Optical studies of metastable properties of a defect with a zero-phonon transition at 0.615 eV in 2-MeV electron-irradiated Czochralski-grown silicon

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Using infrared absorption spectroscopy, a new zero-phonon bound exciton (BE) line is found at 0.615 eV in 2-MeV electron-irradiated Czochralski-grown silicon. The optical properties of this BE reveal an interesting metastability in the neutral charge state of the defect. After cooling the sample in darkness this spectrum is initially very weak, but grows up after optical band-gap excitation for several hours at low temperatures. An activation energy of 0.21 eV is found for the thermal quenching of the line upon heating in darkness. The optical data are explained as connected with a carbon-related complex defect with two different geometrical configurations in the neutral charge state.

Silicon grown by the Czochralski (Cz) technique usually contains isolated oxygen and carbon atoms in concentrations of the order of 10^{18} and 10^{16} atoms/cm^3, respectively. A large number of optical bound-exciton (BE) transitions from oxygen- and carbon-related defects in Cz-grown silicon with no phonon energies between 0.45 and 1.10 eV have been studied during the past decades.[1-10] The majority of the defects causing these transitions are formed by irradiation with high-energy particles such as electrons, neutrons, and protons, but many are also created by heating.

During electron irradiation, vacancies and silicon interstitials are created in the primary damage event. Vacancies are mobile at temperatures exceeding 70 K and are known to form divacancies,[11] and also a complex defect called the A center with an interstitial oxygen atom.[12,13] Vacancies also form complexes with substitutional impurities such as phosphorus.[14]

Silicon interstitials created in the primary damage event are known to be trapped at substitutional carbon (C_s) atoms creating interstitial carbon (C_i) atoms in an exchange event.[15] These interstitial carbon atoms are mobile at room temperature and are known to be trapped at substitutional carbon atoms,[16] interstitial oxygen atoms,[17] and other impurities.

A detailed configurational model of such an impurity pair defect has only been identified for two of these observed BE transitions, namely, the 0.79- and 0.97-eV peaks, frequently called the C and G lines, respectively. The former is identified as a C_i-O_i (Ref. 17) and the latter as a C_s-C_i (Refs. 10 and 16) complex defect. These two peaks are identified as due to bound-exciton transitions associated with the neutral charge state of the defects.

In our present work we discuss a previously unreported zero-phonon peak in silicon at 0.615 eV, with satellite structure at higher energies. The peak has so far only been found in absorption. In our samples the peak grows up only after several hours of optical above-band-gap excitation at low temperatures. An activation energy of 0.21 eV is associated with the thermal quenching of the peak. A model based on a complex defect with two metastable

configurations agrees with the data. Arguments supporting a model for the identity of the defect as a complex involving carbon and interstitial oxygen are presented.

The samples studied are Czochralski-grown phosphorus-doped silicon crystals, with an initial resistivity of 40 Ω cm at room temperature. The samples were polished to obtain optical surfaces and then irradiated with 2-MeV electrons. After the irradiation the samples were highly resistive. The Fermi level was determined at low temperatures (4 K) to be in the middle of the band gap, i.e., between $E_c - 0.40$ and $E_v + 0.23$ eV (as monitored by the optical absorption peaks at 0.34 and 0.31 eV, attributed to the singly negative and singly positive charge states of the divacancy, respectively[18-20]). The samples were not exposed to temperatures exceeding 40 °C during irradiation or storage before the measurements. All measurements were made with a BOMEM DA3.26 Fourier Transform Spectrometer fitted with a liquid-nitrogen-cooled InSb detector and a CaF$_2$ beam splitter. The light source used was a tungsten halogene bulb. The source was filtered with a small silicon or germanium wafer at room temperature during all measurements. The samples were cooled with a helium bath cryostat with a temperature controller.

A typical absorption spectrum from a phosphorus-doped irradiated sample at a temperature of 4.2 K is shown in Fig. 1. At 0.615 eV a no-phonon peak with a full width at half maximum (FWHM) of 0.18 meV is observed, together with a broad optical band with a maximum intensity at 0.630 eV [Fig. 1(a)]. The peak shows no splitting in a magnetic field up to 4 T and therefore corresponds to a singlet-to-singlet transition. An additional peak at 0.779 eV, and a split peak at 0.780 eV (splitting 0.25 meV) together with broader bands at 0.787 and 0.802 eV, are shown in Fig. 1(b). A very weak peak at 0.784 eV is also observed. This absorption structure is superimposed on the high- and low-energy sides of another broad absorption band with an intensity maximum at 0.69 eV, typically observed in irradiated silicon. (This broadband has been attributed to an internal transition within the neutral charge state of the vacancy pair.[21] The peaks marked C_1 to C_5 are due to the C-line BE transitions,[22] i.e., they are related to another defect.)
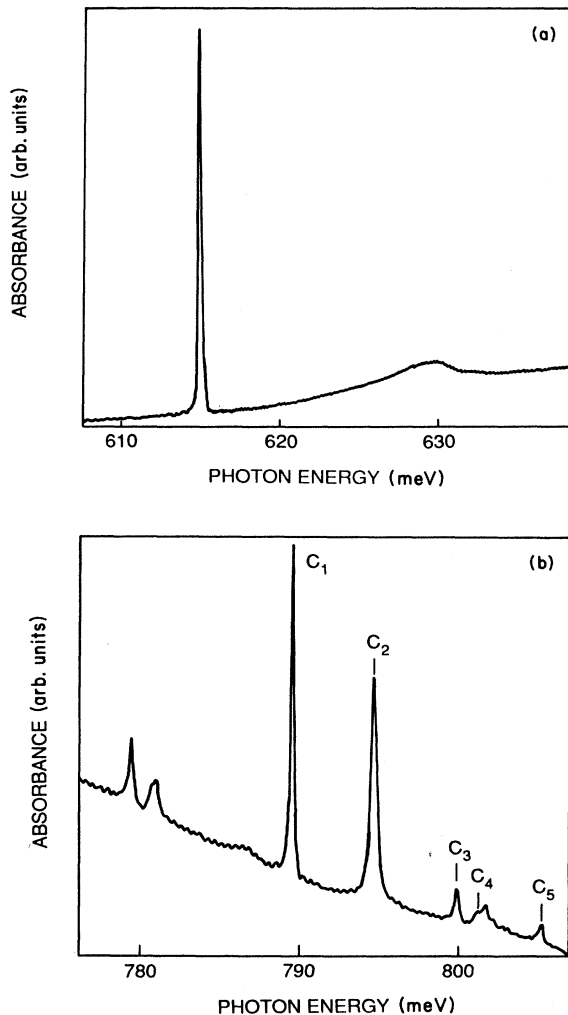
FIG. 1. (a) Absorption spectrum of an irradiated sample after approximately 30 h of optical excitation, showing the no-phonon peak at 615 meV with a TA-phonon replica, and (b) additional optical structure at higher energies. The peaks are superimposed on the high- and low-energy sides of a broad optical band peaking at 0.69 eV (not shown). The peaks marked C_1 to C_5 in (b) are due to the C line. The spectral resolution is 0.062 meV.

These new peaks are initially extremely weak in the samples, but are found to emerge and increase monotonically versus time when the samples are optically excited at low temperatures (< 65 K) without filtering the white-light source. The most prominent peaks of the absorption structure at higher energies grow in 1:1 correspondence with the no-phonon peak at 0.615 eV (the broader bands at 0.787 and 0.802 eV are too weak to make a similar comparison possible). It is not possible to correlate the 0.615-eV peak with any other known zero-phonon peaks found in the sample. The higher-energy peaks can be interpreted either as electronic excited states or as coupling between localized vibration modes of the defect and the zero-phonon transition. It should be noted that the energy displacement from the 0.615-eV line is close to some of

the localized vibrational modes of interstitial oxygen, an argument for the latter interpretation. The displacement of 15 meV from the zero-phonon peak of the broadband is close to the energy of transverse-acoustic (TA) phonons from near the $\langle 111 \rangle$ TA zone boundary.

As mentioned above these absorption peaks are found to grow up upon optical above-band-gap excitation. The intensity increases monotonically versus excitation time at a constant sample temperature, in the range of 4 K to about 65 K. The dependence of the formation rate of the observed defect state associated with the optical peaks on optical excitation intensity is linear. Furthermore, the formation rate of the defect state associated with the peaks is approximately constant at temperatures between 10 and 55 K, but increases at the lowest measured temperature, 4.2 K.

Upon heating in the dark, followed by a measurement at 4.2 K, the concentration of the defect state under consideration is found to remain unchanged up to heating temperatures of 70 K. When heated in darkness at higher temperatures, on the other hand, the intensity of the zero-phonon peak, as well as the associated structure at higher energies, decreases exponentially versus time. The annealing reaction was found to be of first order, as demonstrated in Fig. 2(a), where the normalized intensity of the zero-phonon peak at 4.2 K has been plotted versus annealing time at different temperatures. The data fit a simple exponential decay of the form

$$I_{np}(t) = [I_{np}^0(t) - I_{np}^0(\infty)]\exp(-Rt) + I_{np}^0(\infty), \qquad (1)$$

as expected for first-order kinetics. Here I is the peak intensity at 4.2 K, t is the annealing time, and R is the rate of the reaction. An Arrhenius plot of the reaction is shown in Fig. 2(b), and the kinetics are consistent with the relation

$$R = 1.8 \times 10^{11}\exp[-(0.21 \text{ eV})/k_B T], \qquad (2)$$

in units of sec^{-1}.

Finally we can conclude that this 0.615-eV spectrum only occurs in samples containing carbon. The peak is not observed in other samples with comparable concentrations of oxygen and phosphorus but with a lower concentration of carbon. We suggest that carbon is involved in the defect, possibly together with interstitial oxygen.

In the light of the above experimental results we are led to the following conclusions:

(1) The absorption structure shows considerable similarities concerning FWHM and coupling to lattice phonons with other BE transitions found in irradiated silicon, such as the G line. In this case, the ground state of the transition is the neutral charge state of the defect and the excited state an exciton bound to the neutral center. The singlet nature of the BE line is only consistent with a neutral charge state with a strongly hole-attractive local potential.[23]

(2) The defect is metastable in the observed neutral charge state, and the activation energy of 0.21 eV reflects the energy barrier for a configurational change between a metastable state and the stable state, according to Fig. 3. It is also important to note that a small residual absorp-
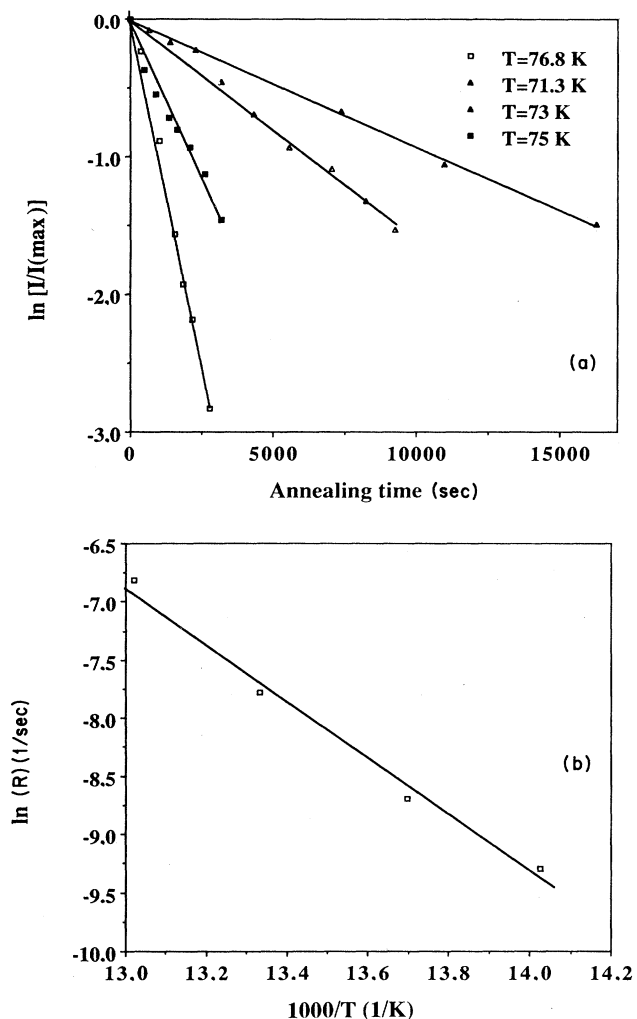
FIG. 2. (a) The logarithm of the relative intensity of the no-phonon peak at 615 meV vs annealing time at different temperatures between 70 and 77 K. The intensity was measured at a sample temperature of 4.2 K. The annealing was performed in darkness. (b) The logarithm of the rate of decay of the 615-meV no-phonon peak, as deduced from (a), is a function of the inverse annealing temperature.

FIG. 3. A schematic illustration of the energy barrier between the stable (marked C) and metastable (marked C^*) configurations of the defect in the neutral charge state vs a normalized defect configuration coordinate, Q.

tion is always found irrespective of what optical filter is being used, most likely reflecting the equilibrium concentration of the two configurations. Annealing in darkness at 80 K does not reduce this residual absorption. It is interesting to note that the activation energy according to Eq. (2) is very close to the energy barrier for the carbon—silicon bond switching governing the bistability of the C_s-C_i pair defect.[10,16]
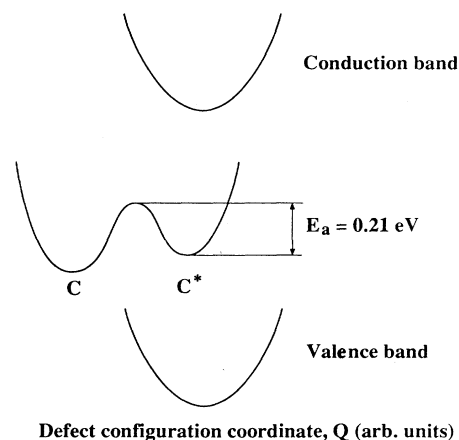
The observed buildup of the metastable neutral charge state of the defect upon above-band-gap excitation agrees with the results obtained for free excitonic Auger recombination into a single deep impurity level in silicon,[24] thus implying that free exciton recombination at the defect site governs the population of the metastable neutral charge state observed as the increase of intensity of the 0.615-eV peak. (These conclusions together with additional experimental data will be discussed in more detail separately.[25])

In summary we have presented an optical investigation of a defect in Czochralski-grown silicon with a new BE zero-phonon peak at 0.615 eV. The peak appears upon optical above-band-gap excitation and disappears upon thermal heating in darkness with an activation energy of 0.21 eV. A model describing the appearance and the thermally induced disappearance of the no-phonon peak as caused by a configurational change in the neutral charge state of the defect, thus reflecting metastable properties of the defect, is found to agree with our experimental results. The thermal energy barrier between the optically active metastable state and the inactive ground state is thus 0.21 eV. We suggest that carbon is involved in the defect, possibly together with interstitial oxygen. The optical technique demonstrated in this work should be a valuable tool to investigate metastable properties of defects in silicon. More detailed results in connection with this work will be presented separately.[25]

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