Electronic structure of a photoluminescent center in silver-doped silicon

N. T. Son,* Mandeep Singh, J. Dalfors, B. Monemar, and E. Janzén
Department of Physics and Measurement Technology, Linköping University, S-581 83 Linköping, Sweden
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In silver-doped silicon, a photoluminescence band is observed with zero-phonon lines at 778.92, 779.85, and 784.31 meV, which is concluded to be associated with the spin-triplet and spin-singlet states of a bound exciton. The photoluminescence excitation spectrum of this defect, with the transitions to *s*-like electronic excited states dominating, is measured using Fourier-transform techniques. The electronic structure of this defect, which is known in the literature as the deep $E_v+0.34$ eV silver donor, is well described by the pseudodonor model.

Silver is one of the common contaminating impurities in silicon and is known to be electrically active. Electrical investigations have shown that silver-related defects give rise to several deep levels in the band gap of silicon. The two most commonly reported levels in silver-doped silicon are the donor and the acceptor at $E_d=E_v+0.34$ eV and $E_a=E_c-0.54$ eV, respectively.[1] These levels are very close to the corresponding donor and acceptor levels reported for gold in silicon. Silver is expected to be paramagnetic and also optically active like gold.[2–6] In the recent optical studies of silver-doped silicon by Olajos, Kleverman, and Grimmeiss,[7] an absorption spectrum with sharp lines corresponding to the excitations to electronic excited states was observed. Based on their binding energies in combination with results from photothermal ionization spectroscopy, these electronic states were identified as those of the deep silver donor.[7] A C_{2v} or lower symmetry of the center was suggested based on the observation of four lines in the $1s(E+T_2)$ multiplet of the excited states. Very recently, the isolated silver center and several silver-related centers were identified by electron paramagnetic resonance (EPR).[8] However, there is still no correlation between magnetic resonance and optical data in the silver case.

For gold in silicon, both absorption and photoluminescence spectra believed to be associated with the deep gold donor and acceptor centers have been reported.[3–6] In particular, the structure of the $1s(E+T_2)$ multiplet of the excited states of the gold donor shows a marked similarity to that of the silver-related center.[7] The observed no-phonon photoluminescence at 793 meV from Si:Au was also attributed to a transition from shallow hydrogenlike levels to the deep donor level.[3] From the similarity in the electronic structure of the gold- and silver-related centers one may expect to observe a similar radiative transition in Si:Ag.

In the present work, we report on our observation of a photoluminescence (PL) spectrum with three no-phonon lines in the 780-meV region in silver-doped silicon. The results from Fourier transform photoluminescence excitation (FTPLE) measurements of this band are also reported. The temperature-dependent photoluminescence studies of this PL spectrum in combination with Zeeman results from Kleverman[9] reveal the singlet-triplet nature of these electronic lines. In comparison with available data on the analogous donorlike defects in silicon, the series of lines observed in PLE are attributed to the optical transitions to effective-mass-like states of a pseudodonor. With the obtained results, the pseudodonor character[10] of the electronic structure of this dominating silver-related defect can be confirmed.

The starting materials for the sample preparation in our investigation were float zone, dislocation free, *n*- and *p*-type silicon with initial resistivities varying from a few to 1000 Ω cm. Silver was introduced into the sample by diffusion in a closed quartz ampoule containing 200 mbar of argon. The diffusion was performed at 1150 °C for 2 h and the samples were quenched to room temperature by dropping the whole ampoule in water. The PL measurements were performed using a BOMEM DA3 Fourier transform spectrometer fitted with a CaF_2 beamsplitter. The PL was excited using the 514.5 nm or the 1090 nm lines of an argon-ion laser. The emission was detected with either a LN_2-cooled North Coast EO-817 Ge detector or a Cincinatti Electronics InSb LN_2-cooled photodiode. The FTPLE measurements were also performed with a BOMEM DA3 spectrometer using its internal tungsten halogen bulb as the excitation source. A short-wavelength pass filter with a 50% transmission at 815 meV was used to limit the modulated (Fourier frequency encoded) light at the high energy side of the triplet zero-phonon lines *A* and *B*. The emission was detected in the phonon sideband of the *A* and *B* zero-phonon lines using a 1700-nm bandpass filter with a bandwidth of about 100 nm. For both PL and FTPLE measurements, a Leybold continuous helium flow cryostat was used.

In all samples, besides some very weak spectra, which were previously reported to be related to copper and nickel, two PL bands were observed. At temperatures below 8 K, the strongest spectrum exhibited two zero-phonon lines denoted *A* and *B* at energies 778.91 and 779.85 meV, respectively, which are well resolved with a separation of 0.94 meV [Fig. 1(a)]. Some quasilocalized phonon replicas were detected with energies about 6 and 15 meV. At energies of 20.7 and 33.1 meV below the *A* line, two broad lines were observed which may be assigned to the transverse-acoustic TA (Λ) and longitudinal-acoustic LA (Λ) phonon replicas, respectively. A broad line at 718.6 meV [Fig. 1(b)] is attributed to the transverse-optical TO (Λ) phonon replica with an en-

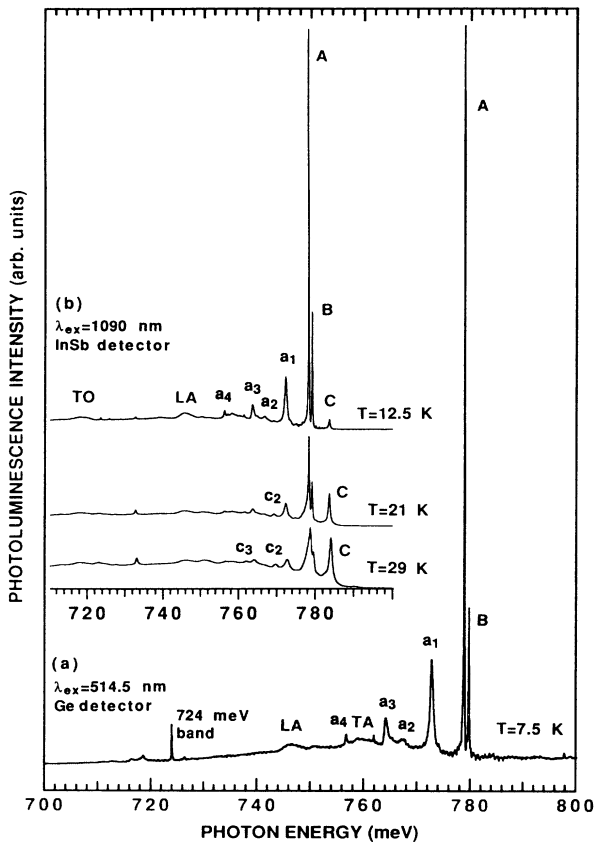

FIG. 1. Photoluminescence from the 780-meV band observed in silver-doped silicon: (a) measured at 7.5 K shows two sharp zero-phonon lines *A* and *B* and some local phonon replicas; (b) another line, labeled *C*, appears at higher energy and the temperature dependence of this PL band. For the assignment of lines, see text and Table I. The spectral resolution is 0.06 meV.

ergy of 60.3 meV. At higher temperatures another line, labeled *C*, appears at 784.31 meV as shown in Fig. 1(b). The intensity of this line rapidly increases with increasing temperature while the intensities of the *A* and *B* lines decrease. At temperatures higher than 20 K some local phonon replicas of the *C* line are also observed. The data for this PL band are presented in Table I. The temperature dependence of this band is illustrated in Fig. 1(b). With the Ag diffusion time varying from 2–16 h no significant change in the intensity of this band could be observed.

At lower photon energies, a new and much weaker PL band at 724 meV with several zero-phonon lines were detected. Since the data of this band is incomplete, its results will not be discussed in this paper. When using the 1090-nm line of the Ar laser, which has a penetration depth larger than the sample dimensions, as the excitation source, only the 780-meV band is observed. The 724-meV band and the Cu- and Ni-related spectra could not be detected. These defects are either not bulk centers like the 780-meV center, but are localized near the surface, or are not efficiently excited by the 1090-nm (below silicon bandgap) excitation. Near room temperature, a broad PL band with a maximum at about 680 meV is still observed.

The FTPLE measurements of the *A* and *B* lines were performed at 7 K and the obtained excitation spectrum with a number of resolved lines in the region from 780–830 meV is shown in Fig. 2. The *A* and *B* lines are also observed in the excitation spectrum but are very weak due to the short pass filter response outlined earlier. The PLE results prove that the *A*,*B*,*C*, and the higher lying lines are related to the same defect. A comparison with the transmission spectrum reported by Olajos, Kleverman, and Grimmeiss[7] shows that the energy positions of all observed lines in the two spectra are identical. In their work, based on the fact that the high-energy limit of the spectrum (825 meV) is close to the ionization energy level of 830 meV of the deep silver donor, and also in comparison with the spectra observed for deep chalcogen donors, the spectrum was believed to be due to a deep silver donor center.[7] The observed lines were described as due to the excitation from the ground state to the effective-mass-like excited electronic states near the conduction band. The *A*,*B*, and *C* lines were also observed but not given a definite assignment. They were suggested to be due to many-particle and spin-orbit effects.[7]

Recently, several neutral defects in silicon with donor-like excited electronic states similar to the silver-related center have been studied.[10–14] The optical-excitation spectra of these defects were shown to be well explained by the pseudodonor model. The optical spectra of such defects are characterized by their bound exciton (BE) states, whose formation is described by Hopfield, Thomas, and Lynch.[15] As suggested recently by Svensson, Monemar, and Janzén,[10] the pseudodonor character seems to be a common feature of the electronic structure of low-symmetry neutral defects in silicon. If the local potential is sufficiently strong, the defect may bind a hole as a primary particle and then possesses an electron-attractive local Coulomb potential. Such a hole can be very localized at the defect and its orbital momentum is then quenched by the low-symmetry local potential.[16] Consequently, a spinlike hole represents the ionized pseudodonor, which can loosely bind an electron in its long-range Coulomb potential. Spin coupling between the spinlike hole and the electron in such a system naturally gives rise to the spin-singlet and spin-triplet states which are the lowest states of the BE (for a detailed description see Ref. 16). The pseudodonor electron is then typically effective-mass (EM) -like and responsible for the observed PLE spectra. The excited states of such defects can be well described in the effective-mass approximation (EMA). However, a deviation from the EMA binding-energy values often occurs for the 1*s* manifold whose wave function has a nonvanishing amplitude at the defects site and, therefore, can be significantly affected by the central-cell potential. In some cases, a negative central-cell shift of the binding energy is observed.[15] A positive shift is always observed for deep pseudodonors, however.[10] It is due to a strong electron-attractive central-cell potential, which may not be effectively compensated in cases when the hole-attractive central-cell potential in the ground state is strongly localized, as discussed by Svensson, Monemar, and Janzén.[10] The major difference between a pseudodonor and a donor spectrum

is that all the $1s$ electronic states are final states in a pseudodonor excitation spectrum, while for a donor, one of the $1s$ states (although sometimes heavily modified) is the initial state of the optical-excitation spectrum.

In the case of this silver-related defect, the energy separation between the B and C lines is about 4.5 meV, which is in the range of typical singlet-triplet separations for complex defects in silicon and can be explained by spin-orbit effects.[16] The separation of 0.94 meV between the A and B lines then corresponds to the splitting of the triplet due to the crystal field. The temperature dependence of the PL intensity is indicative of the singlet-triplet character of the defect. As seen in Fig. 1(b), the temperature dependence of the intensities of the C line and the A and B lines exhibits changes in intensities which are usually observed for the singlet and triplet lines. The C line corresponds to the transition to the spin-singlet state which is an allowed transition and has a much higher transition probability than the nominally-forbidden triplet state. This assumption was recently confirmed by the Zeeman studies of Kleverman.[9]

Following Refs. 7 and 10, the assignment of the lines in the PLE spectrum is given in Table I and also in Fig. 2. For convenience, the T_d labels A_1, E, and T_2 are used here although the symmetry is lower. Attributing the low-energy group of four lines of the PLE spectrum at around 797 meV to the $1s(E+T_2)$ multiplet in agreement with Olajos, Kleverman, and Grimmeiss,[7] the next weak narrow line at 814.53 meV is expected to be the $2p_0$ line. In comparison with the PLE spectrum of the radiation-induced C-line defect in silicon—a shallow pseudodonor[12] —it is shown that the energy positions of the $1s(E+T_2)$ multiplet and the $2p_0$ line in both spectra almost coincide.[10] A marked similarity between the PLE spectra of silver and the C-line defect is also found for the higher s states, which gives further support for the above assignment. In the case of a pseudodonor, the influence of the central-cell potential on the binding energy of the shallow p states and the $ns(E+T_2)$ multiplet is expected to be small since their wave functions have a node at the defect site. The energy position of the ground state is estimated by adding the EMA value of 11.49 meV for the $2p_0$ state taken from Janzén *et al.*[17] to the energy value of the $2p_0$ line. The obtained value is E_c-826 meV. The

TABLE I. Observed electronic transitions energies of lines in the PL and PLE spectra of the 780-meV-PL band and the corresponding binding energies. For comparison, the corresponding EMA values taken from Ref. 17 are also given.

Assignment	Photon energy (meV)	Binding energy (meV)	EMA (meV)
A (triplet, zero-phonon line)	778.92	47.10	31.262
a_1 (6-meV-local phonon)	772.98		
a_2 (12-meV-local phonon)	766.94		
a_3 (14.8-meV-local phonon)	764.12		
a_4 (22-meV-a_1+a_3 phonon)	756.85		
TA (Λ) phonon (20.7 meV)	758.26		
LA (Λ) phonon (33.1 meV)	745.82		
TO (Λ) phonon (60.3 meV)	718.60		
B (triplet, zero-phonon line)	779.85	46.17	31.262
C [singlet, $1s(A_1)$]	784.31	41.71	31.262
c_2 (14.6-meV-local phonon)	769.70		
c_3 (22-meV phonon)	761.74		
$c(x)$	790.48		
$1s(E+T_2)(1)$	795.75	30.27	31.262
$1s(E+T_2)(2)$	796.50	29.52	31.262
$1s(E+T_2)(3)$	797.16	28.86	31.262
$1s(E+T_2)(4)$	797.66	28.56	31.262
$1s(x)$	803.09		
$c(y)$	805.59		
$2p_0$	814.53	11.49	11.492
$2s(A_1)$	816.01	10.01	8.856
$2s(E+T_2)$	817.52	8.50	8.856
$2s(E+T_2)$	817.61	8.41	8.856
$1s(y)$	818.61		
$3p_0$	820.79	5.23	5.485
$3s(A_1)$	821.10	4.92	4.777
$3s(E+T_2)$	821.52	4.50	4.777
$4s(A_1)$	823.19	2.83	2.911
$4s(E+T_2)$	823.47	2.55	2.911
$5s$	824.12	1.90	1.929
$2s(x)$	824.12		
$3s(x)$	827.70		

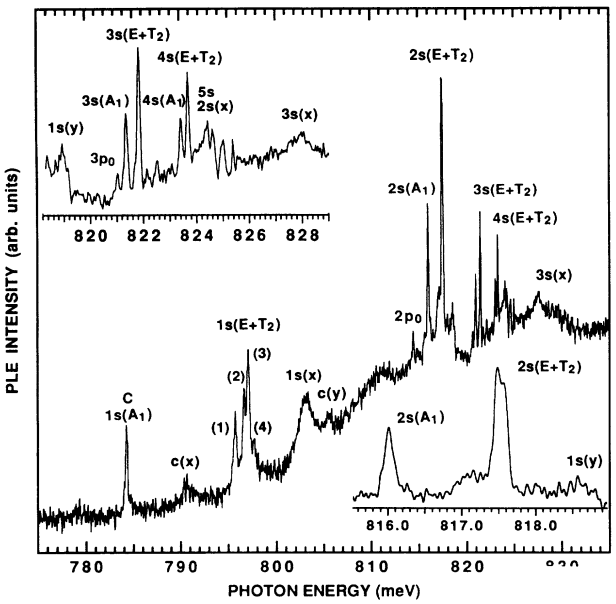

FIG. 2. The FTPLE spectrum of the 780 meV band recorded at 7.5 K using a Ge detector. For the assignment of lines, see text and Table I. The spectral resolution is 0.06 meV.

strong line at 817.59 meV corresponds to the transitions to the unresolved $2s(E+T_2)$ states. This line could be resolved with a higher-resolution scan (Fig. 2). The higher $ns(E+T_2)$ states are assigned as indicated in Fig. 2. Following Svensson, Monemar, and Janzén,[10] the C line of the Ag defect is attributed to the transition from the $1s(A_1)$ state. The transitions from the higher $ns(A_1)$ states are also observed and the deviation in their binding energies is in good agreement with the theoretical estimation (Ref. 10).

The phonon replicas of the excited Coulomb states are also observed in the PLE spectrum. The assignment of these phonon replicas is in agreement with Olajos, Klevermann, and Grimmeiss[7] and is given in Fig. 2 and Table I.

In contrast to the donor spectra in silicon, the transition from s states dominate in the excitation spectrum of the silver-related defect. As seen from Fig. 2, only very weak $2p_0$ and $3p_0$ lines are observed while all transitions to s states are rather strong. The $2p_\pm$ line, which is normally the highest intensity one in donor spectra in silicon, has not been observed. In the case of a donor, optical transitions between the p states and the ground donor states, which is usually the $1s(A_1)$ state, are EMA allowed, while for s states they are forbidden. In the pseudodonor case, the natural ground state of the defect is not a donorlike state, and may have a different orbital symmetry, which causes a change in the selection rules in favor of the transitions from s pseudodonor states.

The observed PLE spectrum, thus, can be explained as being due to a pseudodonor with a small down shift in the binding energy of the $1s(A_1)$ ground state compared to the EMA value. The resolved $1s(E+T_2)$ structure with four lines indicates that the symmetry of the defect can be C_{2v} or lower. Based on the C_{2v} symmetry and the binding energy of the center, which is close to that of the deep silver donor at $E_v+0.34$ eV, Olajos, Kleverman, and Grimmeiss[7] identified the spectrum as originating from the isolated substitutional silver in the vacancy model. In the vacancy model, silver has a closed $4d^{10}$ shell with the remaining electron in a vacancylike t_2 deep level and hence is expected to be paramagnetic as in the case of gold.[2] Our samples were also measured by EPR, but only the spectra of the isolated interstitial Fe_i^0 and Ag_i^0 (both have T_d symmetry) and the trigonal spectrum of the FeAg pair were observed in some samples, particularly those that had undergone long thermal treatments. The concentration of the center studied in this work is probably too low to be detected in our EPR setup. Optically detected magnetic resonance (ODMR) measurements were attempted on our X-band spectrometer but without success.

In summary, we have observed a PL spectra in silver-doped silicon, which is interpreted as being associated with the spin-triplet and spin-singlet states of a BE. The observed PLE spectrum of this PL band provides detailed information about the excited states of the defect. With these results, the electronic structure of this defect is confirmed to be well described by the pseudodonor model. This result leads to a suggestion that the electronic structure of the similar 793-meV-PL center, which is observed in gold-doped silicon and is generally believed to be related to the deep gold donor,[3,6] may also be interpreted by the pseudodonor model. For a conclusive identification and a microscopic model of this silver-related center, more investigations are required, however.

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*Permanent address: Department of Physics, University of Hanoi, Vietnam.

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