lattice parameter [1] and for the effects of isotopic disorder on the phonons [2]. The indirect energy gap has been reported to be 0.9 ± 0.05 meV larger in a mixed $^{74}Ge/^{76}Ge$ crystal than in one of natural isotopic content [3], and a recent pseudopotential–bond-charge-model calculation has predicted a shift of 1.3 meV between these particular crystals [4]. This letter has two aims: firstly, to report accurate measurements of the changes in indirect energy gap by using the no-phonon photoluminescence of excitons bound to shallow donors and acceptors in several isotopically pure Ge crystals and, secondly, to show that it is possible to reproduce the observed shifts using a simple, empirically based calculation.

Single-crystal Ge samples grown with one dominant isotope have been used in this work. For example, the nominal ^{74}Ge sample was shown by SIMS analysis to be 0.5 at.% ^{70}Ge, 0.17 at.% ^{72}Ge, 2.2 at.% ^{73}Ge, 96.8 at.% ^{74}Ge and 0.33 at.% ^{76}Ge, giving an averaged mass number of $A = 73.96$. Donor and acceptor concentrations were typically below 10^{13} cm^{-3}. The luminescence was excited using the 0.5145 μm line of an Ar^+ laser with the samples mounted stress-free immersed in liquid helium at 4.2 K. It was recorded using a Nicolet 60SX Fourier transform spectrometer fitted with a North Coast Ge diode detector cooled to 90 K. Typical photoluminescence spectra obtained from ^{70}Ge and ^{74}Ge single isotope samples containing trace amounts of copper and phosphorus are shown in figure 1.

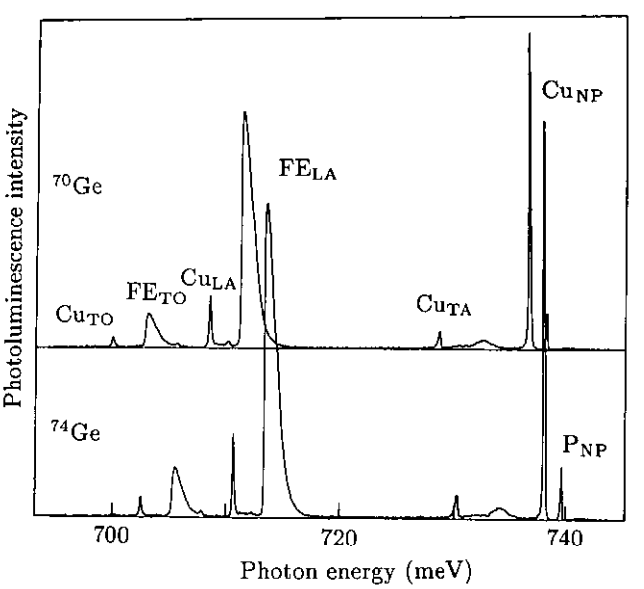

Figure 1. Luminescence, not corrected for the wavelength dependence of the system, from the decay of free excitons and excitons bound to Cu triple acceptors and phosphorus donors in ^{70}Ge and ^{74}Ge at 4.2 K. The subscripts indicate the L-point phonons involved in each transition.

Germanium is an indirect gap semiconductor with its valence band maxima at wavevector $k = 0$ and conduction band minima at the L point. In Ge of natural isotopic content and in the limit of low temperature, the energy of a stationary indirect-energy gap exciton is 740.46 ± 0.03 meV [5]. Luminescence is not ob-

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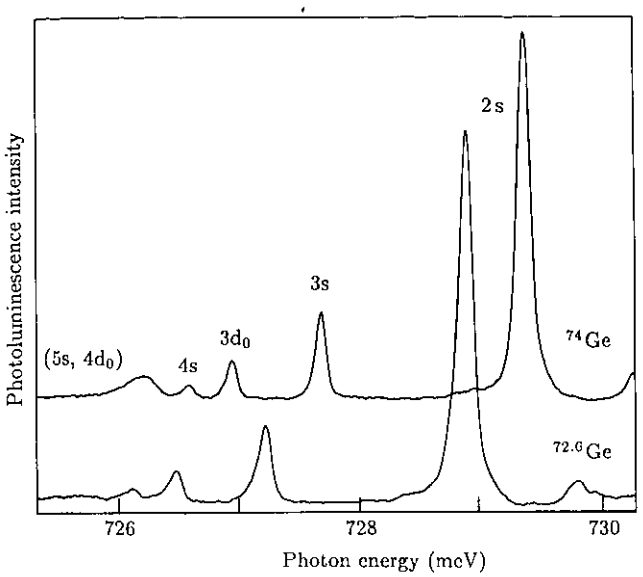

Figure 2. 'Two-electron' luminescence from excitons bound to As donors in ^{74}Ge and natural isotope Ge (effectively $^{72.6}$Ge), leaving the donor in the even parity states as labelled [7]. The separations of the peaks are the same, reflecting the isotopically invariant effective mass states of the donor.

served at this energy because of the need to conserve the wavevector by the emission of a phonon from the L point. All transverse and longitudinal acoustic and optic phonons are observed, with quanta, in natural Ge, of $\hbar\omega^{L}_{TA}$ = 7.9 meV, $\hbar\omega^{L}_{LA}$ = 27.7 meV, $\hbar\omega^{L}_{LO}$ = 30.6 meV and $\hbar\omega^{L}_{TO}$ = 36.1 meV. When the exciton is bound to a neutral shallow donor or acceptor, the localization allows it to decay without phonon emission. The resulting no-phonon line is very well defined and its energy may be accurately measured. The energy E_b binding the exciton to the centre is small for all the centres considered here. For example, for the copper triple acceptor, the deepest centre considered here, E_b = 2.77 meV [6]. Consequently the binding is only a small perturbation to the exciton.

We assume that the binding energies are unchanged by the isotopic content of the lattice, so that the no-phonon energies reflect the isotope-induced changes in the indirect energy gap. As confirmation of this we note first that all the electronic energy states of each centre track together with changes in isotope (figure 2). Secondly, all the no-phonon lines of different shallow centres have the same variation in energy on changing the Ge isotope (figure 3), as expected if the bound excitons are all similar to the free exciton and hence to each other. The rate of change of no-phonon energy E_{NP} with mass number A of the Ge isotope is

$$dE_{NP}/dA = 0.35 \pm 0.02 \text{ meV}. \quad (1)$$

The phonon-assisted luminescence lines are shifted to a photon energy $h\nu = E_{NP} - \hbar\omega$ by the quantum $\hbar\omega$ of the relevant phonon. We find that for all the phonon sidebands of the donors and acceptors investigated here, the change in vibrational quanta are as expected from the mass change using the trivial relationship $\hbar\omega \propto 1/\sqrt{A}$. This result implies that the donor

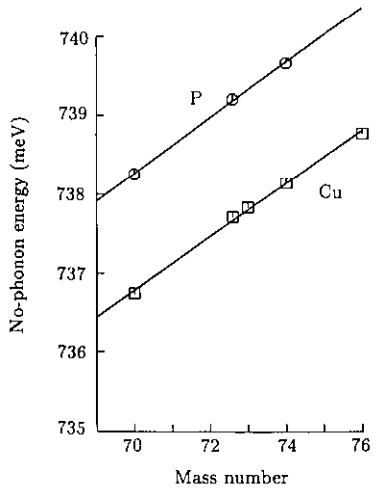

Figure 3. Points show the measured data for the energies of the no-phonon lines of excitons bound to Cu triple acceptors (squares) and P donors (circles).

or acceptor plays a negligible role in determining the effective mass of the phonon modes, consistent with the weakly localized nature of the exciton.

The two main contributions to the isotope dependence of the indirect energy gap are from electron–phonon coupling and from the dependence of the atomic spacing on the isotope. The volume change on changing the isotope from the natural isotopic content (effective mass number 72.6) to nominal ^{74}Ge (with an averaged mass of A = 73.9) has been measured at low temperature [1]:

$$\frac{V^{72.6} - V^{73.9}}{V^{72.6}} = (14.9 \pm 0.3) \times 10^{-6}. \quad (2)$$

The change in energy with volume of the indirect gap is also known [8]:

$$a = V dE/dV = -3800 \text{ meV}. \quad (3)$$

Consequently the change in exciton energy with mass number A from the volume change is only about 12% of the total shift:

$$(dE/dA)_{vol} = 0.044 \text{ meV} \quad (4)$$

and most of the shift arises from the isotope dependence of the electron–phonon coupling. A simple estimate of this contribution to the energy shift can be made from measurements of the temperature dependence of the indirect energy gap. The reasoning is as follows. First we recognize that with increasing temperature the energy gap decreases simply as a result of lattice expansion. This contribution can be calculated explicitly using the deformation potential (equation (3)) and the known volume expansion of Ge; it will be shown to contribute only a minor part of the change. The dominant contributions to the temperature dependence of the energy gap come from structure factors, which contain Debye–Waller terms, and from self-energy terms [4]. When either of these terms is expanded as a power series in the atomic displacements,

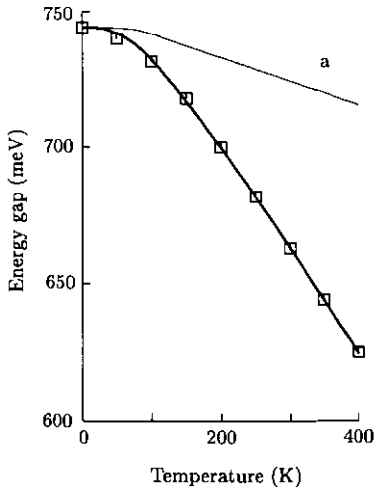

Figure 4. Temperature dependence of the lowest indirect energy gap of Ge. Points show the trend of experimental data from [9], the fine curve 'a' shows the effect of volume expansion and the full curve shows the total fit of equation (5) with $p = 0.4$.

the leading terms are proportional to the mean-square displacements $\langle u^2 \rangle$ of each atom. For a harmonic oscillator of angular frequency ω, mass m and in its nth quantum state, $\langle u^2 \rangle = \hbar(n + \frac{1}{2})/m\omega$. With increasing temperature, the mean quantum state n increases, producing a temperature-dependent change in the energy gap. At low temperature, $\langle u^2 \rangle \propto 1/m\omega$, and so depends on mass as $\langle u^2 \rangle \propto 1/\sqrt{m}$, producing the isotope effects.

We therefore write the temperature dependence of the energy gap as

$$E(T) = E_0 + \int \mathrm{d}\omega f(\omega)[n(\omega, T) + \tfrac{1}{2}] - a(c_{11} + 2c_{12})\frac{\Delta V(T)}{3V} \qquad (5)$$

where the energy gap at $T = 0$ is $E_0 + \int \mathrm{d}\omega f(\omega)/2$. Here, $f(\omega)\mathrm{d}\omega$ is the difference in the electron–phonon coupling for the conduction band minima and the valence band maximum for those modes in the frequency range ω to $\omega + \mathrm{d}\omega$ and the integral is over all the lattice modes. The last term in equation (5) is the volume expansion term.

Figure 4 shows the measured indirect energy gap between 0 and 400 K [9]. Since the maximum vibrational quantum of Ge with natural abundances is equivalent to 440 K, this temperature range is sufficient to sample all the lattice phonons of Ge. The curve 'a' on the figure shows the relatively small contribution from the lattice expansion. The remainder of the shift is produced by the term $\int \mathrm{d}\omega f(\omega) n(\omega, T)$ in equation (5). The functional form of f is unknown. We have assumed that it is determined by the density $g(\omega)$ of phonon states of Ge [10] modified by the phonon frequency in some power law, i.e.

$$f(\omega) = c\omega^p g(\omega). \qquad (6)$$

We find that the temperature dependence of the energy gap may be fitted with $p = 0.4 \pm 0.4$ (figure 4).

Knowing the best-fitting values of c from the fit on figure 4 we can now calculate explicitly the isotopically induced shift $E^i - E^j$ at 0 K between two isotopes of atomic mass number A^i and A^j:

$$E^i - E^j = \tfrac{1}{2}(\sqrt{A^j/A^i} - 1) \int \mathrm{d}\omega f(\omega). \qquad (7)$$

Evaluation yields, for the range $p = 0$–0.8, an electron–phonon contribution of

$$(\mathrm{d}E/\mathrm{d}A)_{\mathrm{e-ph}} = 0.22\text{–}0.30 \text{ meV}. \qquad (8)$$

The total predicted shift is the sum of the contributions in equations (4) and (8) and is

$$(\mathrm{d}E/\mathrm{d}A)_{\mathrm{tot}} = 0.26\text{–}0.34 \text{ meV}. \qquad (9)$$

In this letter we have presented accurate data on the effect of changing the isotope of the Ge lattice on the no-phonon luminescence from excitons bound to shallow donors and acceptors. We have shown that the indirect energy gap increases with mass number as $\mathrm{d}E/\mathrm{d}A = 0.35 \pm 0.02$ meV. A slightly smaller value, $(\mathrm{d}E/\mathrm{d}A)_{\mathrm{tot}} = 0.3 \pm 0.04$ meV, has been predicted using a simple empirical calculation. In contrast, a recent first-principles calculation predicts $(\mathrm{d}E/\mathrm{d}A)_{\mathrm{e-ph}} = 0.42$ meV [4], to which must be added the volume term (equation (4)), giving $(\mathrm{d}E/\mathrm{d}A)_{\mathrm{tot}} = 0.46$ meV.

This work was supported by the Science and Engineering Research Council and by NASA Award W17605 under Interagency Agreement, Office of Health and Environmental Research of the US Department of Energy under Contract Numbers DE-AC03-76SF00098 and DE-AC03-76SF00515.

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