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Mechanism of photoluminescence of Si nanocrystals fabricated in a SiO₂ matrix

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The luminescence properties of silicon nanocrystals fabricated by Si ion implantation into a SiO_2 matrix and subsequent thermal annealing have been studied. To identify the mechanism of photoluminescence of Si nanocrystals, the dependencies of the steady-state photoluminescence on temperature and excitation power density, and the time-resolved photoluminescence have been investigated. The experimental results point to the mechanism of recombination via the levels of centers which are presumably localized at the silicon nanocrystal–silicon dioxide boundary. © 1998 American Institute of Physics. [S0003-6951(98)02046-4]

The observation of intense photoluminescence (PL) of porous silicon at room temperature by Canham¹ has stimulated extensive investigation of the emission properties of different kinds of nanocrystal structures, motivated by the need to integrate optical and electronic devices on silicon chips. Silicon nanocrystals fabricated by Si ion implantation into silicon oxide with subsequent thermal annealing are promising candidates as light emitters. In these nanocrystals the visible and near-infrared PL in the 1.5-1.7 eV range was observed,²⁻⁵ the nature of which is still under debate. Recently, two different mechanisms of radiative recombination in silicon nanocrystals were discussed in the literature—^{4,6} the recombination between quantum confinement levels, and recombination via levels of defects localized either inside the nanocrystals or on the interface of nanocrystals with amorphous silicon oxide, with different experimental and computational results pointing to either of the two mechanisms. To verify the mechanism of radiative recombination in Si nanocrystals fabricated by thermal annealing of SiO₂ layers implanted with Si, we report here the results of an investigation of kinetics, excitation power, and temperature dependencies of the PL of Si nanocrystals. The experimental data point to the mechanism of recombination via the levels of defect, localized presumably on the nanocrystal-matrix boundary.

The preparation of the samples studied in this work was described in detail in the paper by Kachurin and co-workers.⁵ Briefly, 500 nm thick layers of SiO₂ grown on Si were implanted with 200 and 100 keV Si⁺ at a doze of 1×10^{17} cm⁻², and then annealed at 1200 °C for 1 s and at 400 °C for 30 min. As reported in that study, the results of transmission electron micrography and Raman scattering investigations evidenced the formation of crystalline silicon clusters with an average size of 3.5 nm. An Ar⁺ laser operating at a wavelength $\lambda = 488$ nm and a maximum power density of 2.5 kW/cm² at the sample surface was used for excitation of steady-state PL, while for transient PL excitation a frequency-doubled Q-switched Nd:YAG laser (λ

=532 nm, pulse duration 0.15 μ s, peak power density 0.4 kW/cm²) or a N₂ laser (λ = 337 nm, pulse duration 7 ns, peak power density 100 kW/cm²) was used. The photoluminescence measurements were carried out using a double diffraction grating monochromator equipped with a cooled S-1 photomultiplier operated in the photon counting mode. The PL spectra were corrected for the wavelength-depended sensitivity of the system, which was determined through blackbody-radiation measurements.

In Fig. 1 a typical room-temperature steady-state PL spectrum of Si nanocrystals is shown. The spectrum comprises an asymmetrical band around 1.5 eV with a width of about 300 meV. An arrow in Fig. 1 marks the band position calculated by Khurgin *et al.*⁷ for the 3.5 nm cluster size. It is seen that the band maximum in the calculated spectrum is shifted to larger energies in comparison with the experimental one, and has its position at 2.1 eV. In Fig. 2 a dependence of the steady-state PL intensity (I_{PL}) on excitation power (P)and its approximation by a power-law function $I_{\rm PL} \sim P^{\gamma}$ are shown. The dependence has an overall sublinear character. At the lowest excitation powers a linear relationship is observed ($\gamma = 1$), while at higher powers it becomes sublinear with $\gamma = 0.5$. It is necessary to note that the shape of the band does not change with excitation power. With temperature decreased, the band exhibits a shift at a rate of -0.1 meV/K.



FIG. 1. Room temperature steady-state PL spectrum of Si nanocrystals. The arrow indicates the calculated band position of 3.5 nm Si nanocrystals according to Khurgin *et al.* (Ref. 7).

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FIG. 2. Dependence of the steady-state PL intensity of the nanocrystals on the excitation power at room temperature.

In Fig. 3 a set of time-resolved PL spectra measured at 300 K is shown as a function of the delay time after the excitation pulse. It is seen that the shape of the spectrum does not change with the delay time. The inset to Fig. 3 shows decay curves integrated over the spectrum taken at several temperatures on a wider time scale. At all temperatures the decay is nonexponential, the curves are approximated by stretched exponential functions. The 1/e decay time is 450, 65, and 20 μ s at 4.2, 77, and 295 K, respectively. Though the temperature decrease leads to a considerable increase of the decay time accompanied by a slight increase of the steady-state PL intensity, we did not observe any change of the band shape with delay time in this temperature.

The above results support the assumption that radiative recombination in silicon nanocrystals is mediated by some defect levels. The following observations point to this conclusion. First, the energy of radiative recombination is considerably less than the expected energy of optical transitions between the quantum-confined levels (see Fig. 1). Second, the sublinear dependence of PL intensity on the excitation power indicates that the recombination is mediated by some localized centers which saturate at high excitation powers⁸ and thus let charge carriers recombine via competing nonra-



FIG. 3. Evolution of the transient PL spectrum of Si nanocrystals with time at room temperature. The spectra were taken at delays of 0.25, 1, 3, 8, 15, 25, and 50 µs. The inset shows the decay curves integrated over the band spectrum at 4.2, 77, and 300 K (from upper to lower).

diative channels. In the opposite case of excitonic recombination in quantum dots, the saturation of the ground-level PL is accompanied by the onset of the PL of the excited states of the dots.^{9,10} Since we do not observe any change in the spectral shape of the band with excitation intensity, a sublinear dependence should not be expected for the recombination between quantum-confined levels in nanocrystals in our experimental conditions. Third, the absence of the spectral dependence of PL kinetics also points to recombination via local centers. On the contrary, in the case of the quantumconfinement recombination model, the PL decay should proceed faster on the shorter wavelength side of the spectrum because of the strong dependencies of both the recombination probability and energy of optical transitions on nanocrystal radii,^{7,11} resulting in a redshift of the band with time.

Let us speculate on the nature of the recombination center. Recently, a center of recombination on the Si nanocrystal-silicon dioxide boundary that is responsible for 1.5 eV luminescence was considered by Allan et al.⁶ They have shown that a single covalent bond, for example a Si-Si bond, can act as a trap and a recombination center. Their calculation shows that a metastable recombination state, separated from the excited state by an energy barrier, can exist on the boundary of small nanocrystals. The nonexponential decay kinetics can be expected in such centers if the barriers between excited and metastable states of the centers would have a certain energy spread and, consequently, the probability of carrier transition from the excited to recombination state would differ. In our case, since the recombination centers are localized on the boundaries of nanocrystals, the barrier height can depend on the local environment.

A particular qualitative characteristic of the center can be inferred from the temperature dependence of its PL band energy. It is known that the temperature dependence of the band energy of a center that is strongly bound with crystal lattice differs from that of the band gap of the host crystal. According to the configuration diagram model,^{12,13} the direction of the PL band shift with temperature is determined by the ratio of the frequencies of vibration modes of the ground and excited states of the center. The blueshift of the band with decreased temperature that we observe experimentally enables us to conclude that in our case the frequency of the vibration mode of the ground state of the center is higher.

In conclusion, we have studied the steady-state and timeresolved luminescence of 3.5 nm silicon nanocrystals fabricated by Si ion implantation into a SiO₂ matrix. We observed that the 1.5 eV PL band that is usually attributed to the recombination of quantum-confined carriers in silicon quantum dots displayed a sublinear intensity dependence on the excitation power, a spectrally uniform decay after transient excitation, and besides that, the estimated energy position of the band differs strongly from the experimentally observed. These data enable us to conclude that the characteristic 1.5 eV luminescence of Si nanoclusters is governed by the recombination via the levels of some defect-related centers, which are presumably localized at the silicon nanocrystal– silicon dioxide boundary.

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