Two - Color Mid-Infrared Spectroscopy of Isoelectronic Centers in Silicon

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ABSTRACT

One of the open questions in semiconductor physics is the origin of the small splittings of the excited states of bound excitons in silicon. A free electron laser as a tunable source of the mid-infrared radiation (MIR) can be used to investigate such splittings of the excited states of optical centers created by transition metal dopants in silicon. In the current study, the photoluminescence from silver and copper doped silicon is investigated by two color spectroscopy in the visible and the MIR. It is shown the PL due recombination of exciton bound to Ag and Cu is quenched upon application of the MIR beam. The time-resolved photoluminescence measurements and the quenching effects of these bands are presented. By scanning the wavelength of the free-electron laser ionization spectra of relevant traps involved in photoluminescence are obtained. The formation and dissociation of the bound excitons, and the small splittings of the effective-mass excited states are discussed. The applied experimental method allows correlation of DLTS data on trapping centers to specific channels of radiative recombination. It can be applied for spectroscopic analysis in materials science of semiconductors.

INTRODUCTION

Bound exciton recombination gives sharp luminescence lines in the near band-gap region of most semiconductors. Shallow donors and aceptors as well as isoelectronic impurities are known as exciton binding centers. The binding energy of excitons bond to isoelectronic centers does not follow simple systematics. This is due to a more complicated binding mechanism in these complexes. An electron bound to a positive charge core of a neutral defect experiences two partly overlapping potentials: central-cell potential with a short range interation and the Coulond potential with a long range interaction. The Coulomb potential of the positive charge localized at the core gives rise to hydrogenlike excited states described by the effective-mass approximation (EMA).

The photoluminescence (PL) of silver-doped silicon has been investigated in the past and in generation of a characteristic low temperature emission spectrum at 780 meV [1-5] has been concluded. In the photoluminescent spectrum, narrow no-phonon lines (termed A, B, and C with energies of 778.9, 779.9 meV and 784.4 meV, respectively) 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. The PL spectrum of copper-doped silicon has two bands at 1014.7 meV [6] and 943.7 meV [7], each of them featuring several replicated PL lines.

EXPERIMENTAL

Samples for this study were prepared from low resistivity p-type float-zone silicon. Silver or copper was evaporated on both sides of a sample and then diffused at 1150oC 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 that, the surface layers were mechanically lapped and etched in a mixture of HF and HNO_3 (1:3).

The experiments have been performed at the free electron laser for infrared experiments (FELIX) users facility at the FOM institute for Plasma Physics “Rijhuizen”. For band-to-band excitation, a second harmonics of a pulsed Nd:YAG laser operating at λ_{YAG} = 532 nm was used. Following the pump pulse, a secondary pulse from the free electron laser (FEL) is applied with a tunable delay time at the wavelength of choice and a variable power. For spectroscopic measurements, our studies were performed in two specific ranges of photon energies between 70-170 meV and 35-65 meV. The sample is places in a helium gas flow variable temperature cryostat (Oxford Instruments Optistat). The emerging luminescence is dispersed by a spectrometer (Triax 320) and detected with a PMT detector (Hamamatsu R5509-72).

RESULTS AND DISCUSSION

Figure 1 shows the effect of the FEL pulse, at photon energy of 88meV) on the emission due to excitons bound at the Ag-related center. The effect of the FEL is shown for two different delay times between the pump and the FEL pulses Δt= -100 μs, -250 μs. Similar, the quenching effect on the Cu-related PL signal is observed. As can be seen, the FEL pulse leads to a

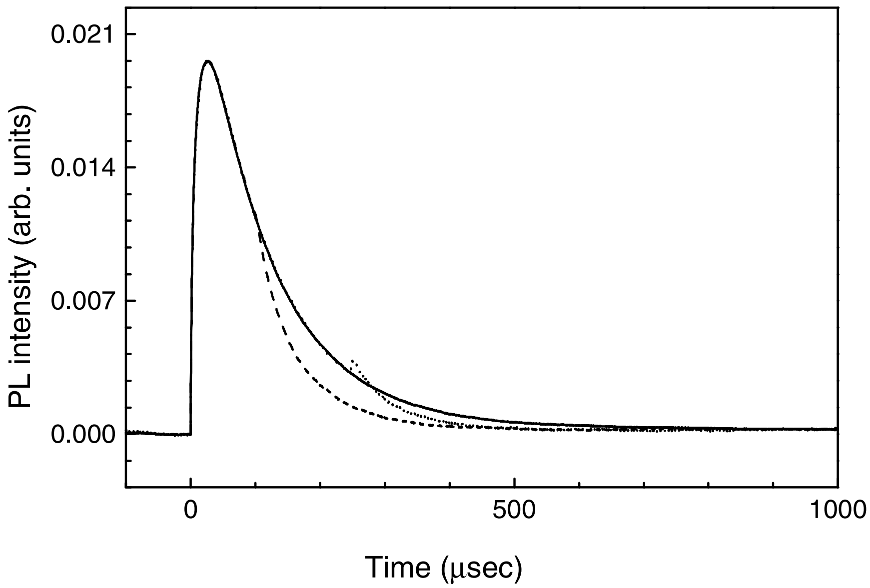

Figure1. Quenching of the emission from Ag-related center by application of the FEL at photon energy of 88 meV with two different delay times between the pump and the FEL pulses of 100 μs and 250 μs.

considerable quenching of the intensity of the PL signal. In order to understand the actual role played by the FEL pulse, we scan the wavelength of FEL.

Figure2 shows the quenching effect as a function of photon energy, normalized for a few values of constant MIR flux density. An onset is shown with a maximum of quench at 47 meV. When we assume that the quenching effect is related to ionization of an effective-mass shallow state, then its ionization energy can be calculated as formula $h\nu = 10/7\ E_{ion} \approx 33$ meV. Since the emission from Ag-related center has photon energy of 780 meV, then taking into account the band-gap energy of silicon at low temperature, we calculate the localization energy of a hole at Ag-related center as 357 meV. This is in agreement with the existing reports on DLTS measurements on Si:Ag. Exciton binding energy is asymmetric with primary localization of a hole by a strong local potential; subsequently an electron is localized in a Coulombic potential forming effective-mass-theory donor-like states. Also for copper in silicon, we have shown from the quenching effect as function of FEL photon energy, that two ionization energies of the shallow trap are 32 and 36 meV. The ionization energy in the 35 meV range is typical for the

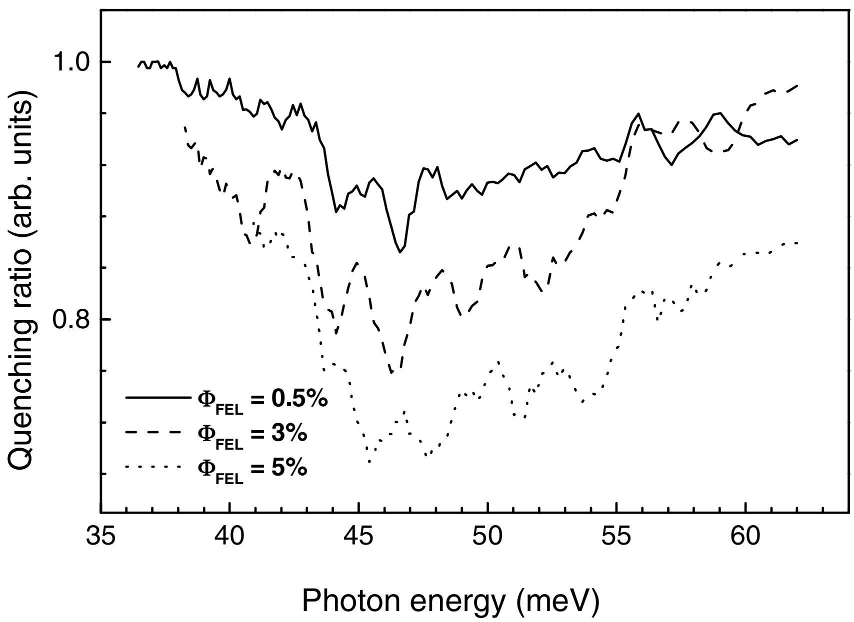

Figure 2. The quenching effect of PL of silver in silicon is a function of photon energy, for three different flux densities.

effective-mass-theory shallow states in silicon, confirming the bound exciton model developed in the past for isoelectronic centers formed by Ag and Cu doping of Si.

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