Time-resolved free-electron laser spectroscopy of a copper isoelectronic center in silicon

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Time-resolved "two color" photoluminescence is reported from the 944 meV band produced by a low concentration of copper in silicon. Photoluminescence has been generated by a pulsed pump beam, and then partially quenched by a probe beam from a free-electron laser. The kinetics of the quenching allow the absorption cross section for photoionization of the center to be determined without knowing its concentration in the sample. The time-resolved data demonstrate a partial recovery of the luminescence after photoionization, due to repopulation of the ionized traps.

I. INTRODUCTION

At low temperature, the radiative lifetime of the luminescence emitted by most optical centers in silicon is long, of the order of 100 μs. Consequently, these centers, many of which are well characterized, can be used to investigate nonradiative processes. For example, it is well established that most of the strongly luminescent centers are in the neutral charge state, isoelectronic with the lattice, because a charged center could preferentially de-excite by an Auger emission of the excess charge. A very simple picture has been developed for the excited states of the majority of the isoelectronic centers. Excitation of the center is equivalent to exciting one charge (hole or electron) to a higher energy state at the center, leaving the core of the center charged (negative or positive, respectively). The high permittivity of silicon and the low effective masses of the electrons and holes result in the excited charge moving into an effective-mass state. The effective-mass particle may be the hole, for example, at the carbon-related "T" center,[1] or the electron, as in the example discussed in this paper. By using the known properties of the extremes of the valence or conduction bands, it is possible to understand in detail many properties, such as the response of the states to perturbations,[2] or to link the relative optical transition probabilities of different excited states to the electron-phonon coupling at the center.[3] The partial separation of the electron and hole states results in the long radiative lifetimes and, consequently, in very weak absorption strengths, but the localization of the energy produces apparently high quantum efficiencies at low temperatures. Photoluminescence (PL) spectroscopy and associated techniques have therefore been the preferred optical probes of the centers. For example, for some centers, the Rydberg-like series of excited states have been detected by PL excitation spectroscopy.[4] The long lifetimes in the excited states also favor two-color spectroscopy, in which one "pump" beam (of photon energy of the order of the band gap) excites the center, and a second mid-infrared "probe" beam (with photons of the order of 10 to 100 meV) excites transitions within the effective-mass states.[5,6] Precision measurements of the effective-mass states have been reported using high spectral resolution in the probe beam. Additionally, in a "two-color"

experiment, the selection rules for transitions induced by the probe allow states to be investigated that are not observed by direct PL measurements.

To date, the two-color experiments have used steady-state excitation (strictly, low-frequency modulated for lock-in detection). This approach allows high spectral resolution. However, the concentrations of the optical centers are usually not known with any precision, and the fraction of them in the excited states is also unknown, so that data cannot be obtained on the kinetics of the processes. In this paper we report time-resolved two-color excitation, in which a pulsed probe beam has been obtained from a free-electron laser (FEL). These measurements allow the photoexcitation cross section of transitions from the excited states to be determined without knowing the concentration of the excited optical centers, and they demonstrate that a carrier that has been photoionized from an optical center may be recaptured by it.

We consider here a luminescence center produced by copper in silicon. The properties of copper in silicon have considerable relevance to silicon-based technology. Copper is used for interconnects in recent generations of microchips.[7] Due to its high solubility and rapid diffusion (as a positively charged species), copper is one of major contaminants in silicon. The behavior of copper in silicon has been studied extensively.[8] In an isolated form, Cu has been found to take a somewhat distorted substitutional position.[9] At low temperatures it precipitates and clusters with other defects. Many of these centers exhibit electrical activity; some are involved in radiative recombinations. The most familiar PL system produced by Cu in Si has a zero-phonon line (ZPL) at 1014.7 meV. This band is highly characterized. It occurs from a center of trigonal symmetry,[10] and the excited states can be described in terms of an effective-mass electron orbiting in the local trigonal field.[11] The binding energy of the electron is estimated to be 32 meV from the thermal quenching of luminescence from the center.[10] In the positive charge state, the tightly bound hole state is observed in deep-level transient spectroscopy (DLTS) at $E_v+0.1$ eV.[12] The vibronic sideband is characterized by a low-energy resonance phonon of 7 meV, identified as a highly localized, in-phase motion of the nearest-neighbor substitutional-interstitial copper pair forming the center.[13] In this paper we present data on a lesser
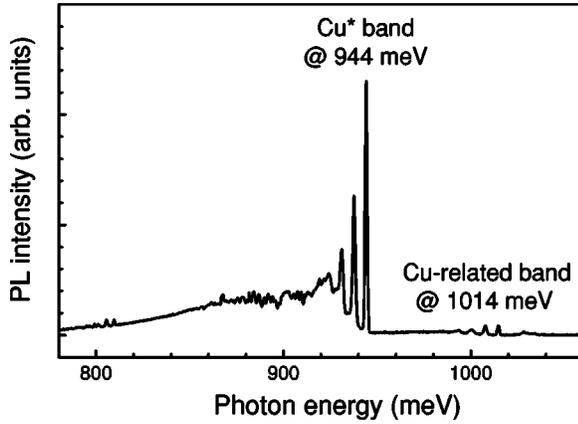
FIG. 1. The 944 meV Cu* PL band observed in this project ($T = 4.2$ K, Ar$^+$-ion laser excitation). In addition, the 1014 meV Cu-related band of lower intensity can be distinguished.

investigated Cu center, known as Cu*, which is produced by a lower contamination with Cu. The PL band has a very similar shape to that of the 1014 meV band, and only differs by having its ZPL shifted by 70 meV to lower energy to 944 meV.[14] Correspondingly, we expect that the deep hole state will be shifted deeper into the gap by the same amount, because, for this type of center, the sum of the hole level, the energy of the ZPL, the binding energy of the electron (again assuming ~ 30 meV for an effective-mass electron in silicon), and the exciton binding energy (15 meV) will be close to the indirect energy gap (1170 meV at low temperatures). The associated hole level is located at $E_v + 0.185$ eV.[15] Recent *ab initio* calculations suggest that the Cu* center consists of a substitutional Cu atom with an interstitial Cu atom located near the third-neighbor tetrahedral site.[16] This assignment disagrees with published uniaxial stress perturbations of the line, but those data were measured only for low stresses and they are not fully understood.[17] For present purposes it is sufficient to know (from the DLTS data) that the center has a deep-hole shallow-electron structure, and that it is produced with low metallic contamination.

II. SAMPLE PREPARATION AND EXPERIMENT

The p-type samples for the current study were prepared by evaporating copper on both sides of a sample. The metal was in-diffused by heating for 4 h at 1150 °C in a closed quartz ampoule containing 100 mbar of argon. After the diffusion step, the ampoule was quenched to room temperature in water and the samples were etched to remove 70 μm of the surface layers. The PL spectrum of the investigated sample is shown in Fig. 1. It has been taken at low temperature $T = 4.2$ K under continuous wave excitation with a 514.5 nm line of Ar$^+$-ion laser. As can be seen about, 97% of the PL (amplitude) detected at 4.2 K from the samples came from the Cu* band, 3% from the 1014 meV Cu-related band, and the remainder from the boron doping and the Ag-related 780 meV band.

For the two-color measurements reported here, the pump beam was the second harmonic of a Nd:YAG laser (532 nm)
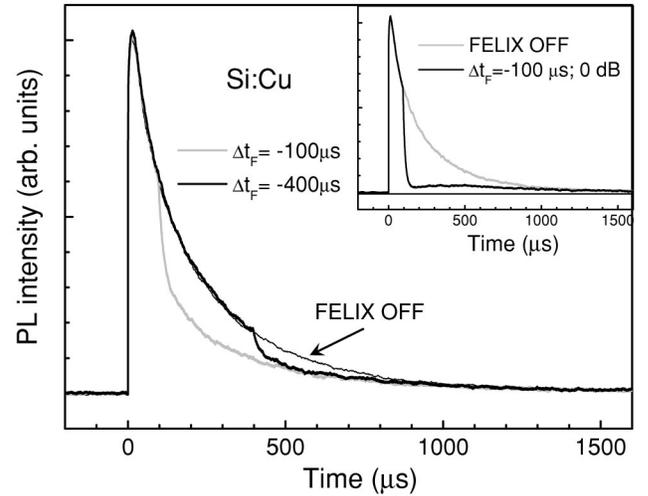
FIG. 2. The quenching of Cu-related PL band (944 meV) by the FEL probe pulse. The effect is illustrated for a photon energy of 60 meV with the probe pulse applied 100 and 400 μs after the YAG-laser excitation (denoted by $\Delta t_F = -100, -400$ μs). The inset shows the recovery of the PL signal after termination of the probe pulse (set to a maximum intensity of the MIR probe photons).

with a repetition rate of 5 Hz and a pulse duration of 100 ps. A mid-infrared (MIR) probe pulse was provided by the Dutch Free Electron Laser for Infrared eXperiments (FELIX) users facility at the FOM Institute for Plasma Physics "Rijnhuizen" in Niewegein, The Netherlands. The MIR beam features short micropulses, which have a nominal duration of 1 ps and separated by intervals of 1 ns (1 GHz). The micropulses form a train (the macropulse) with a duration of ~ 5 μs. The wavelength of the FEL is tunable between 35 and 65 meV and can be activated with a selected time delay Δt_F with respect to the Nd:YAG laser pulse. Measurements were carried with the sample fixed on the cold finger of a flow cryostat resulting in a sample temperature of 16 K. The emerging Er PL is dispersed through the spectrometer, and detected with an InP/InGaAs nitrogen-cooled photomultiplier tube (Hamamatsu R5509-72) with a flat response over the wavelength from 300 to 1600 nm. The experimentally measured system response time is $\tau_{det} \approx 30$ μs. More details on the experimental setup for the two-color spectroscopy with FEL can be found in Refs. 18 and 19.

III. RESULTS AND DISCUSSION

Figure 2 shows the decay of the 944 meV PL band after excitation by the pump pulse. The figure also shows the effect on the decay curves of FEL pulses applied with delay times of 100 and 400 μs. For these data, the FEL pulse had a photon energy set to $E_{ph} = 60$ meV, and a sufficiently low power to avoid complete quenching of the PL (with 10 dB attenuation). Using only the pump pulse, the PL intensity decays exponentially with a decay rate of $W_1 = 4.4 \times 10^3$ s^{-1}. Applying a FEL probe pulse produces a strong quenching of the PL (Fig. 2). The quenching effect is not observed when the FEL photons are applied prior to the pump excitation pulse, ruling out sample heating by the FEL pulse as the

cause of the quenching. Figure 2 also shows that after a rapid decrease during the FEL pulse, the decay curve continues with the same exponential decay time as without the FEL pulse; PL quenching takes place only during the FEL pulse. For a fixed photon energy E_{ph} and a photon flux ϕ of the FEL, the fraction of the PL signal that is quenched is independent of the delay time; that is, the quenching is proportional to the concentration of the emitting centers available at the moment when the FEL is fired. All data have been taken in the regime in which the PL quenching effect depends linearly on the pump power to avoid saturation effects. In the absence of the FEL pulse, the decay of the population N in the luminescing state therefore follows the usual rate equation $dN/dt = -W_1 N$. During the FEL pulse, this becomes modified to $dN/dt = -W_1 N - W_q N$, where W_q is the decay rate induced by the FEL pulse. This induced decay rate is found to be proportional to the FEL photon flux ϕ, $W_q = \sigma \phi$, at a fixed photon energy E_{ph}. The physical meaning of σ is therefore that of the cross section for the absorption of photons from the excited state at each of the centers. We define R as the "time-integrated" ratio of the PL intensity observed with and without the FEL pulse, where the integral is from the time chosen for the pulse to infinity. We approximate the FEL pulse by a square pulse of duration τ. In the limit that $W_q \gg W_1$, which is valid here, we expect that the quenching ratio, measured from the time of switching off the FEL pulse ($t=0$), is given simply by

$$R = \frac{\exp(-W_q\tau)\int_0^\infty \exp(-W_1 t)dt}{\int_0^\infty \exp(-W_1 t)} = \exp(-W_q\tau). \quad (1)$$

However, there is a further complication in that when the power of the FEL pulse is increased so that there is almost complete quenching of the Cu signal, a recovery is observed, commencing after the quenching (inset to Fig. 2). Integrating the PL to long time shows that $29 \pm 3\%$ of the quenched Cu signal recovers after the FEL pulse. Where the recovered fraction can be accurately measured, it is found to be independent of the photon energy and also of the flux of the FEL beam. It is proportional to the signal level after the FEL pulse, so that in the simple description employed here it increases the numerator of Eq. (1) by a constant factor.

The origin of the quenching is established by Fig. 3, where the FEL quenching rate is plotted as a function of the FEL photon energy E_{ph} for three different FEL fluxes, all sufficiently low that the quenching rate is linearly dependent on the flux. The quenching rate W_q is known directly as $-\ln(R)/\tau$ [Eq. (1)], and has been normalized to constant FEL flux density. (We assume that the signal recovered after the FEL pulse is constant and equal to 29% of the quenched signal.) The threshold, near the energy expected for ionization of the effective-mass electron, establishes that the quenching process is simply the photoionization of the electron. The photoionization cross section σ into a continuum of states is expected to depend on the photon energy E_{ph} as
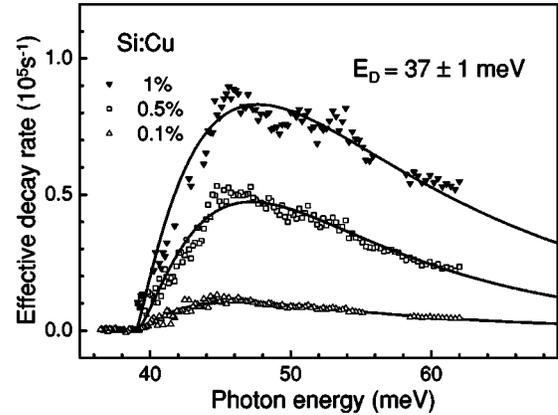
FIG. 3. The effective decay rate W_q induced by the FEL pulse of Si:Cu sample as a function of FEL photon energy, for three different values flux of the MIR photon.

$$\sigma(E_{ph}) \propto \frac{(E_{ph} - E_D)^{3/2}}{(E_{ph})^{3+2\gamma}}, \quad (2)$$

where E_D is the threshold energy for the ionization, and γ is an adjustable parameter of the order of unity. The lines in Fig. 3 are a fit of Eq. (2) with $\gamma = 1.6$, and define the threshold as $E_D = 37 \pm 1$ meV. For a silver-doped silicon material, which forms a similar bound exciton optical center giving rise to PL band at 780 meV, a fit to photoionization data produces $E_D = 39 \pm 1$ meV (see Fig. 4).

Figure 5 plots the quenching rate W_q against the FEL flux ϕ for three values of the FEL photon energy E_{ph}. Since W_1 and τ are known, a least-squares fit to W_q ($=\sigma\phi$) gives σ for each value of E_{ph}. The values of σ decrease from $\sigma = 1.1 \times 10^{-14}$ cm^2 at $E_{ph} = 45$ meV to 8.7×10^{-15} cm^2 and 5.6×10^{-15} cm^2 at 54 and 62 meV, respectively, where allowance has been made for reflection losses at the surface of the sample.
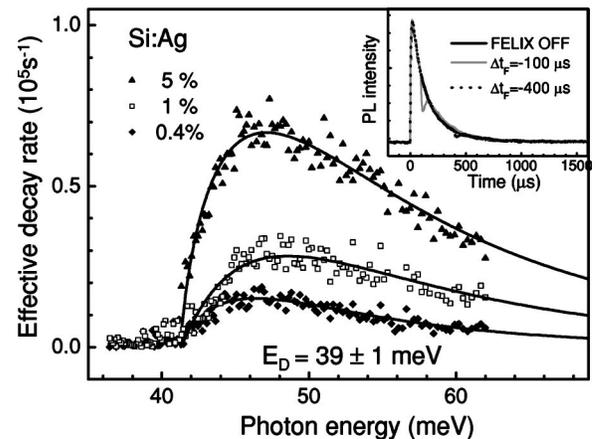
FIG. 4. The effective decay rate W_q induced by the FEL pulse as a function of FEL photon energy, for three different flux values of the MIR photon for Si:Ag sample. The inset shows the quenching of Ag-related 780 meV PL band by the FEL probe pulse with a photon energy of 60 meV and the probe pulse applied 100 and 400 μs after the YAG:Nd laser excitation.
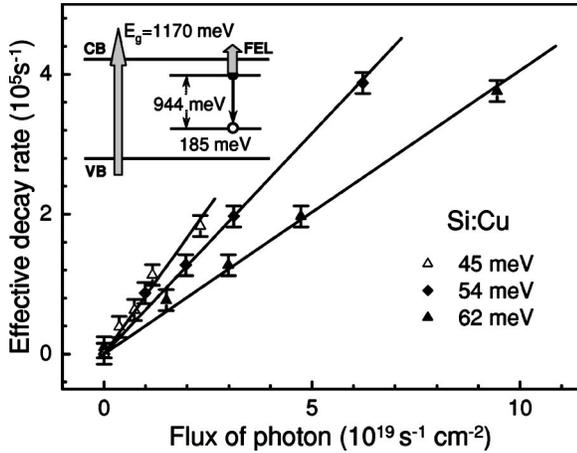
FIG. 5. The flux dependence of the MIR-induced quenching PL for photon energies of 45, 54, and 62 meV and a delay time of $\Delta t_F = -200$ μs. The inset shows the model for the quenching effect.

The ratios of the values for σ are in close agreement with the ratios of the cross sections at those photon energies shown in Fig. 3. To check the order of magnitude of the cross sections, we note that the absorption coefficient μ is related to the cross section σ by $\mu = \sigma N$, where N is the concentration of the optical center. The excited state of the Cu center consists of an effective-mass electron orbiting a positive hole—a configuration very similar to an electron orbiting a phosphorus donor. The ionization continuum of the P donor has a cross section of $\sigma = \mu/N \sim 2 \times 10^{-15}$ cm^2,[20] of the same order as the values obtained here for Cu*.

We have noted that the fraction of the signal that recovers after the FEL pulse is independent of the properties of the FEL pulse, but is proportional to the signal after the pulse; that is, it is proportional to the effect of the pump beam. It could therefore be an intrinsic property of the center, or it could be an effect of the pump beam ionizing other centers. A similar effect has been observed for Si:Ag (Fig. 4, inset).[21] A time-dependent measurement allows the recovered fraction to be observed, in contrast to a steady-state measurement, such as when measuring the loss of PL as the temperature is increased, where the recovered fraction is simply observed as an indistinguishable part of the total signal.

One of the unanswered questions concerning the class of isoelectronic centers is the ionization mechanism. Thermal quenching of the PL may have an activation energy equal to the ionization of the shallow particle, for example, at the 780 meV Ag center,[22] it may be equal to the binding energy of the tightly bound particle, as at the sulfur-related centers,[23] or it may equal the exciton binding energy. We have seen that following photoionization of the Cu* center, there is a transient increase in the PL signal (Fig. 2, inset). First, consider the situation with a low concentration of Cu-related centers. In contrast to ionizing a gas atom, where by definition the electron travels away from the ion, an electron ionized from a center in a crystal can lose energy as it comes to thermal equilibrium with the lattice. For example, an electron of

mass $0.1m_e$ and kinetic energy 20 meV would travel a total distance of about 100 to 1000 atomic spacings in 10^{-13} to 10^{-12} s, which we take as the time to come to thermal equilibrium. The Coulomb potential attracting the electron to the ionized center is then at least 5 to 0.5 meV in magnitude, comparable with the thermal energy of about 1.4 meV (16 K). With no externally applied electric field, recapture of the ionized electron is quite probable. With increasing temperature, the probability that the electron will escape increases, and indeed the experimental results show that the magnitude of the PL recovery process is strongly temperature dependent and does not occur for $T > \sim 40$ K. With a weak Coulomb potential, as at the 780 meV center, recapture is likely to affect predominantly the emission rate, and thus is not obvious in a steady-state measurement. With a deep potential, as at the sulfur-related centers with electron binding energies of about 60 meV, thermal ionization of the shallow particle alone may be prohibited.

On the other hand, for a high concentration of Cu-related centers, a different scenario might be applicable. We note that the cross section for electron capture in a cascade process, as applicable for a shallow, effective-mass state has a relatively high value, of the order of $\sigma \approx 10^{-11}$ cm^2. Assuming a reasonable value of average thermal velocity of electrons in Si at cryogenic temperature, $\langle v_{th} \rangle \approx 10^6$ cm s^{-1}, the characteristic time constant of the recapture process is $\tau_{cap} = [N\sigma_{cap}\langle v_{th} \rangle]^{-1} \approx 0.1$ ns for a concentration of the Cu-related traps of 10^{15} cm^{-3}. At this concentration the average distance between the centers would be of an order of $d = 100$ nm, comparable to the effective capture radius $r_{eff} = e^2/\kappa kT \approx 50$ nm, for the Si dielectric constant $\kappa = 11.6$ and $kT = 3$ meV. In this case, if all the copper was present as Cu* centers, optical ionization would be a transient phenomenon, taking place only during the FEL pulse, with the full recovery of the PL signal upon termination of the pulse. At higher temperatures, the capture cross section decreases, leading to a decrease of the effective capture radius and an increased capture time. In both the low and high concentration limits, a recovery in the PL emission is not unexpected. In the present study the concentration of the different copper-related centers is not known, although the Cu* PL band is reported to be observed at low copper doping levels.

IV. CONCLUSIONS

In conclusion, we have demonstrated, using a Cu center in silicon, that the ionization cross section can be measured for unknown concentrations of centers from the kinetics of the two-color excitation measurements. We have verified the value by comparison with the absorption coefficient reported using known concentrations of shallow donors. Further, we have presented evidence the recapture of charge photoionized from the center.

ACKNOWLEDGMENTS

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