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Time-resolved photoluminescence study of Si : Ag

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Abstract

Photoluminescence band at 780 meV, previously assigned to silver-related centers in Si on basis of indirect arguments, is investigated in detail. For that purpose specially prepared samples doped with isotopically enriched silver are used. The photoluminescence spectrum exhibits characteristic structure consisting of narrow no-phonon lines and lower-energy phonon replicas. We observe isotope shift of the three main no-phonon lines which conclusively shows that silver is incorporated in the microscopic structure of the luminescent defect. From time-resolved photoluminescence lifetime of a few 100 μs is determined. This is a characteristic fingerprint for recombination of excitons bound to isoelectronic centers. Further insight in the nature of the optically active Ag-related center is obtained from the temperature dependence of the lifetime.

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1. Introduction

Like other noble metals, silver is an important impurity in silicon. This is due to its interesting physical properties as well as possible applications for device manufacturing. When introduced into silicon, silver gives rise to two levels: an acceptor at $E_c - 0.54$ eV and a donor level at $E_v + 0.34$ eV [1]. The donor level has been observed in optical absorption [2]. Transition at the acceptor were not observed. Also low-temperature photoluminescence (PL) from Si : Ag has been reported. It has been found that silver-doped silicon exhibits a characteristic emission spectrum at 780 meV [3–5]. The photoluminescence spectrum consists of narrow no-phonon lines (termed A, B, C at energies 778.91, 779.85 and 784.31 meV, respectively) which are replicated at lower energies by local phonons. From replica of lines A and B, local phonon energies of approximately 6 and 15 meV were determined. At temperatures higher than 20 K phonon replicas of the C line were also observed. The structure of the 780 meV band was identified as transitions from the effective-mass-theory electronic states near the conduction band to the ground state.

In the present work, we report on observation of the silver isotope 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. Also, the decay time of these lines and its temperature dependence have been determined.

2. Experimental

The starting material for sample preparation was float-zone, p-type silicon, with resistivity of 75–125 Ω cm. Silver was introduced into the sample by evaporation, followed by diffusion at 1150°C for 4 h in a closed quartz ampoule containing 100 mbar of argon. After the diffusion step, samples were quenched to room temperature in water and chemically cleaned to remove the silver-rich surface layer. For diffusion both natural and isotopically enriched silver (99.5% of ^{107}Ag and 99.4% ^{109}Ag isotope) were used.

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

Time-resolved measurements were carried out using a digital oscilloscope (Tektronic TDS 3000) in combination with an InP/InGaAs nitrogen-cooled photomultiplier tube (Hamamatsu R5509-72). For transient excitation a laser beam (at a 1 W continuous power) was passed through a pinhole and mechanical chopping (200 Hz). In this configuration, the experimentally measured system response time was 38 μs.

3. Results and discussion

3.1. Isotope measurements

For all the investigated samples photoluminescence was measured for the energy range between the band gap energy of silicon and approximately 700 meV. Fig. 1 shows typical photoluminescence spectra obtained in this study from silver-doped silicon samples at 10 and 20 K. The band around 780 meV is similar to that observed earlier [3–5], and ascribed to silver on basis of sample preparation. In addition to that, two new and weaker PL bands at 806 and 811 meV, labeled D and E, respectively, were detected.

Fig. 2 presents high-resolution photoluminescence spectra of the 780 meV band recorded for samples doped with silver isotope ^{107}Ag, silver isotope ^{109}Ag and natural silver. The spectra of samples doped with isotopically enriched silver are similar to that in Fig. 1

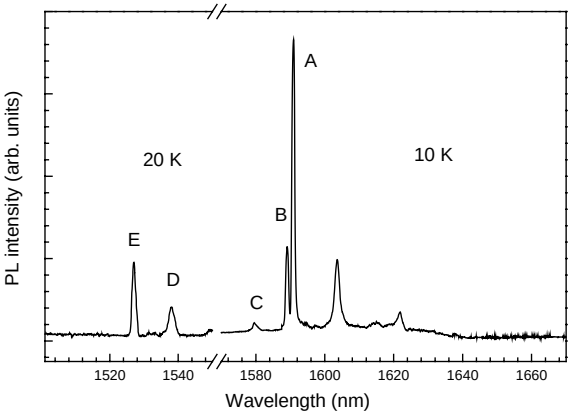

Fig. 1. 780 meV PL band observed in silver-doped silicon at $T = 10$ and 20 K.

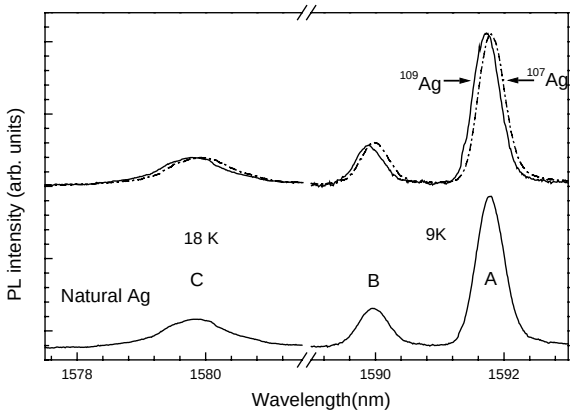

Fig. 2. A, B and C PL lines measured in silicon doped with isotopically enriched silver (upper curves) and natural silver (lower curve).

but with positions of ABC structure were shifted by ~ -0.017 meV for ^{107}Ag-doped silicon, and by $\sim +0.017$ meV for ^{109}Ag-doped silicon. We also note that PL lines in sample diffused with natural silver ([^{107}Ag]:[^{109}Ag] as 52:48) are distinctly broader than those for ^{107}Ag or ^{109}Ag-doping. These results provide direct evidence that silver is involved in the microscopic structure of the center responsible for this emission.

The isotope shifts were observed also for the phonon satellites and are illustrated in Fig. 3 for the 773 and 765 meV replicas of lines A and B. Isotope shifts of luminescence lines are a convenient tool for the identification of the chemical nature of the optically active centers. The isotope effect for the bound exciton photoluminescence is related to the zero vibrations of the center and leads usually to an increase of the recombination energy for heavier nuclei [6,7]. For isoelectronic impurities in silicon such an effect has been experimentally observed for the copper–copper pair [8]. In this case, a 0.1 nm difference of the position of the PL line for the samples doped with ^{63}Cu and ^{65}Cu copper isotopes has been concluded.

In Fig. 4 high-resolution PL spectra of D and E bands at 25 K recorded in samples doped with monoisotopic silver are compared. In this case no isotope shift is observed and we can not conclude whether these lines are silver-related.

3.2. Luminescence decay time measurements

We have examined decay characteristics of A, B and C lines. The decay times are exponential over the entire temperature range and identical for all the components. Fig. 5 shows decay of A line experimentally measured at 4 and 20 K. The lifetimes measured for A line at 4 and 20 K are 248 ± 3 μs, and 130 ± 5 μs, respectively. The

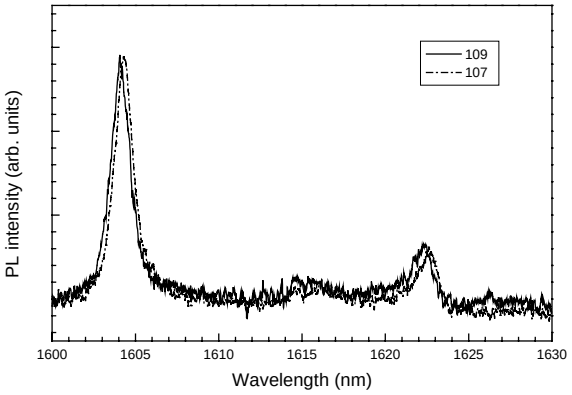

Fig. 3. Isotope effect for the phonon replicas of A and B lines.

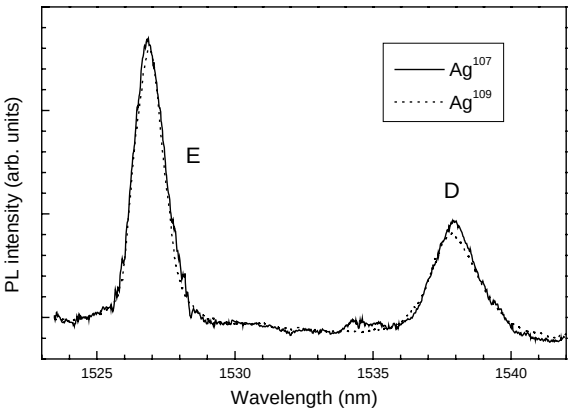

Fig. 4. Isotope effect for D and E PL lines.

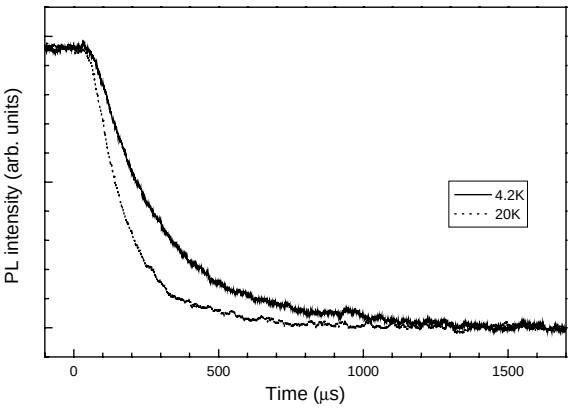

Fig. 5. Decay time for the A line of the 780 PL band measured at 4 and 20 K.

temperature dependence of the lifetime is depicted in Fig. 6. From the comparison with the temperature dependence of PL intensity [3], we assign the

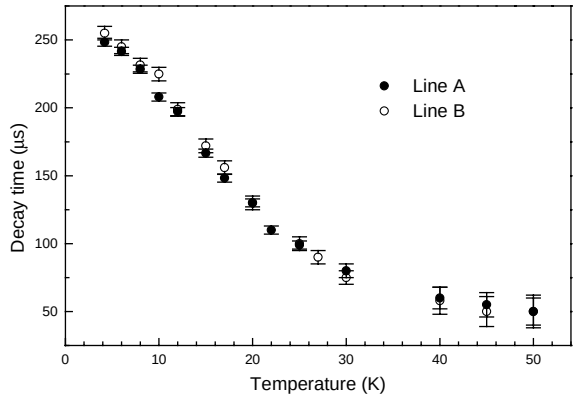

Fig. 6. The temperature dependence of decay times of A and B lines.

high-temperature decrease ($T \geqslant 30$ K) of the lifetime to dissociation of the exciton. The identical decay time of A, B and C lines is in agreement with the hypothesis that these lines originate from three thermalizing states of the same center [5]. At low temperatures, we obtain long decay times of about 250 μs. This value is large when compared with the lifetimes of donor or acceptor bound excitons in silicon, which are in the ns range. For excitons bound to a donor or acceptor, the lifetimes strongly depend on the impurity binding energy E_i. Experimentally, approximate dependencies $\tau \propto E_i^{-4.6}$ for acceptor or $\tau \propto E_i^{-3.9}$ for donor were reported and the lifetime shortening was attributed to a localized phononless Auger recombination process [9]. For example, for excitons localized at In acceptors in silicon with $E_i = 154$ meV, the lifetime of $\tau = 2.7$ ns has been determined [9]. The lifetimes measured in this study are by a factor 10^5 longer and are consistent with a model that the A, B and C lines are due to recombinations of excitons bound at an isoelectronic trap [10,11].

5. Conclusion

The 780 meV luminescence lines observed in silver-doped silicon samples have been studied. For samples doped with isotopically enriched silver, we present conclusive microscopic evidence on participation of silver in the optically active center responsible for the 780 meV PL band. The experimentally measured long lifetimes of the three dominant no-phonon lines of the 780 meV band are in agreement with a model of radiative recombination of an exciton localized at an isoelectronic center.

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