Further evidence for the C-line pseudodonor model in irradiated Czochralski-grown silicon

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Photocurrent spectroscopy and photothermal ionization spectroscopy have been performed on electron-irradiated Czochralski-grown silicon. Two series of lines are observed, one starting with the *C* line at 790 meV, and another starting at about 30 meV higher energy. The lines are shown to belong to the same continuum, indicating that they are all associated with the same center. A continuum is also observed, and in this part of the spectrum Fano resonances are seen. The analysis of these resonances implies that the free-carrier states couple with an *f* TO phonon, and this confirms the view that the center is donorlike.

INTRODUCTION

Czochralski-grown silicon contains, in general, oxygen and carbon impurity concentrations of up to 10^{17} cm^{-3}. In samples irradiated with high-energy electrons, intrinsic defects are created which react with impurities resulting in a variety of electrically and optically active centers. Rather detailed studies have been performed on two of these defects, namely the vacancy-oxygen (*V*-O) or the *A* center[1,2] and the so-called *C* line.[3] Although the microscopic structure of the latter defect is not completely known, it has been shown, by isotopic substitution, that both oxygen and carbon are involved in the defect.[4,5] Foy[6] used absorption spectroscopy and Wagner *et al.*[7] photoluminescence excitation spectroscopy to investigate the defect in more detail. With both these methods a very prominent no-phonon line at 790 meV and several other lines at somewhat higher energies were observed.

From uniaxial stress experiments, Foy[6] was able to show that the *C* line has C_{1h} point-group symmetry, but no further information was given about the microscopic nature of the center. Later, Thonke *et al.*[8] performed a more detailed analysis of the results reported by Foy and found that the symmetry indeed was as low as C_{1h}, but the deviation from the tetragonal D_{2d} point-group symmetry was very small. Their analysis is mainly based on the concept of bound excitons. According to this model a hole is tightly bound to the neutral defect with a binding energy of 341.2 meV. This positively charged center then binds an electron with an energy of only 38.3 meV. The bound hole and the electron are envisaged as a pseudodonor. As in the case of the hydrogen atom, the electron experiences an attractive Coulomb-like potential, and thus has an infinite number of bound states. Those bound states which have fairly extended electron wave functions can be described with some accuracy by effective-mass theory (EMT).[9] The more localized states are not so well described by EMT, since, in addition to the Coulomb potential, the electron also feels a central cell potential. The pseudodonor model by Thonke *et al.*,[8] in conjunction with a modified deformation potential theory, was able to explain the uniaxial stress data. The purpose of our investigation was to examine the model further by studying the temperature dependence of the photoconductivity spectra, and to investigate whether or not the excitation spectra show Fano resonances.

In photoconductivity only those charge carriers which are excited to a band contribute to the signal. In particular, excitation of carriers to free states in the bands are readily studied by photoconductivity, resulting in a continuum with a photoionization edge. However, a modification of this technique is needed when the objects of study are transitions between bound states in the forbidden gap, e.g., between the ground state and the excited states of a defect, since these transitions do not create any

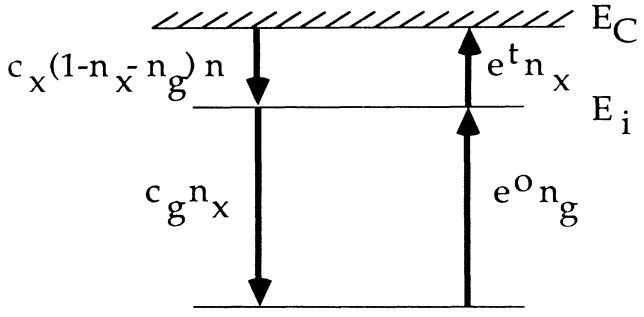

FIG. 1. Photothermal free-carrier generation via an excited state. Carriers are excited optically from the ground state to an excited state, and from there to the conduction band by phonon absorption. The concentration of neutral centers is n_g, the concentration of centers with an excited electron is n_x and n is the carrier concentration in the band. The thermal emission rate e^t is proportional to a factor $\exp[-(E_C-E_i)/AkT]$, where E_C-E_i is the distance between the excited state and the band, and A is a factor between 1 and 2 (see text).

free carriers. This complication may be circumvented by combining optical and thermal excitation, and using the so-called photothermal ionization spectroscopy (PTIS), as reviewed by Kogan and Lifshits.[10] With reference to Fig. 1, the method could be described as follows. A carrier is optically excited from the ground state to a bound excited state, and from there to a free state in the band by phonon absorption, thereby increasing the free-carrier concentration, and hence also the photoconductivity. So, even if the primary optical excitation does not generate any free carriers, a conductivity signal can nevertheless be obtained.

In PTIS the increase in free-carrier concentration therefore depends not only on the photon energy, but also on the temperature. The increase in carrier concentration is approximately proportional to a factor $\exp[-(E_C-E_i)/AkT]$, where E_C-E_i is the thermal activation energy, as defined in Fig. 1, k is Boltzmann's constant, T the absolute temperature, and A a number between 1 and 2. The value of A depends on the thermal excitation process, i.e., whether the thermal contribution is small or large relative to the total concentration of the free carriers studied. If the contribution is small the value of A is 1, but if most of the carriers arise from the thermal process the value is 2. At low temperatures, transitions to excited states near the continuum edge will be favored, due to their small binding energies, and the deeper levels will not be seen as positive peaks. Sometimes they are observed as negative dips, since they still absorb photons and thus take photons from other photoconductivity processes.

EXPERIMENTAL DETAILS

The samples used were originally n-type phosphorus-doped Czochralski-grown silicon crystals with a resistivity of 54 Ω cm. The polished samples were irradiated by 2.0 MeV electrons to a dose of 5×10^{17} cm^{-2}. During irradiation the samples were kept at room temperature. The crystals were then sawed into smaller pieces, approximately $2\times2\times6$ mm^3. Ohmic contacts were obtained by scratching and rubbing the samples with an aluminum rod covered with a small amount of gallium. The irradiation made the samples highly resistive. No treatment after irradiation was allowed to cause the sample temperature to increase over 40 °C.

The photocurrent and PTIS measurements were performed using a BOMEM series DA3.01 Fourier-transform spectrometer with a Keithly 427 current amplifier. The temperature of the sample was controlled in a Leybold cryostat, and the temperature was monitored by a gold-iron–Chromel thermocouple. A voltage of about 70 V was applied to the samples.

RESULTS

The photoconductivity spectra were obtained for different temperatures between 8 and 78 K. Figure 2 shows a typical spectrum. An ionization edge is observed at approximately 6650 cm^{-1}. This feature is due to a normal photoconductivity signal caused by the optical excitation of free carriers from the ground state into the continuum. At lower energies, between 6350 and 6650 cm^{-1}, a line spectrum is seen, which is very similar to the photoluminescence excitation (PLE) spectrum obtained by Wagner *et al.*[7] The labeling of these lines is according to the EMT model suggested by Thonke *et al.*,[8] where the s states are split in the C_{1h} strain field of the defect. The six A_1, E, and T_2 valley-orbit-split states, which arise from the loosely bound electron experiencing a field of T_d point-group symmetry, are further split in C_{1h} symmetry giving six lines. The splitting between the T_x

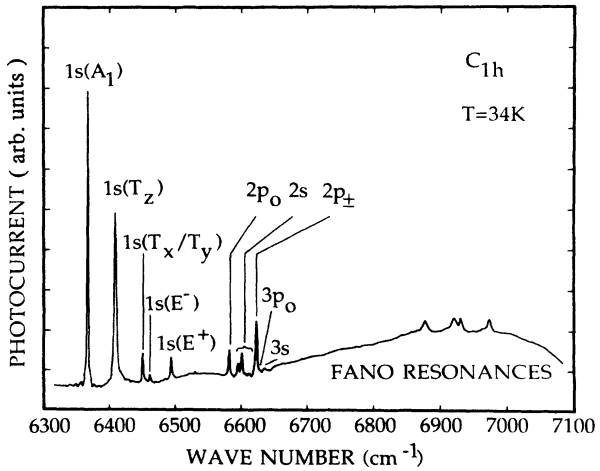

FIG. 2. Photocurrent as a function of photon energy. The continuum part is due to ordinary photoionization, but the sharp peaks are PTIS signals (see text). The spectrum is not normalized in terms of the photon flux.

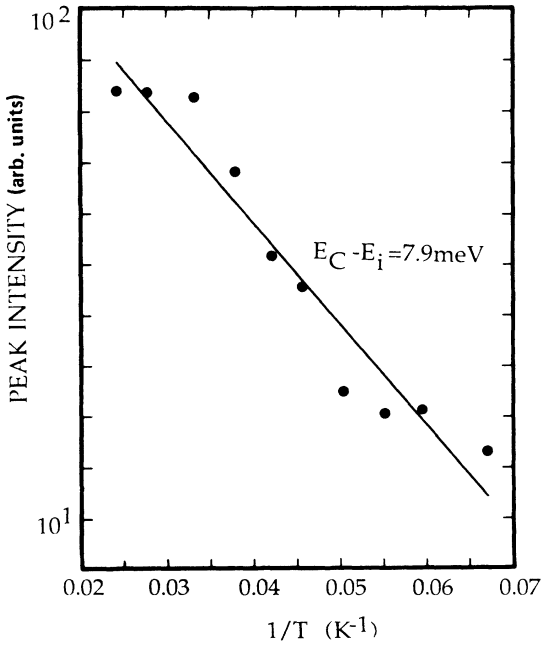

FIG. 3. A typical Arrhenius plot for the line at 6625.0 cm^{-1}, showing the integrated peak intensity as a function of $1/T$. From the regression line an activation energy, E_C-E_i, has been calculated, assuming $A=2$ (see text).

and T_y states in C_{1h} is not resolved, due to the fact that for the defect studied, the deviation from D_{2d}, where they are degenerate, is very small.[8]

The lines between 6570 and 6625 cm^{-1} are attributed to excitation to the $2p$ and $2s$ states. The $2s$ lines are in principle split in the same way as the $1s$ lines, but, due to the much smaller probability of the electron being found at the origin, the splitting is much smaller. Furthermore, the $2s(T_x)$ and $2s(T_y)$ states cannot be resolved from the $2s(E^+)$ state.

The intensities of the peaks vary with temperature, since the thermal excitation is different for different temperatures, as discussed above. The logarithms of the intensities for one of the lines as a function of $1/T$ are plotted in Fig. 3. From the slopes of the straight lines, and assuming $A=2$, the respective activation energies can be calculated. Since the peaks appear superimposed on a much stronger background signal in the original spectra, it is reasonable to assume that if the peaks produce charge carriers of the same type as the background signal, then $A \approx 1$, but if different carriers are obtained, then $A \approx 2$. The energies obtained in this way correspond to the thermal activation energy for the excitation of an electron from a bound state given by a particular line, to the conduction-band continuum. If all the lines in the spectra belong to the same center then all the lines should be correlated to the same continuum. When the activation energies $E_C - E_i$ calculated from the Arrhenius plot with $A=2$ are plotted against the transition energies, a linear relation should therefore be obtained, as in Fig. 4. The slope of the regression line is 0.8, which is close to the expected value of 1, if our assumption of $A=2$ is valid. The crossing point of the regression line with the baseline gives a value of about 828.7 meV. This value is very near the value of 828.3 meV, which Thonke *et al.*[8] obtained by fitting an EMT model to photoluminescence excitation data. If we take the transition energies to the $2p_0$ and the $2p_\pm$ states from our data, and add the EMT values for the binding energies of these states,[11] we obtain a continuum energy of 827.8 meV.

In the continuum part of the spectrum, between 6800 and 7000 cm^{-1}, some structure can be seen. A closer inspection shows that this structure is similar to the sharp line spectrum observed at lower energies, with respect to number of lines and relative energy spacings (see Fig. 5). Since these additional structures appear at about an energy of an optical phonon above the pseudodonor lines, they are interpreted as Fano resonances. Similar resonances have been seen both for donors[12,13] and for acceptors,[14,15] and have been proven to be Fano resonances.[16] These resonances could arise when there is a discrete state degenerate with a continuum of states and some interaction between them. In this case the continuum consists of the conduction-band states, and the discrete states of the bound excited states plus a phonon. The relevant phonons are those which couple to the continuum states in question. For donors coupling with f TO (59.1 meV), and g LO (63.9 meV) phonons have been reported,[12,13] and for acceptors with O^Γ phonons (64.5 meV).[14,15] The phonons involved are thus characteristic for donors or acceptors. For the center discussed in this paper, the pairing of a fundamental line with a corresponding resonance structure using the appropriate phonon is somewhat difficult, due to two facts. Firstly, the energies of the O^Γ phonons (64.5 meV) and the g LO (63.9 meV)

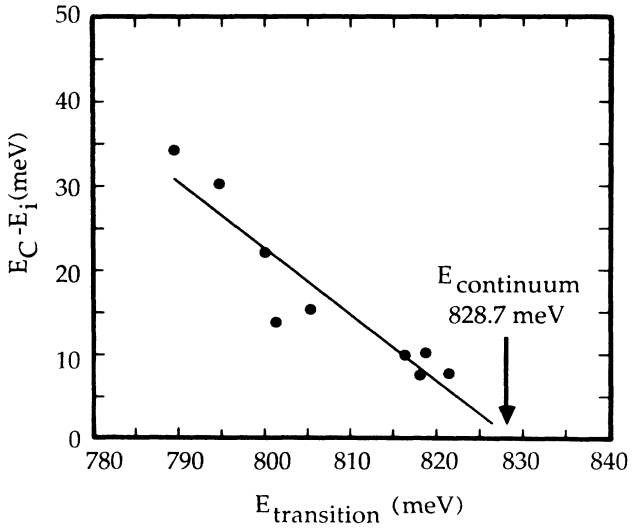

FIG. 4. The thermal activation energy as a function of the optical transition energy for all the lines. The continuum value is obtained by extrapolation of the regression line to $E_C - E_i = 0$.

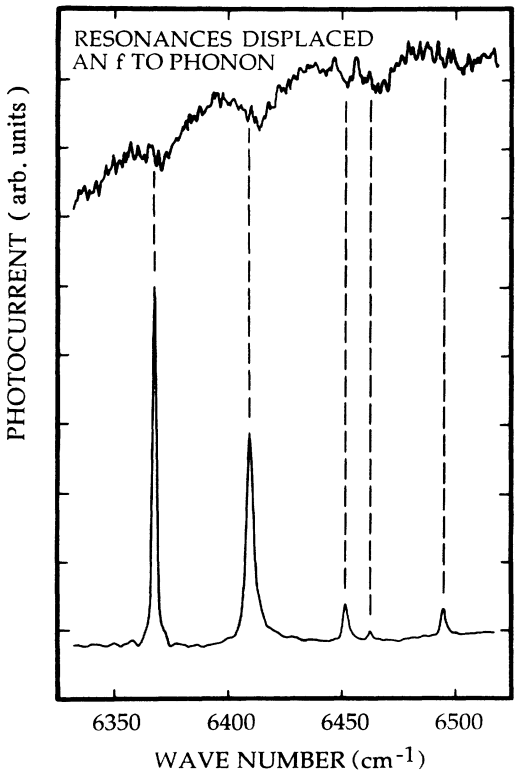

FIG. 5. The upper part of the spectrum shows the Fano resonances in the continuum of the spectrum and the lower the fundamental spectrum. The resonance spectrum is shifted by an energy corresponding to an f TO phonon (476.7 cm^{-1}).

phonons are very similar, and secondly, the difference between any of these phonons and the f TO phonons is very similar to the difference between the most prominent fundamental peaks, which is about 5 meV. In our case the assignment was made by pairing a resonance dip at 6850 cm^{-1} with the line at 6368 cm^{-1}, which implies a phonon with an energy of not greater than 60 meV, i.e., the f TO. This shows not only that the center causing the line at 6368 cm^{-1} is donorlike, but also, since all the lines have been shown to belong to the same continuum, that all the lines are associated with the same donor. This argument gives additional strength to the explanation by Thonke *et al.*[8] that the center is a pseudodonor. We were unable to prove whether or not the g LO phonons are also involved, due to the difficulties discussed above.

No Fano resonances for the $2p$, $2s$, $3p$, and $3s$ states were observed. All resonances were seen as typical resonance structures (peaks and dips) at higher temperature, but only as dips at lower temperatures. The resonance of the $1s(A_1)$ line plus the f TO phonon was only seen at temperatures around 8 K.

With decreasing temperature the positive peaks become smaller and dips arise. Each dip corresponds to a peak with the dips shifted about 1.6 cm^{-1} towards higher energies. The amplitudes of the dips seem to be constant with temperature, and their being visible or not depends only on the magnitude of the positive peaks. Only the peak observed at 6625.0 cm^{-1}, which lies only 38.7 cm^{-1} (4.8 meV) from the continuum edge, was positive for all temperatures.

CONCLUSIONS

Our analysis of the Fano resonances gives evidence for all the observed lines associated with the C line being donorlike, and is in agreement with the pseudodonor model of Thonke.[8] The C line is another example of a system whose interpretation benefits from the use of several different measurement techniques, since the crucial point in our argument, the Fano resonances, have only been seen in absorption and photoconductivity, and not in luminescence.

ACKNOWLEDGMENTS

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