Photoluminescence of Silicon Nanoparticles under the Action of Infrared Femtosecond Laser Pulses[1]

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Abstract—We present the experimental results for the absorption spectra and photoluminescence of silicon nanoparticles synthesized by femtosecond laser ablation in distilled water under action of femtosecond laser pulses at a wavelength of 1048 nm with intensities in the range from 10^{10} to 10^{12} W/cm^2.

INTRODUCTION

Silicon nanoparticles have a number of unique physical and chemical properties [1], in particular: resistance to photobleaching, size dependence of the emission spectrum, and low toxicity. Accordingly, silicon nanoparticles are considered to be a promising material in photonics [2–4], optoelectronics [5, 6] alternative energy [7], biology, and medicine [8–11].

Optical and electronic properties of silicon significantly change when its dimensions are close to the Bohr radius. In this case, due to an increase in probability of radiative recombination as a result of interband transitions, the intensity of photoluminescence of silicon nanoparticles can increase significantly compared to the bulk sample. Despite the fact that the study of specific properties of silicon nanoparticles has been carried out for several decades, the debates about the possible mechanisms and the sources of their unique properties still exist.

The most common methods of synthesis of silicon nanoparticles include electrochemical etching [9, 12, 13], chemical [14, 15] and physicochemical synthesis (in particular, laser-induced decomposition of silane [16, 17]), heating degradation [18], and pulsed laser ablation [19]. In the latter case, irradiation of target (Si wafer) is performed using nanosecond [19, 20] or femtosecond laser pulses [11, 21–23]. This technique does not require use of additional chemicals. Moreover, the size of the particles can be easily tuned by controlling the experimental parameters. Femtosecond laser ablation of silicon in a liquid is one of the simple and common synthesis methods, which makes it possible to obtain biocompatible silicon nanoparticles.

The size of the silicon particles depends significantly on various parameters of the synthesis such as the pressure of the inert gas in the chamber [24], the characteristics of the laser radiation (pulse repetition frequency [25], pulse duration [26], and the energy of pulses [10]), and the composition of the buffer medium [11, 25, 27].

In most cases, xenon arc lamps [9, 20] as well as argon (wavelength λ of 488 nm) [26] and nitrogen lasers [21] or higher harmonics of solid-state lasers (second harmonic of Nd:YVO4 [18] or the fourth harmonic of Nd:YAG [16]) are used for excitation of photoluminescence. In recent years, femtosecond lasers have been applied to study the characteristics of photoluminescence of various silicon nanostructures [28–30]. Using ultrafast laser sources make it possible to carry out time-resolved spectroscopy of the processes related to photoluminescence as well as to study the multiphoton excitation of silicon nanoparticles.

In our paper, we present the experimental results for the photoluminescence spectra of silicon particles at extremely high intensities, at which the formation of high electron density in the conduction band as well as the anomalous luminescence yield become possible. Experiments were carried out at combined system of femtosecond laser tweezers-scalpel based on an inverted optical microscope developed at the Joint Institute for High Temperatures, RAS [31].

SYNTHESIS OF SILICON NANOPARTICLES

At the first stage of research we conducted the synthesis of silicon nanoparticles. Synthesis was performed by femtosecond laser ablation in a liquid. In the experiments we used a femtosecond laser system with an active medium on the basis of a tungstate crystal doped with ytterbium (Yb:KYW). Laser pulses were generated at λ = 1028 nm with a spectral width of 10 nm, the maximum pulse energy of 120 μJ, and a repetition rate of 5 kHz. The laser system consisted of a fiber master oscillator, a regenerative amplifier and a compressor. Amplified pulse duration was 285 fs.

The laser beam was focused on the sample by LOMO 10× microscope objective with numerical

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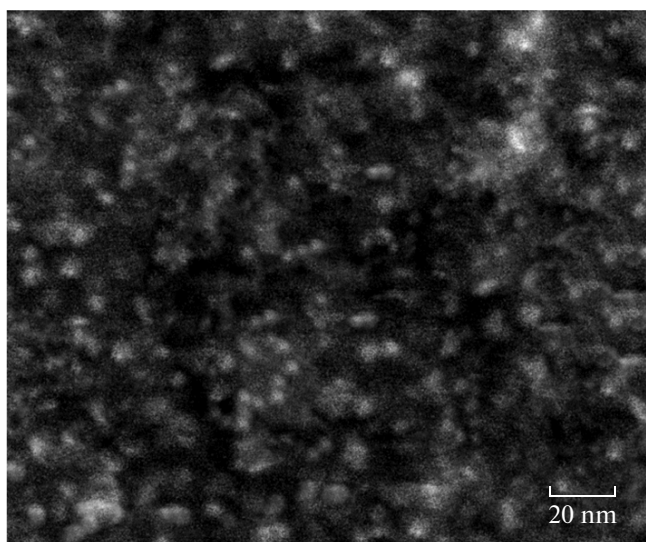[1] The article is published in the original.

Fig. 1. SEM image of silicon nanoparticles.

Fig. 2. Size distribution of silicon nanoparticles.

aperture $NA = 0.25$. The target was constantly moving using a motorized microscope stage during the synthesis of nanoparticles. The spot size on the sample was determined according to standard technique [32], which resulted in the dependence of the squared radius of the ablation crater on the energy logarithm of the laser pulse. Linear approximation of the experimental data allowed us to determine the parameter r_0 of the Gaussian beam, which amounted to 3.2 μm at the $1/e$ level, as well as the fluence of ablation threshold $F_a = 0.45 \pm 0.05$ J/cm^2.

The target was a plane-parallel plate of polished crystalline silicon (KEF, 111-orientation, n-type) 400 μm thick; target area was about 1 cm^2. The sample was placed into a Petri dish with a silica glass bottom 170 μm thick; it was filled with 2 mL of distilled water. The thickness of water layer above the sample was 2 mm. Petri dish with a target was installed on an *XY* software-controlled motorized microscope stage, which continuously moved along a predetermined path under unceasing action of laser pulses.

Synthesis of nanoparticles was carried out for an hour at energy density of the incident laser radiation on the surface of the silicon target, exceeding the ablation threshold F_a by 50 times. In order to reduce the particle size dispersion, obtained solution of nanoparticles was subjected to a multistage centrifugation with spin frequency of 3000 min^{-1}. Centrifugation process lasted for 20 min.

All the experiments were performed within one day after the synthesis of nanoparticles. Figure 1 shows scanning electron microscope (SEM) image of nanoparticles. The sample was prepared by drying the drops of the nanoparticles on the silicon substrate.

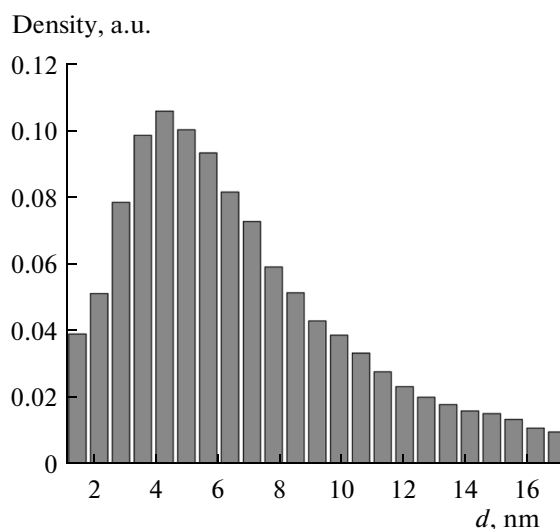Figure 2 shows the distribution of nanoparticles depending on the diameter. Mean diameter was between 4 and 6 nm.

ABSORPTION SPECTRA

Measurement of the absorption spectra of nanoparticles in the solution of distilled water in the visible wavelength range was carried out in a quartz cuvette 10 mm thick using AvaSpec-2048 spectrometer (Avantes). Halogen photometric lamp DH-2000 (Ocean Optics) was applied as a source of radiation. The measured absorption spectra of the synthesized nanoparticles of silicon before and after centrifugation are shown.

Figure 3 demonstrates that absorption spectrum after centrifugation becomes narrower as compared to the spectrum of the original nanoparticle solution, and the infrared absorption edge is shifted towards the shorter wavelengths. The maximum absorption also
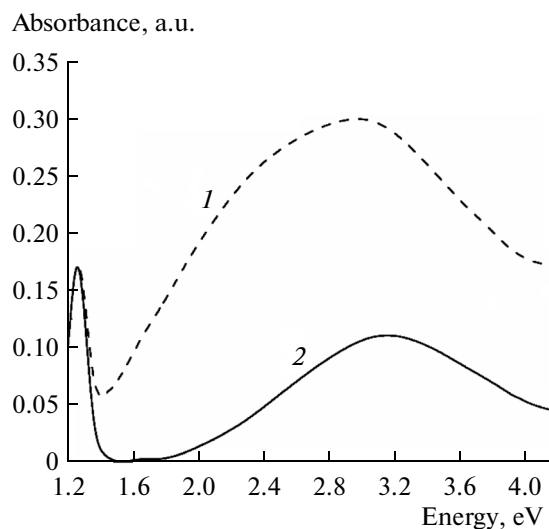

Fig. 3. Absorption spectra of silicon nanoparticles: *1*—mother solution, *2*—after centrifugation.
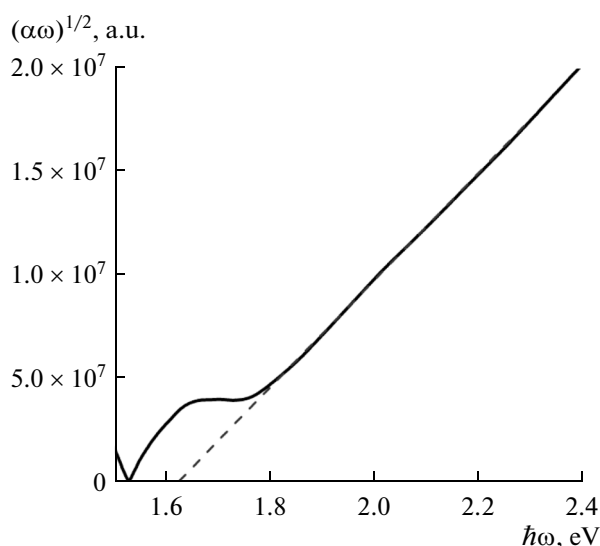
$(\alpha\omega)^{1/2}$, a.u.

Fig. 4. The edge of the optical absorption of nanoparticles in the low energy range.

shifts to shorter wavelengths, indicating that smaller particles prevail in the solution.

On the basis of measured absorption spectra it is possible to obtain information about the change in band structure as a function of the size of nanoparticles, compared with the band structure of the bulk silicon, as well as to define the width of the forbidden band. To do this, the natural absorption coefficient α should be determined according to the experimental data:

$$\alpha = 2.3A/l,$$

where A is the measured optical density of the solution of nanoparticles, and l is the cell thickness with solution. Then one should plot the values of $(\alpha(\hbar\omega)\omega)^{1/2}$ as a function of photon energy $\hbar\omega$. Obtained linear dependence, shown in Fig. 4, corresponds to semiconductors with indirect transitions. According to [18], the bandgap width for such type of semiconductors can be determined as follows:

$$\alpha(\hbar\omega) \propto \omega^{-1}(\hbar\omega - E_g)^2,$$

where E_g is the bandgap. Therefore, E_g of silicon nanoparticles can be obtained as the intersection point of the linear approximation of the experimental data with the x-axis (dashed line in Fig. 4).

The bandgap of nanoparticles determined by this method corresponds to 1.62 eV, which is approximately 1.5 times greater than that of bulk silicon ($E_0 = 1.12$ eV). Using the expression of size dependence of the bandgap of nanoparticles [33, 34]:

$$E_g = E_0 + 3.73/d^{1.39},$$

one can determine the appropriate diameter of the nanoparticles d (nm). For the bandgap $E_g = 1.6$ eV, diameter of nanoparticles is 4.2 nm, which correlates well with SEM imaging. The peculiarity of spectrum shape at energies lower than 1.6 eV is due to the presence of particles with larger size in the solution.

PHOTOLUMINESCENCE SPECTRA

Experimental setup for measuring the photoluminescence spectra of silicon nanoparticles at multiphoton absorption of infrared femtosecond laser pulses has been implemented on the basis of inverted microscope Olympus IX-71, similar to [35, 36]. The luminescence was excited by the radiation of infrared laser TEMA "Avesta Project" at wavelength of 1048 nm, with pulse duration of 110 fs, and pulse repetition rate of 71 MHz.

The laser beam was focused on the sample by microscope objective LOMO 20× with numerical aperture $NA = 0.4$ to a spot 1.6 µm in diameter. The maximum energy density at the sample reached 100 mJ/cm². Luminescence emission collected by microscope objective was directed onto the entrance slit of the spectrograph Acton SP2300i. A ruled diffraction grating of 50 lines/mm (Richardson gratings) with maximum reflection efficiency at $\lambda = 600$ nm was installed in the spectrograph. Using a low-dispersion grating made it possible to record spectra in the range between 400 and 650 nm at once. The limits of spectral measurement were defined by the detector sensitivity in the red region of spectrum and the grating efficiency in the blue one.

We used a highly sensitive CCD-camera with image intensifier (PI-MAX) as a detector. To protect the CCD camera from laser radiation at $\lambda = 1048$ nm we installed a bandpass filter between the spectrograph slit and the microscope objective lens. The exposure time of a single frame of CCD camera was 25 ms. Experimental setup was spectrally calibrated using a blackbody source at a temperature of 3000 K [37].

A sample for studying the photoluminescence spectra was prepared in a similar manner as for electron microscope studies, but we used a cover glass 170 µm thick as a substrate. Figure 5 shows the photoluminescence spectra of silicon nanoparticles excited by femtosecond infrared laser pulses at different energy densities. The spectra were obtained by summing over 20 frames of CCD camera and adjusted for instrument function of spectral transmission of the system.

Our experiments show that there is a very weak luminescence emission in the wavelength range of 450–650 nm for energy density less than 20 mJ/cm². When increasing the energy density of laser pulse up to 30 mJ/cm² a sharp increase in the yield of luminescence in the range of 500–650 nm is observed, with a pronounced maximum at 575 nm. For energy density in the range between 40 and 90 mJ/cm² almost no increase of the luminescence radiation as well as the saturation is observed. This effect is shown in Fig. 6, which demonstrates the integral yield of photoluminescence of silicon nanoparticles as a function of the
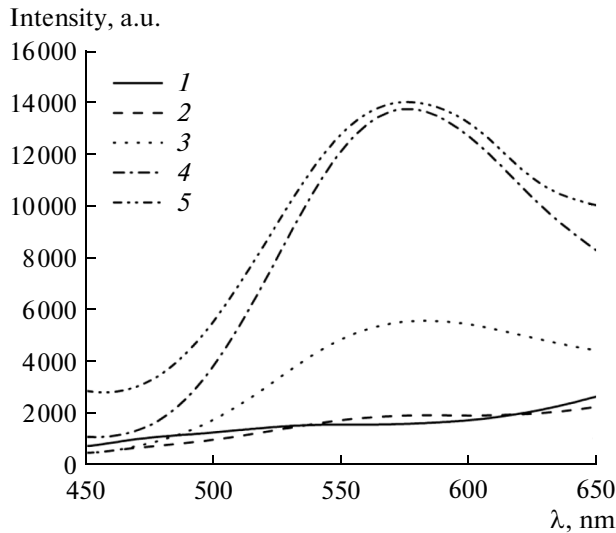
The photoluminescence spectra of silicon nanoparticles at multiphoton excitation by femtosecond laser pulses at wavelength of 1048 nm with a photon energy less than the bandgap were investigated. Photoluminescence spectra of silicon nanoparticles at laser intensities not exceeding the melting threshold ($I < 10^{12}$ W/cm^2) were measured for the first time under conditions of high electron density in the conduction band up to 10^{21} cm^{-3}.

The measured spectra are similar in form to the photoluminescence spectra obtained at single-photon excitation (when the energy of the exciting photon $\hbar\omega$ is larger than the bandgap E_g) and low intensities [29, 30]. Perhaps this is due to the fact that the spectra were measured without temporal resolution and a high electron density in the conduction band existed for a very short time (about a few picoseconds).

The radiation yield of luminescence at low laser intensities is quadratic, as might be expected when two-photon absorption occurs. However, in contrast to [29, 30], when reaching a certain threshold intensity, a clearly seen saturation is observed.

Fig. 5. Typical photoluminescence spectra of silicon nanoparticles excited by femtosecond laser pulses at $\lambda = 1048$ nm at different energy densities: *1*—7, *2*—14, *3*—29, *4*—43, *5*—87 mJ/cm^2.
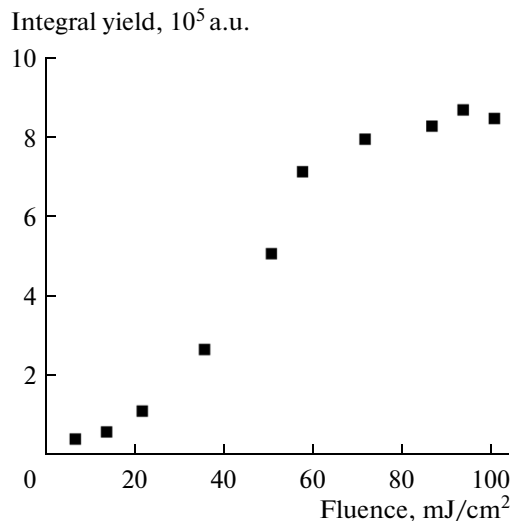
Fig. 6. The yield of photoluminescence of silicon nanoparticles integrated over the spectrum as a function of the femtosecond laser pulse fluence.

energy density of femtosecond laser pulses incident on the sample.

CONCLUSIONS

In this work we performed the synthesis of nanoparticles with an average size of 5 nm at the incident energy of the laser pulse of 2 mJ by femtosecond laser ablation of silicon in distilled water. The estimates of both the bandgap $E_g = 1.62$ eV and the particle size were derived from absorption spectra; obtained data correlate well with the results of electron microscopy.

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