

780-meV photoluminescence band in silver-doped silicon: Isotope effect and time-resolved spectroscopy

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(Received 10 July 2001; published 28 December 2001)

Silver doping of silicon crystals results in intense emission at 780 meV which consists of narrow no-phonon *A-B-C* lines and phonon replicas. Observation of an isotope shift confirms participation of a silver atom in the microscopic structure of the defect center responsible for this emission. Decay times of the three no-phonon lines of the 780 meV band are measured and found to be of the order of 100 μ s. These long decay times are consistent with a model which assigns the investigated band to recombination of an exciton bound to an isoelectronic center.

DOI: 10.1103/PhysRevB.65.033202

PACS number(s): 78.55.Ap, 78.47.+p, 61.72.Ji

I. INTRODUCTION

Deep impurities which introduce energy levels near the middle of the forbidden gap influence electrical conductivity and the free-carrier lifetime of semiconductors. Like other noble metals, silver is an important impurity in silicon. Electrical properties of silver in silicon were extensively studied and a number of Ag-related deep levels have been reported.^{1,2} In a deep-level transient spectroscopy (DLTS) study, Baber *et al.*³ reported that silver creates an acceptor level at $E_c - 0.54$ eV and a donor level at $E_v + 0.34$ eV. An absorption spectrum in the 6200–6700 cm^{-1} energy range observed in a silver-doped silicon sample was attributed to transitions of the silver donor.⁴ Transitions of the Ag-related acceptor were not found. Silver-doped silicon was also thoroughly studied by electron paramagnetic resonance (EPR); following analyses of the EPR spectra, microscopic models of several Ag-related centers were proposed.^{5,6}

Also, the photoluminescence (PL) of silver-doped silicon has been investigated. It has been found that silver doping of silicon crystals results in generation of a characteristic low-temperature emission spectrum at 780 meV.^{7–10} In the photoluminescence spectrum narrow no-phonon lines (termed *A*, *B*, and *C*) and lower-energy phonon replicas have been distinguished. The observed structure was identified as transitions from the effective-mass-like electronic states near the conduction band to the ground state. At temperatures below 8 K, the spectrum was dominated by two no-phonon lines *A* and *B* with energies of 778.91 and 779.85 meV, respectively.⁹ Both lines produced phonon replicas with local phonon energies of approximately 6 and 15 meV. At energies of 20.7 and 33.1 meV below the *A* line, two broad features were observed and assigned to the transverse-acoustic (TA) and longitudinal-acoustic (LA) silicon phonon replicas, respectively. At higher temperatures a third no-phonon line *C*, appeared at 784.31 meV. The intensity of this line rapidly increases with temperature while the intensities of the *A* and *B* lines decrease, and the *A-B-C* system thermalizes.⁸ At temperatures higher than 20 K some local phonon replicas of the *C* line were also observed.

In the present work, we report observation of a silver-isotope-dependent shift of the no-phonon *A*, *B*, and *C* lines of the 780-meV band, providing direct microscopic evidence of silver involvement in the center responsible for this emission. The decay time of these lines is also investigated.

II. EXPERIMENTAL DETAILS

Silver-doped silicon samples for the present study were prepared from 75–125 Ω cm *p*-type float-zone silicon by diffusion. Thin silver layers were evaporated on both sides of the silicon samples. The diffusion was performed for 4 h at 1150 $^{\circ}\text{C}$ in a closed quartz ampoule containing 100 mbar of argon. Following the diffusion step, the samples were quenched to room temperature by dropping the whole ampoule in water. After diffusion, the surface layers were mechanically lapped and etched in a mixture of HF and HNO₃ (1:3). For the diffusion, both natural and isotopically enriched silver (99.5% and 99.4% of ¹⁰⁷Ag and ¹⁰⁹Ag isotopes, respectively) were used.

The PL experiments were performed with a variable-temperature continuous-flow cryostat accessing the 1.5–300 K range (Oxford Instruments Optistat CF). The samples were excited using a cw argon-ion laser operating at 514.5 nm. All spectra were obtained with a 1.5-m *F*/12 monochromator (Jobin-Yvon THR-1500) and detected by a high-sensitivity germanium detector (Edinburgh Instruments).

Time-resolved measurements were carried out using a digital oscilloscope (Tektronix TDS 3032) in combination with an InP/InGaAs nitrogen-cooled photomultiplier tube Hamamatsu R5509-72. Transient excitation was achieved by using a pinhole and mechanical chopping (200 Hz) of the 514-nm line of an Ar⁺-ion laser. In this configuration, the experimentally measured system response time was 38 μ s.

III. EXPERIMENTAL RESULTS

For all the investigated samples photoluminescence was measured for the spectral energy range between the silicon band gap energy and approximately 700 meV. Figure 1

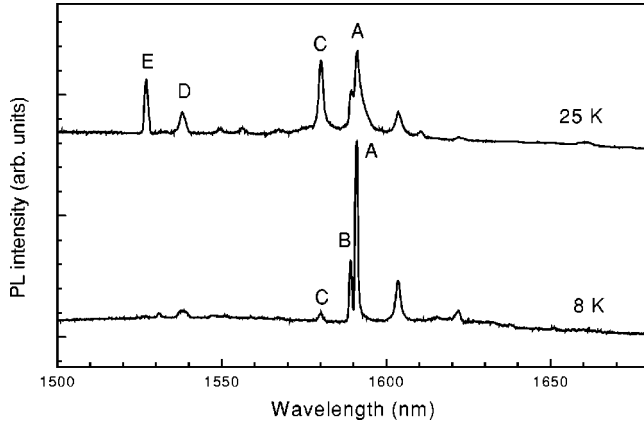


FIG. 1. The 780-meV PL band observed in silver-doped silicon at $T=8$ and 25 K.

shows typical photoluminescence spectra obtained in this study from silver-doped silicon samples at 8 and 25 K. The band around 780 meV is similar to that observed earlier,^{7–10} and ascribed to silver on the basis of sample preparation. In addition to that two new PL bands at 806 and 811 meV, labeled *D* and *E* lines, respectively, were detected. Also, a weak PL band at approximately 724 meV, reported before in Ag-doped silicon,⁹ could be distinguished.

Figure 2 compares the high-resolution photoluminescence spectra of the 780-meV band recorded for three samples: doped with silver isotope ^{107}Ag , silver isotope ^{109}Ag , and natural silver (52% ^{107}Ag +48% ^{109}Ag). While all three spectra show a similar A-B-C structure, the linewidth for samples doped with a single silver isotope is smaller and the position of lines is shifted by ~ -0.017 meV for ^{107}Ag -doped silicon and by $\sim +0.017$ meV for ^{109}Ag -doped silicon. Also, related shifts of the phonon satellites were observed. We note that the A-B-C lines in the sample containing natural silver are somewhat broader than those observed for ^{107}Ag or ^{109}Ag doping. The temperature dependence of the A-B-C lines in the samples doped with the

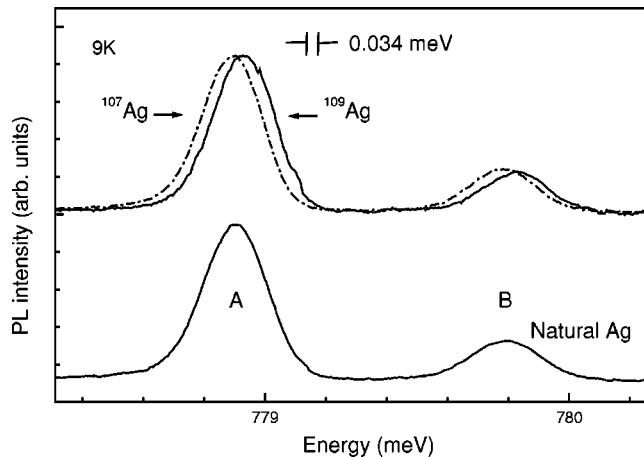


FIG. 2. A, B, and C lines in silicon doped with isotopically enriched silver (upper curves) and natural silver (lower curve).

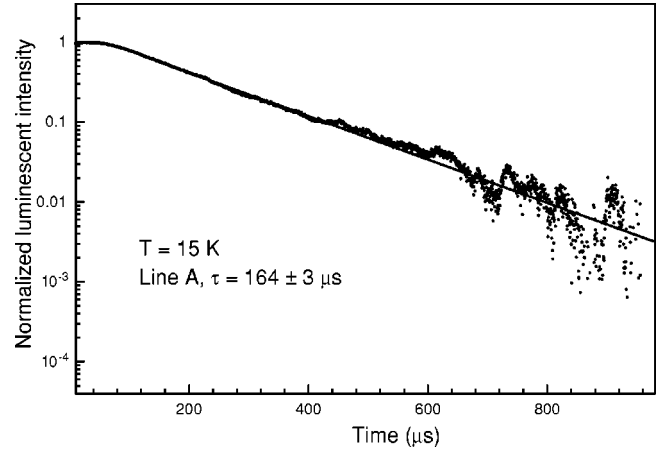


FIG. 3. Decay time characteristics for the A line of the 780-PL band measured at 15 K.

monoisotopic silver was found to be in agreement with the earlier report.⁸

Also, the *D* and *E* lines, as well as the 724-meV band, were detected in samples doped with monoisotopic silver. These were, however, considerably broader than the A-B-C lines. This obscured a reliable observation of the isotope effect. Therefore, participation of silver atom(s) in the microscopic structure of defects responsible for these emissions could not be unambiguously established and remains open for future investigations.

We have examined the decay characteristics of the A-B-C no-phonon system. The measured decay times were found to be exponential over the entire temperature range and identical within the experimental error for all the components. This serves as an independent confirmation that the whole band corresponds to transitions at the same center. Figure 3 illustrates intensity decay of the A line experimentally measured at 15 K. A lifetime of $\sim 150 \mu\text{s}$ can be determined. The decay time constants were found to decrease for higher temperatures, as depicted in Fig. 4.

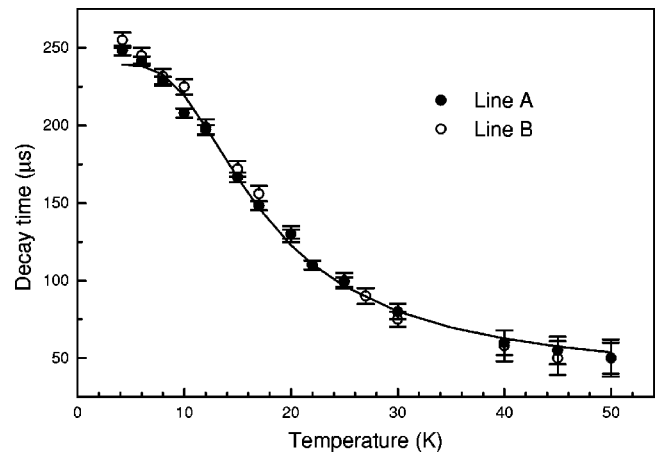


FIG. 4. The temperature dependence of the decay time for the A and B lines. The solid line represents a fit with Eq. (7)—for an explanation, see the text.

IV. DISCUSSION

A. Isotope measurements

The observation of isotope shifts for A , B , and C lines provide conclusive microscopic evidence that the 780-meV band is related to silver.

Isotope shifts of luminescence lines are convenient for identification of the chemical nature of such centers.¹¹ Heine and Henry¹² gave a quantitative description of the isotope shift of no-phonon optical transitions at defects in semiconductors. If the force constant in the initial and/or final electronic state will change on isotopic substitution, an isotope splitting of the no-phonon optical transition will result. In their model, the shift of the no-phonon energy S is related to a softening effect of the electron and hole on the modes of the perfect lattice. When the force constants between the atoms change, the state of the electronic system alters. The effect is related to the temperature dependence of the band gap of the pure material. The presence of a carrier c ($c=e$ for an electron and $c=h$ for a hole) on an atom lowers the interatomic elastic constant Λ by a fraction $\gamma_c P_c$:

$$\Lambda' = \Lambda[1 - \gamma_c P_c], \quad (1)$$

where P_c is the probability of the carrier being at the impurity atom and γ_c is the effect of the carrier.

The sum of the effects of a free e - h pair $\gamma = (\gamma_e + \gamma_h)$ can be found from the temperature dependence of the band gap energy. At temperatures well above the Debye temperature this is given as¹³

$$-\frac{dE_g}{dT} = \frac{3}{4}k(\gamma_e + \gamma_h), \quad (2)$$

where T denotes temperature and k is Boltzmann's constant. From analysis of the data for several defects, Heine and Henry concluded that

$$\gamma_h = (3.6 \pm 1.0)\gamma_e. \quad (3)$$

The presence of either a hole or an extra electron will soften lattice modes, the effect of a hole being significantly larger than that of an electron. The total value of the isotope shift can then be given by¹²

$$S = \frac{2\hbar\omega_D}{5} \left(\frac{M_0}{M} \right)^{1/2} \frac{\Delta M}{M} \frac{\gamma_c}{\gamma} \left(-\frac{dE_g}{dT} \right)_{HT} P_c. \quad (4)$$

In Eq. (4), ω_D is Debye cutoff frequency (for silicon $\hbar\omega_D = 55.6$ meV), M_0 is the atomic mass of a host semiconductor, and M is the mass of a particular impurity atom ($M \approx 108$ for silver with natural isotopic composition). ΔM is the mass difference introduced by isotope substitution: $\Delta M = \pm 1$ for ¹⁰⁹Ag and ¹⁰⁷Ag impurities, respectively.

In order to calculate P_c , one must determine the wave function of the carrier bound to the defect center in either the initial or the final state (or both). Assuming that the 780-meV band originates from recombination at an isoelectronic center with a local hole binding potential,⁴ we roughly estimate the

probability P_c to be about 1. Further, we take dE_g/dT for silicon to be -2.1 k at room temperature,¹⁴ and from Eq. (2) we have

$$\gamma_e + \gamma_h = 2.8. \quad (5)$$

Finally, substituting the mentioned values into Eq. (4), we evaluate the difference in zero-point energy to be

$$S = 0.015 \pm 0.001 \text{ meV}, \quad (6)$$

in good agreement with the experimentally measured value of 0.017 meV.

B. Luminescence decay time measurements

As one can see from Fig. 4, a strong variation of the decay times with temperature has been determined in the experiment. From a comparison with the temperature dependence of the PL intensity,⁷ it seems natural to assume that the high-temperature decrease ($T \geq 30$ K) of the lifetime is due to the dissociation of the exciton. From the experiment we can conclude that the decay times of the A and B lines are identical. Also, the decay time of line C , whose intensity allowed accurate measurements for $T \geq 10$ K, has a similar value. Such a situation is in agreement with the hypothesis that the A , B , and C PL lines are due to transitions originating from three thermalizing states of the same center.⁸ At low temperatures, we obtain long decay times of about 250 μ s. This value is large when compared to the lifetimes of donor or acceptor bound excitons in silicon, which are in the nanosecond range. For excitons bound to a donor or to an acceptor, the lifetime strongly depends on the impurity binding energy E_i . Experimentally, approximate dependences $\tau \propto E_i^{-4.6}$ for an acceptor or $\tau \propto E_i^{-3.9}$ for a donor were reported and the lifetime shortening was attributed to a localized phononless Auger recombination process.^{15,16} For example, for excitons localized at In acceptors in silicon with $E_i = 154$ meV, a lifetime of $\tau = 2.7$ ns has been determined.¹⁷ The lifetimes measured in this study are longer by factor of 10^5 . This indicates that nonradiative lifetime shortening processes are absent, or heavily suppressed, in this case. For silicon such a situation would occur for an exciton trapped at an isoelectronic center.

In the past, PL bands with long decay times were frequently reported in the low-temperature spectra of crystalline silicon.^{18–21} Optical excitation spectra and decay times of these centers were shown to be well explained by a microscopic model of an exciton bound at an isoelectronic center. In that case, a hole or an electron can be localized at the defect by a local (core) potential. Upon localization of the primary particle, the secondary particle can be captured by Coulomb field into a shallow, effective-mass-theory state. An electron and a hole may couple to form an exciton with states of a different total momentum. The observed temperature dependence of the decay time can then be described by thermal population of two states where the lower one has a much longer lifetime than the higher one, denoted τ_L and τ_H , re-

spectively. Under these assumptions, an expression for the temperature dependence of the lifetime can be derived as,^{20,21}

$$\tau_{\text{exp}}(T) = \tau_L \frac{1 + g_2/g_1 \exp(-\Delta E/kT)}{1 + g_2/g_1 \gamma \exp(-\Delta E/kT)}. \quad (7)$$

Here $\gamma = \tau_L/\tau_H$ and ΔE denotes the energy splitting between the lower and upper levels with degeneracies g_1 and g_2 , respectively.

We will now use the above expression to describe the temperature dependence of the *A-B-C* band lifetime depicted in Fig. 4. In the description we take also into account the thermally induced intensity changes of the individual lines. In our model we assume that the *A* and *B* lines correspond to transitions of a low probability, characterized by a long and identical lifetime $\tau_A = \tau_B = \tau_L$, while the upper level responsible for the *C* line has a considerably shorter lifetime $\tau_C = \tau_H$. Since the precise origin of the *A*, *B*, and *C* lines is not known, we assume identical multiplicity of the levels and take therefore the degeneracy ratio as $g_2/g_1 = 0.5$. As can be concluded from Fig. 4, under the above assumptions a satisfactory fit to the experimental data can be obtained. The solid line in the figure corresponds to the following values of the fitting parameters: $\tau_L = \tau_A = \tau_B = 240 \pm 3 \mu\text{s}$, $\tau_H = \tau_C = 11 \pm 1 \mu\text{s}$, and $\Delta E = 4.1 \pm 0.2 \text{ meV}$.

We note that the fitted value of the activation energy responsible for the lifetime shortening is close to the spectroscopic separation between the *A/B* and *C* lines. Also, the obtained lifetime ratio of the “slow” and “fast” components of $(\tau_A = \tau_B)/\tau_C = 240 \mu\text{s}/11 \mu\text{s} \approx 22$ is close to the intensity ratio $I_C/(I_A = I_B)$ extrapolated from the temperature dependence,^{8,9} supporting the model used to describe the temperature dependence of the decay time of the *A-B-C* system.

V. CONCLUSION

We presented conclusive microscopic evidence for the participation of silver in the optically active center responsible for the 780-meV PL band. The appearance of this emission has been frequently reported in silver-doped silicon and attributed to a silver-related defect on basis of sample preparation conditions. The experimentally determined long lifetimes of the three dominant no-phonon lines of the 780-meV band are in agreement with a model of an exciton localized at an isoelectronic center.

ACKNOWLEDGMENTS

The authors gratefully acknowledge the cooperation of Dr. P.N. Hai, and Dr. Pham Thanh Huy at various stages of the project.

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