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Photoluminescence of Ge/Si heterostructures with quantum dots created by epitaxy from ion-molecular beams

© Zh.V. Smagina[1], V.A. Zinovyev[1], A.V. Mudryi[2], O.M. Borodavchenko[2], A.O. Bazhenov[1,3], A.V. Dvurechenskii[1], V.D. Zhivulko[2]

[1] Rzhanov Institute of Semiconductor Physics, Siberian Branch, Russian Academy of Sciences,
630090 Novosibirsk, Russia
[2] „Scientific and Practical Materials Research Center, National Academy of Sciences of Belarus",
220072 Minsk, Belarus
[3] Novosibirsk State University,
630090 Novosibirsk, Russia

E-mail: smagina@isp.nsc.ru

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The comparative analysis of the structural and luminescent characteristics of nanostructures with quantum dots created during Ge epitaxy on Si(100) under conditions of irradiation with and without Ge^+ ions with an energy of ~ 2 keV has been carried out. It was found that irradiation with Ge^+ ions used in the heteroepitaxy process increases the photoluminescence intensity by 3 times compared with samples created without ion irradiation. In the irradiated samples, a shift of the maximum of the photoluminescence band of Ge Si quantum dots by ~ 25 meV to a lower-energy region was detected. Based on the analysis of the temperature dependences of photoluminescence spectra in the range of 5–300 K, the activation energies of the thermal quenching of the band associated with quantum dots are determined.

Keywords: GeSi quantum dots, epitaxy, ion irradiation, photoluminescence.

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1. Introduction

The main problem in creating highly efficient silicon-based radiation sources is related to its indirect-gap energy structure. Ge/Si heterosystem with quantum dots (QDs) is one of the promising systems capable of solving this problem [1–5]. However, conventional epitaxial structures with GeSi QD do not provide a noticeable gain in the rate of radiative recombination. One of the ways to increase the radiation efficiency of silicon-based structures is to introduce defects of various types created by ion irradiation [6–9]. Depending on the ion energy, radiation dose, ion type, and annealing temperature, defect complexes can form that emit light at various wavelengths in the infrared region of the spectrum. For example, at annealing temperatures below 600 °C, the photoluminescence (PL) spectra are dominated by lines of point defect complexes, including the so-called „W"-, „X"-, „G"- and „S"-centers [5,10–13]. Systems based on these centers in silicon have been used to create LEDs in cryogenic optoelectronic circuits. Implantation of Er^+ [14] and Si^+ [15] ions into silicon, followed by annealing of the structures, made it possible to obtain a variant of dislocation electroluminescence LEDs operating at room temperature. Attempts are also being made to use the luminescence of {113} defects generated by O^+ ions and emitting at a wavelength of 1.37 microns [9]. We obtained earlier in Ref. [16] the luminescence in the near-IR range on structures synthesized by ion implantation of germanium into silicon (ion energy — 80 keV, radiation dose — $10^{15}\,cm^{-2}$, thermal annealing — (600–800 °C)), which was observed up to room temperature. It has been shown that the emission intensity of structures annealed under optimal conditions is many times higher than the emission intensity of epitaxial structures with GeSi QD obtained without ion irradiation. Structural studies have made it possible to attribute the signal to Ge nanoclusters formed as a result of annealing of irradiated structures and containing optically active defect centers. Studies of the power and temperature dependence of PL have shown that the peak of PL at ~ 0.79 eV is characterized by a high (~ 330 meV) activation energy of PL temperature quenching and an almost linear dependence of PL intensity on the power of laser excitation, which is typical for direct optical transitions. Similar structures with GeSi QD containing radiative recombination centers ([110]-split internodes) were obtained at the University of Linz [17,18] when ion irradiation Ge^+ was applied during QD growth. Due to the high efficiency of radiative recombination and direct optical transitions, the radiation intensity increased by two orders of magnitude compared to structures obtained without ion irradiation, and the effect of laser generation was observed [18]. The authors attribute the results obtained to the introduction of [110]-split internodes into the layers of the QD. At the same time, the effects associated with changes in QD parameters, such as size, density, and composition, which may clarify the role of quantum limitations of charge carriers in zero-dimensional structures, are not discussed in any way. In this regard, it is important to conduct additional studies to establish the effect of ion irradiation on the formation of QDs and their parameters, and to clarify the nature of PL amplification in structures with ion irradiation.

In this work, Ge/Si heterostructures with QD were studied using a modified method of molecular beam epitaxy (MBE) with simultaneous irradiation with Ge^+ ions with energy of ~ 2 keV. The method makes it possible to change the energy of Ge^+ ions and the ion exposure time in a controllable manner during growth by applying a negative electric potential to a silicon substrate. This paper presents new results on the comparative analysis of the temperature dependence of the photoluminescence of Ge/Si nanostructures with QD grown under ion irradiation and without it.

2. Experimental procedure

Ge/Si structures (with and without ion irradiation) were grown in the Riber SIVA-21 MBE system. The Si(100) substrates were loaded into the chamber of the system after a standard chemical cleaning procedure [19]. The procedure for cleaning the substrate surface was completed by removing the protective layer SiO_2 at a temperature of 750 °C in a weak silicon stream. Next, a buffer layer of Si (~ 100 nm) was deposited on the substrate with a gradual increase in the growth temperature from 500 to 600 °C. Then, the structure itself was grown on the surface of the buffer layer, which was either an open layer of germanium (for studying surface morphology), or a stack of 10 layers of GeSi QD. The QD stack was formed by sequential deposition of layers of germanium (each layer with a thickness of ~ 0.8 nm) alternating with layers of silicon. The germanium growth temperature was 500 °C. Silicon interlayers with a thickness of ~ 15 nm were formed at a temperature that was gradually raised from 500 to 600 °C. At the last stage of growth, the structure was covered with a silicon layer 40 nm thick, also with an increase in temperature from 500 to 600 °C. An increase in the growth temperature of the Si separating layers to 600 °C was undertaken to reduce the number of defects that can become centers of nonradiative recombination. Ge layers were deposited in two ways: conventional MBE (sample 1) and MBE with simultaneous irradiation with Ge^+ ions with energy of ~ 2 keV (sample 2). Germanium ion irradiation was carried out by applying a negative electric potential (-2 kV) to the substrate. The applied voltage, in turn, accelerated Ge^+ ions flying out of the electron beam evaporator towards the substrate.

The surface morphology of the grown single-layer structures with QD was studied using an atomic force microscope (AFM) SolverPRO from NT-MDT. PL of Ge/Si nanostructures was studied using a spectroscopic system based on a diffraction monochromator MDR-23U with an inverse linear dispersion of 26 Å/mm. A solid-state laser operating at a wavelength of 405 nm was used as the source of exciting radiation. Optical signals were detected by a temperature-cooled ~ 80 K Ge $p-i-n$ type EO-817H detector. Temperature measurements in the range of $5-300$ K were carried out using a special optical cryostat model ARS CS202E-DMX.

3. Results and discussion

Figure 1 shows typical AFM images of a surface with three-dimensional islands obtained after deposition of 0.8 nm of Ge onto the surface of Si(100) for two types

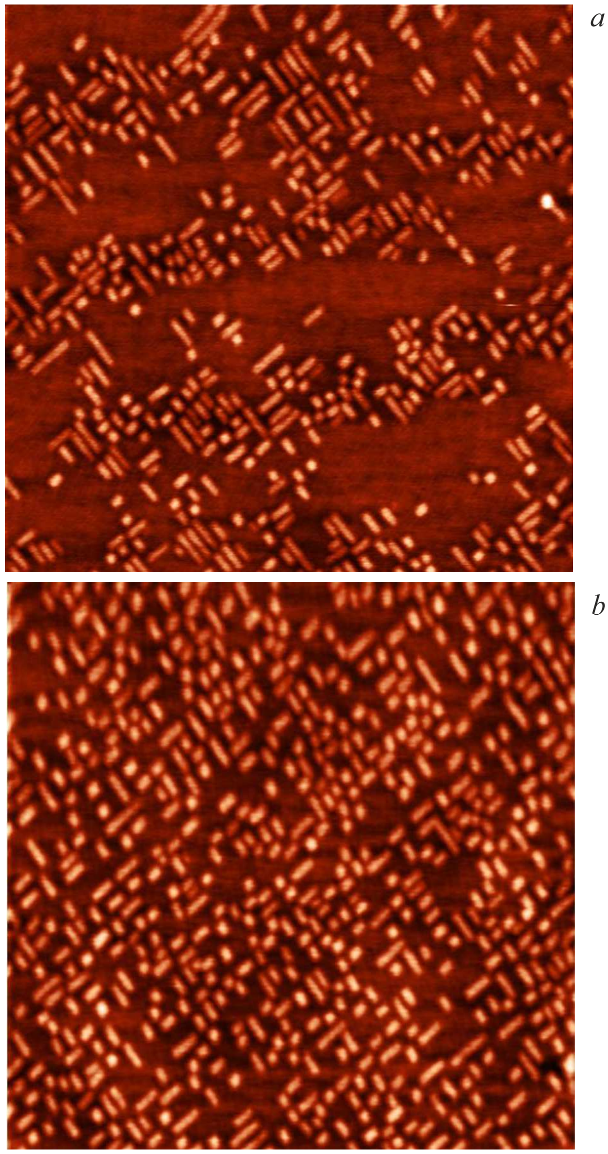

Figure 1. AFM images (1×1 microns) of a surface with three-dimensional islands obtained by deposition of 0.8 nm Ge onto a Si(100) substrate at a temperature of 550 °C, for two types of experiments: *a* — MBE Ge on Si; *b* — MBE with irradiation by Ge^+ ions. Ion energy is ~ 2 keV.

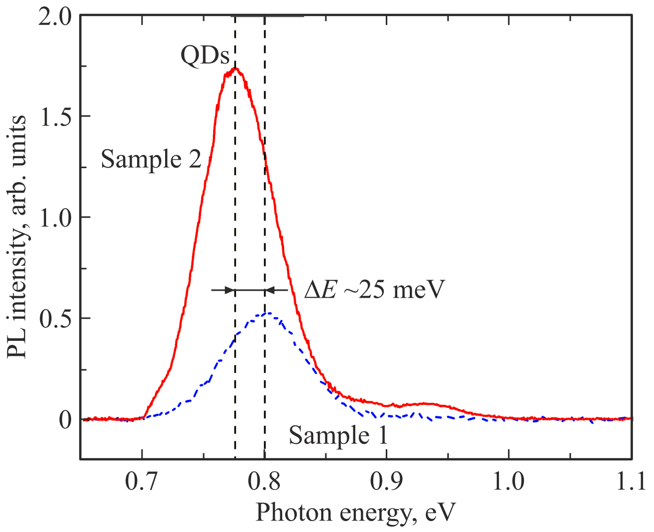

Figure 2. PL spectra from 10-layer structures with GeSi QD grown at 500°C: sample 1 — molecular beam epitaxy, sample 2 — MBE with simultaneous irradiation by Ge^+ ions (energy is ~ 2 keV). The spectra were measured at 78 K. Laser excitation power density is $\sim 8.5\,W/cm^2$. A laser with a wavelength of 405 nm was used.

of experiment: *a* — conventional MBE and *b* — epitaxy with ion irradiation. In experiments without ion irradiation, the density of nanoislands was $\sim 4 \cdot 10^{10}\,cm^{-2}$, while with ion irradiation, the density of nanoislands increased by ~ 1.5 times ($\sim 6 \cdot 10^{10}\,cm^{-2}$). The average transverse size of the base of the three-dimensional islands in the case of epitaxy without ion irradiation is 1.2 times smaller (21.5 ± 2 nm) than the average size of the nanoislands (25 ± 5 nm) obtained by ion irradiation. The average heights of the islands were: 2.26 ± 0.3 nm and 2.4 ± 0.4 nm for conventional MBE and MBE with ion irradiation, respectively. The three-dimensional islands had the shape of *hut*-clusters in both types of growth experiments [20,21], however, in the case of epitaxy without ion irradiation, the nanostructures had a base of a more elongated (rectangular) shape.

The effect of ion irradiation on the properties of nanostructures (quantum dots) can also be traced in their luminescent properties. As can be seen from the PL spectra (Figure 2) obtained at a temperature of 78 K, wide bands associated with GeSi QD radiation are present in the energy range from 0.7 to 0.9 eV. The spectral position of the PL band in structures without ion irradiation is ~ 0.8 eV (Figure 2, sample 1). For samples grown under ion irradiation conditions (Figure 2, sample 2), the PL band from the QD shifts to a lower-energy region of ~ 0.775 eV. The shift of the PL band from quantum dots by $\Delta E \approx 25$ meV to a lower-energy region in the case of ion irradiation may be associated with both an increase in the size of QDs and the formation of defects yielding deeper energy levels than the levels of charge carriers in QDs created without ion irradiation. The intensity of the PL band from QD in irradiated structures (Figure 2, sample 2) turned out to be 3 times higher than the intensity of the PL band from QD in non-irradiated structures. It is obvious that the implantation of Ge^+ ions accelerated by voltage of -2,kV, contributes to an increase in QD radiation intensity.

An additional band is present in the PL spectra in the energy range of ~ 0.932 eV. It disappears at temperatures of > 125 K. This band may be associated with defects of the type {113} generated by ion irradiation [22–24]. The temperature dependences of PL spectra for Ge/Si heterostructures with QDs created with and without ion irradiation showed that with PL from GeSi QDs is quenched with the increase of the measurement temperature for both types of structures (Figure 3).

The temperature dependences of the integral intensity of PL in the range from 0.7 to 0.9 eV was analyzed using the expression [25]:

$$I(T) = I_0/[1 + A\exp(-E_a/k_B T)], \qquad (1)$$

where I_0 is the maximum PL intensity, I is the band intensity at experimental temperature, A is the fitting parameter, k_B is the Boltzmann constantE_a is the activation energy.

As a result, the characteristic activation energies for radiative recombination processes were determined to be $E_a \sim 47$ meV and $\sim E_a^* \sim 72.7$ meV for samples 1 and 2, respectively. The difference in activation energies for the two types of structures is 25.7 meV. It is interesting to note that the obtained value practically coincides with the shift of the maximum of the GeSi QD radiation band found for structures created by ion irradiation (Figure 2). This indicates that the change in the characteristic energies of the radiative transitions ΔE in the studied structures is most

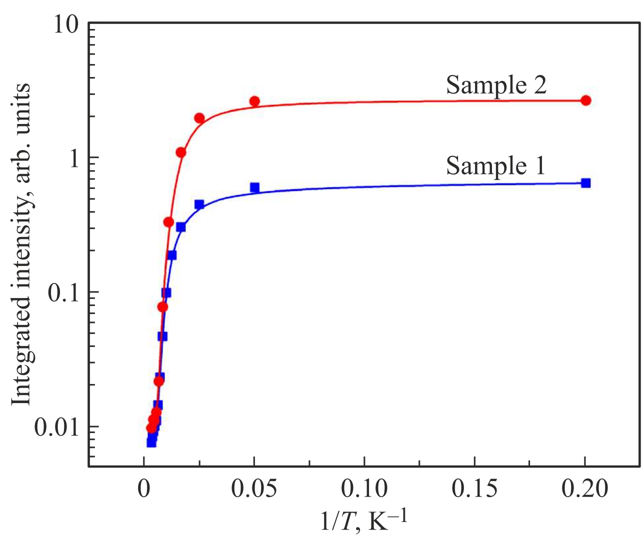

Figure 3. Temperature dependence of the variation of intensity of PL bands on quantum dots created with simultaneous irradiation with Ge^+ ions with energy of ~ 2 keV (sample 2) and without it (sample 1).

likely attributable to a change in the depth of the levels of electronic states in the QD layers.

The conducted studies have shown a higher temperature stability of electronic optical transitions up to room temperature (~ 300 K) and, accordingly, a higher activation energy value for nanostructures with GeSi QD created under conditions of irradiation by Ge^+ ions (sample 2). This result is consistent with the data obtained in the papers of the Austrian researchers in Refs. [17,18] for heterostructures with GeSi QD, which were formed by the MBE method with simultaneous irradiation by Ge^+ ions. The authors of these papers hypothesize that deep centers are created in the layers with QD in case of irradiation by Ge^+ ions, through which effective radiative recombination takes place. It should be noted that in these studies, the activation energy of the temperature quenching of PL was ~ 350 meV for structures with ion irradiation, which, apparently, is a manifestation of the dependence of the activation energy on the intensity of photoexcitation [26]. Whereas for structures created without ion irradiation, the activation energy is equal to ~ 80 meV. Several studies conducted by Austrian researchers use the micro-PL method and a higher power density of photoexcitation than in our work. At the same time, they report that the activation energy under these conditions is determined by the thermal emission of holes into the valence band of silicon [17]. At low levels of laser photoexcitation, the activation energy can be determined by the thermal emission of electrons into the conduction band of silicon. Accordingly, a deepening of the levels of electronic states in the QD layers most likely really takes place in our experiments.

4. Conclusion

As a result of the conducted studies, it was shown that irradiation by Ge^+ ions with energy of ~ 2 keV during molecular beam epitaxy leads to an increase in QD density. It has been found that ion irradiation used in the process of Ge-Si heteroepitaxy contributes to a 3-fold increase in PL intensity compared with samples grown without it. A shift of the PL maximum from GeSi QD by 25 meV to the long-wavelength radiation region was found in case of samples created under ion irradiation growth conditions. The shift can be associated with both an increase in the size of the QD and the formation of defects that produce deeper energy levels than the levels of charge carriers on the QD created without ion irradiation. The activation energies of the temperature quenching of the PL band associated with the radiative recombination of charge carriers in QDs were determined based on the data obtained on the temperature dependence of the change in PL intensity. The activation energies were ~ 47 and ~ 72.7 meV for samples created by epitaxy without irradiation and epitaxy with irradiation by Ge^+ ions, respectively. The results obtained indicate a higher temperature stability of the photoluminescence of GeSi QDs created under ion irradiation conditions.

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Conflict of interest

The authors declare no conflict of interest.

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