Photoluminescence studies of implantation damage centers in ^{30}Si

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We report photoluminescence (PL) studies of implant-damage centers in ^{30}Si. The *X* and *W* zero-phonon lines (ZPLs) shift by +1.55(5) and +1.27(5) meV, respectively, between ^{nat}Si and ^{30}Si. Using a simple empirical approach, we calculate the shifts to within ~20%. Local vibrational modes are identified at the *X* center and confirmed at the *W* center, supporting the assignment of these centers to self-interstitial clusters. All the strong PL lines produced by ion implantation in the sample have isotope shifts characteristic of ZPLs; they all correspond to independent defect centers, the majority of which have undetermined structures. © *2004 American Institute of Physics*.
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There is currently considerable interest in the properties of single-isotope silicon.[1,2] For example, disorder effects, present in a silicon crystal of natural isotopic abundances, are removed in single-isotope material, increasing the thermal conductivity[3] and clarifying optical spectra.[4,5] In the harmonic approximation, changing the lattice isotope changes the vibrational frequencies of the lattice and of the impurities,[6] and the anharmonicity of the vibrational potential results in a change in bond length.[7] Because the electrons are coupled to the phonons, the electronic band structure is modified.[4] Recently we have presented the effects of changing the lattice isotopes on the electronic states and local-vibrational modes of point defects generated in silicon by electron radiation damage.[8] In this paper we examine the effects of changing the lattice isotopes on defects produced in silicon by ion implantation.

Ion implantation is an important tool for controlling the doping of impurities in semiconductor devices. Inevitably, implantation with energetic ions also introduces radiation damage centers into the crystal, many of which are observable by photoluminescence.[9] The evolution of these unwanted damage centers with annealing has been studies in detail for several decades,[10–13] but a detailed model of the damage reactions is not yet available, and many of the atomic-sized defects are not yet identified. We report here high-resolution photoluminescence (PL) spectra of an isotopically enriched ^{30}Si single crystal that has been implanted with high-energy $^{30}Si^+$ ions. The isotope-induced changes in energy of the zero-phonon lines (ZPLs) of the implant-damage centers are reported and are shown to arise predominantly from the electron-phonon coupling to the continuum of lattice modes. We use the isotope effects to identify the local vibrational modes (LVMs) of the well-known *X* center, and demonstrate that all the strong sharp lines observed in the PL spectra originate from ZPLs.

The Si sample used in this work is isotopically enriched, Czochralski-grown ^{30}Si with abundances ^{28}Si (0.67%), ^{29}Si (0.59%), and ^{30}Si (98.74%), giving a mean mass of 29.98. It contains relatively high concentrations of substitutional carbon and interstitial oxygen.[8] The sample is lightly doped with boron and has also been found to contain small traces of phosphorus, arsenic, and aluminum.[8] Opposite faces of the sample were implanted with 1.5 MeV $^{30}Si^+$ ions at room temperature to doses of 10^{11} and 10^{13} cm^{-2} using that 2 MV van de Graaff ion accelerator at the Surrey Ion Beam Centre.

The PL data were collected using a Bomem DA8 Fourier transform spectrometer fitted with a fast-response Ge diode detector. PL was generated by the 514.5 nm line Ar^+ laser with an incident power of ~300 mW. The spectra reported here have not been corrected for the wavelength dependence of the spectrometer and detector response. The temperature of the samples was maintained by an Oxford Instruments ITC controller with a stability of better than ±1 K. Spectra were taken after the samples had been annealed for 30 min at each temperature from 150 to 700 °C at 50 °C steps in a constant flow of argon in a quartz tube.

Self-ion implantation of silicon followed by annealing to different temperatures generates a wide range of photoluminescence centers (Fig. 1). The lines at 1041.25(5), 1019.47(5), 970.34(2), and 950.81(2) meV in ^{30}Si are the ZPLs of the *X* (I_3), *W*, *G* (C_iC_s, two carbon atoms), and *F* (carbon-related) centers, respectively. In this paper we will focus particularly on the *X* and *W* centers which are believed to be intrinsic defects.[12,13] These centers are commonly observed in irradiated, implanted, and neutron bombarded Si.[10,12] There is no evidence that any impurities are involved in the *X* center. The exact formation process of these centers is currently unknown, but they are thought to be created when a migrating self-interstitial is captured by an interstitial-related defect core. The symmetry of the *W* line has been identified as trigonal.[11]

Detailed *ab initio* calculations of the structures of self-interstitial and vacancy clusters have recently been carried out.[13–15] These calculations have shown that a tetrainterstitial

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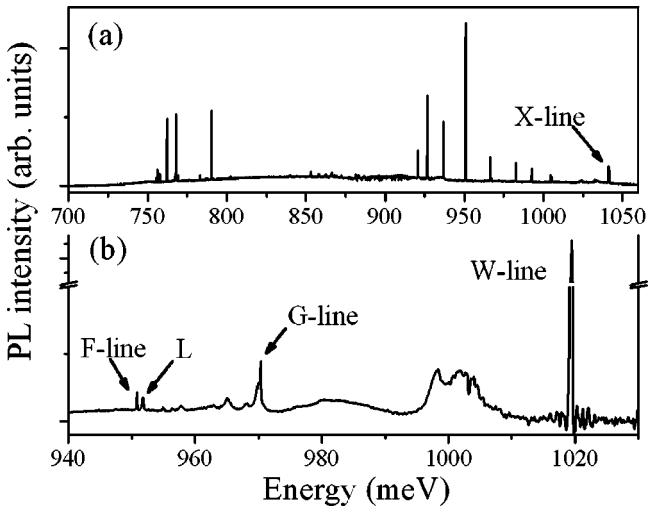

FIG. 1. Photoluminescence from CZ-grown ^{30}Si, (a) implanted with 10^{11} cm^{-2} Si^{+} ions and annealed at 400 °C and (b) implanted with 10^{13} cm^{-2} Si^{+} ions and annealed at 250 °C. The spectra were measured at 4.2 K. L is the 62.7(2) meV LVM of the *W* line in ^{30}Si.

TABLE I. Summary of the measured ZPL energies in self-ion implanted and annealed Si.

^{30}Si (±0.05 meV)	^{nat}Si (±0.05 meV)	Measured shift (±0.01 meV)
737.0	735.4	1.6
747.2	745.7	1.5
762.3	760.8	1.5
767.3	766.5	0.8
856.4	855.4	1.0
920.6	919.7	0.9
982.6	981.5	1.1
986.7	985.1	1.6
992.5	991.3	1.2
1004.4	1003.4	1.0
1005.3	1004.0	1.3
1019.47(5) (*W* line)	1018.20(5)	1.27(7)
1024.4	1022.8	1.6
1032.3	1030.8	1.5
1041.25(5) (*X* line)	1039.70(5)	1.55(7)

center and a tri-interstitial center possess several LVMs, whereas no high-frequency LVMs were identified for vacancy clusters. These finding have led Coomer and co-workers[13,15] to deduce that the *X* and *W* centers are interstitial-related rather than vacancy-related centers, and to suggest the tetrainterstitial and tri-interstitial centers as possible candidates for the *X* and *W* centers respectively.

A single LVM with 70.0(2) meV energy, just above the Raman cutoff edge of 65 meV, has been associated with the *W* line in ^{nat}Si.[11] In ^{30}Si, we observe that this LVM is shifted by −2.3(2) meV relative to the *W* ZPL (Fig. 1). This value is in close agreement with the value expected from the virtual crystal approximation (VCA) if the mode involves only the host atom: $\Delta\hbar\omega_{VCA}=\hbar\omega_{nat}(\sqrt{28.1/29.98}-1)=-2.2(2)$ meV. No LVMs have previously been assigned to the *X* center. In Fig. 2 we see that three weak features at about 974, 972, and 971 meV are consistently observed in the PL spectra of the *X* line measured from proton-irradiated ^{nat}Si. Similar features are also seen in the spectra of implanted ^{30}Si, but they are shifted by −2.1(5), −2.3(2), and −2.1(2) meV, respectively, relative to the *X* ZPL. These isotope shifts are again in good agreement with VCA predictions if the mode involves only the host atoms, establishing that they are LVMs of the *X* center with quanta of 66.2, 67.9, and 69.0 meV in ^{nat}Si. The atoms involved in these modes are predominantly Si atoms, suggesting that the *X*-center is an intrinsic defect.

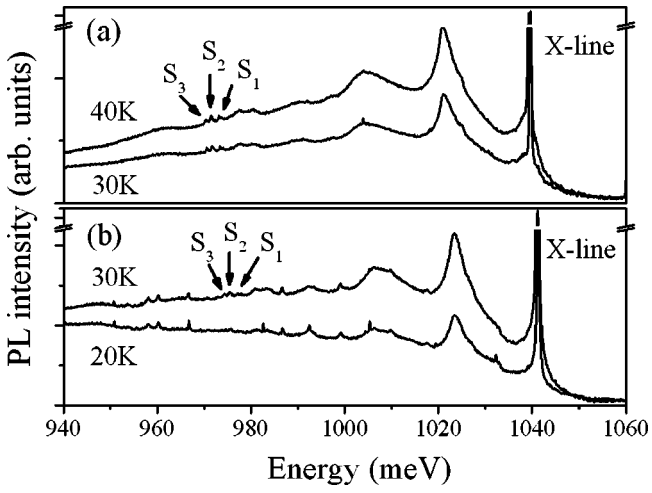

FIG. 2. Photoluminescence spectra of the *X*-line system measured from (a) ^{nat}Si irradiated with protons and annealed at 500 °C, and (b) ^{30}Si implanted with 10^{13} cm^{2} Si^{+} ions and annealed at 450 °C. The LVMs of the *X* line with quanta 66.2, 67.9, and 69.0 meV are labeled S_1, S_2, and S_3, respectively.

In ^{30}Si the *X*- and *W*-ZPLs and shifted by +1.55(5) and +1.27(5) meV, respectively, compared to those in natural-isotope CS Si that has been treated in the same way (Table I). Part of the shift comes from the lattice volume change between ^{30}Si and ^{nat}Si, which is estimated to be $\Delta V/V=-1.32(1)\times10^{-4}$.[7] The deformation potentials ($\Xi=-VdE/dV$) of the *X* and *W* lines are known from uniaxial stress measurements[11,16] as $\Xi_X=2000$ meV and $\Xi_W=-450$ meV, resulting in a contribution to the shifts from the lattice volume change of only $\Delta E_X^V\sim-0.26$ and $\Delta E_W^V\sim+0.06$ meV.

The remainder of the shift can be expressed as the sum over all the changes in the zero-point vibrational energies of the excited and ground electronic states.[17] A mode of mass m_1 with quantum $\hbar\omega_e$ in the excited electronic state and $\hbar\omega_e$ in the ground electronic state contributes $(\hbar\omega_e-\hbar\omega_g)/2$ to the energy of the ZPL. Changing the mass of the mode to m_2 results in a change $(\sqrt{m_1/m_2}-1)(\hbar\omega_e-\hbar\omega_g)/2$ to the ZPL. It is convenient to consider first the LVMs. Unfortunately, the quanta of the LVMs in the excited electronic states are not known for the *X* or *W* centers. In the ground state of the *X* center, we now know that three LVMs have quanta of 66.2, 67.9, and 69.0 meV in ^{nat}Si. We assume that in the excited electronic state these LVMs have quanta 3.5% smaller, as for the LVMs of the C center.[8] These LVMs then only contribute $\Delta E_X^L=+0.11$ meV to the isotope shift of the *X* ZPL. For the *W* line, only one mode with 70 meV energy has so far been identified and nothing appears to be known about the excited state of the *W* center. Assuming again that this LVM softens by 3.5% in the excited electronic state, it will only contribute

$\Delta E_W^L = +0.04$ meV to the ZPL isotope shift. Even if there are several LVMs, the total LVM contribution to the shift will still be a small fraction of the observed shift.

The dominant contribution is from the change in zero-point energy in the continuum of lattice phonons. In principle, this term can be determined from the temperature dependence of the ZPL energy. However, these data are not readily available for the majority of the ZPLs, since their PL is fully quenched at a temperature below ~80 K. Therefore, we have developed an empirical method for predicting the electron-phonon contribution to the isotope shift, which makes use of the well-known temperature dependence of the lowest indirect energy gap.[8] This approach assumes that the strength of the electron-phonon interaction can be estimated with reasonable accuracy by scaling the temperature dependence of the ZPL energy to the temperature dependence of the lowest indirect energy gap. Clearly, this approach is only valid when the two temperature dependencies have a similar form. Here, we will again use this empirical approach to calculate the electron-phonon contribution to the X and W ZPLs.

Between ^{nat}Si and ^{30}Si, the indirect energy gap changes by +1.94(3) meV, of which $\Delta E_g - 2.09$ meV is the calculated electron-phonon contribution.[8] The measured shifts between 0 and 80 K of the X and W lines are −3.5(3) and −2.9(3), respectively. In this temperature range, the indirect gap is shifted by −4.3 meV. Scaling ΔE_{ep} by the temperature-dependence ratio gives electron-phonon contributions to the isotope shifts of $\Delta E_X^{ep} = (3.5/4.3)\Delta E_g = 1.70(5)$ meV and $\Delta E_W^{ep} = 1.41(5)$ meV for the X and W lines, respectively. The total predicted shift is then $\Delta E_X^V + \Delta E_X^L + \Delta E_X^{ep} = 1.55$ meV, in agreement with experiment, and 1.51 meV for W, within 20% of experiment.

Finally, the isotopic shifts of other sharp lines are shown in Table I. Although these PL features are readily observed in heavily damaged Si, the identities of these lines have not yet been established. Here we note that the isotopic shifts of these lines (~1 to 2 meV) are within the range of the observed shifts of the X, W, and other ZPLs,[8] while we have seen that LVMs move significantly more. The widths of these lines, being narrower than 0.15 meV, also show that they are ZPLs. We therefore suggest that all the strong lines visible in the spectra and listed in Table I are ZPLs, rather than LVMs, which means in practice that they all correspond to independent defect centers, the majority of which have completely undetermined structures.

In summary, we have presented data on the host-isotope effects on the ZPLs of the X and W centers. We have shown that the dominant contribution to the ZPL shifts arises from the effects of the electron-phonon coupling to the continuum of lattice modes. We have shown that the X centers has LVMs of quanta 66.2, 67.9, and 69.0 meV in ^{nat}Si, and confirmed that the W center has an LVM of 70.0 meV. The existence of these modes supports the assignment of the X and W centers to self-interstitial clusters.

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