

Quasi-direct optical transitions in Ge nanocrystals embedded in GeO₂ matrix

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GeO₂ films with germanium nanocrystals (NCs) were deposited from supersaturated GeO vapor with subsequent dissociation on Ge:GeO₂. The films were studied using photoluminescence (PL), Raman scattering, IR-spectroscopy techniques. Ge NCs in initial film have sizes about 6–8 nm and have no visible PL signal. The broad green-red PL peak was detected in Ge:GeO₂ films after thermal annealings. According to effective mass approach, maximum of PL signal from such relatively big Ge NCs should be in IR region. The experimentally observed PL signal is presumably originated due to quasi-direct $L_1-L'_3$ optical transitions “folded” in germanium NCs.

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The nanometer-sized semiconductor nanocrystals (NCs), embedded in wide-gap insulating matrices, have shown significant promises for a wide range of nanoelectronics and optoelectronics applications. Quantum effects in such hetero-systems become brightly apparent at room temperature, and because in some experiments a single NC reveal delta-function-like energy spectra [1] it can be called quantum dots. So, these heterostructures are interesting for both fundamental and applied points of view.

Unlike quite long and well studied Si NCs in porous Si and SiO₂ matrix [1–6], very little work has been performed on relative Ge:GeO₂ heterostructures. A comparison of group IV semiconductors (Si and Ge) reveals that, from the technological point of view, germanium has several advantages over silicon. First of all, the melting point of Ge is sufficiently low as compared to Si (940 versus 1420 °C), causing lower crystallization temperature of Ge. The germanium monoxide, GeO, is volatile and readily sublimates at sufficiently low temperature (~500 °C), forming the bases for the development of different technologies utilizing the mass-transfer reactions. Besides, the energy gap values of Ge and Si NCs become equal when their sizes reach 2.3 nm. Further decrease of sizes down to 1.5 nm causes an abrupt increase in Ge gap up to 3 eV, which exceeds by 0.7 eV the gap of Si NCs with the same size. This is the reason for an intensive and useful blue shift of Ge-based light-emitting nanostructures. Ge has a larger exci-

ton Bohr radius (4.9 nm for Si and 24.3 nm for Ge). Thus, the quantum-confinement-related positive effects in Ge manifest themselves at larger sizes, which can be reached with less difficulty. The valence and conduction bands discontinuities in Ge-GeO₂ hetero-system is favorable for charge carrier injection. This important feature can increase the efficiency of the injection-type devices produced on the basis of Ge-GeO₂ system. Germanium is a high-refractive-index semiconductor ($n = 4.12$ at 2.0 μm), valuable for filling the interstitial voids in opals and producing photonic crystals with a complete photonic band gap. Germanium oxides and nitrides have higher dielectric constant than silicon based dielectrics, for example, measured dielectric constant for amorphous GeO₂ is 5.1–5.3 [7], germanium also has higher dielectric constant than silicon, so the exciton binding energy in Ge NCs is smaller than in Si NCs and limit for “blue-shift” for excitons in Ge NCs is higher and energy of optical transitions can reach UV diapason. So, the relatively old [8] obtained, but still not intensively studied Ge:GeO₂ heterostructures attract more attention to researchers recent years [9–15].

The GeO₂ films with Ge NCs were deposited on silicon substrates from supersaturated GeO vapor with subsequent dissociation of meta-stable (in solid state) Ge monoxide on hetero-system Ge:GeO₂. The scheme of reactor is shown in Fig.1. The reactor contains evaporation zone A and deposition zone B. The growth rate depends on gas flow, GeO vapor partial pressure and temperature of substrates. The bearing gas is Ar with impurities of O₂ and H₂O. Oxygen and water reacts with

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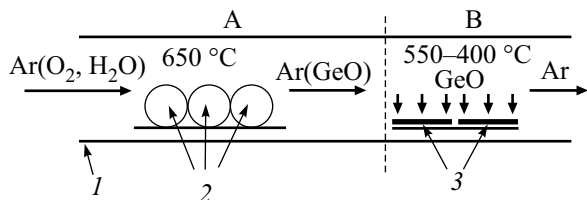
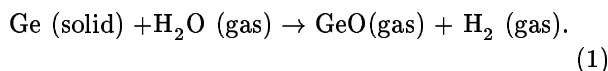
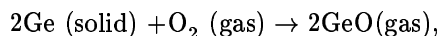
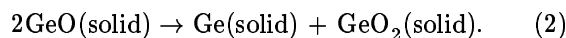


Fig.1. The scheme of growth reactor. 1 – quartz tube; 2 – Ge plates; 3 – substrates for Ge:GeO₂ films

Ge plates in evaporation zone with formation of GeO gas according to chemical reactions:



The pressure of GeO gas in deposition zone is higher than saturation pressure, and GeO precipitate on substrate in the deposition zone. The solid GeO films is meta-stable and decompose in Ge and GeO₂ at relatively low temperatures (about 350 °C and higher) according to reverse chemical reaction:



Depending on growth condition one can obtain GeO₂ films with amorphous Ge nanoclusters or Ge NCs.

The obtained films were studied with the use of photoluminescence (PL) spectroscopy, Raman scattering spectroscopy, IR-spectroscopy techniques. Experimental Raman spectra were registered in quasi back-scattering geometry, the 514.5 nm Ar⁺ laser lines was used. The PL spectra were registered at room and low temperatures using cw HeCd (325 nm), Ar⁺ (488 nm and 514.5 nm lines) He-Ne (633 nm), pulse N₂ (337 nm) lasers and mercury lamp for pumping. The normal incidence IR absorption measurements were carried out with a resolution of 4 cm⁻¹. Some samples were annealed in high-vacuum quartz tube with a tubular oven. The heating rate was 10 °C min⁻¹. When the annealing temperature was reached, the oven was removed and the films cooled naturally. To avoid the evaporation of Ge:GeO₂ films its was covered by cap layer from 50 nm thick SiO₂ deposited at temperature 100 °C and pressure equal to 10⁻⁸ Torr using electron beam gun evaporation of silica.

Figure 2 presents the IR absorption spectrum of initial Ge:GeO₂ film in range from 700 to 1200 cm⁻¹. The observed peak is assigned to Ge-O-Ge stretching vibration mode. It is known, that in GeO_x films this peaks approximately linearly shift from about 820–830 cm⁻¹ for $x = 1$ to about 870–880 cm⁻¹ for $x = 2$ [11, 16]. The experimental peak position (Fig.2) is about 870–880 cm-

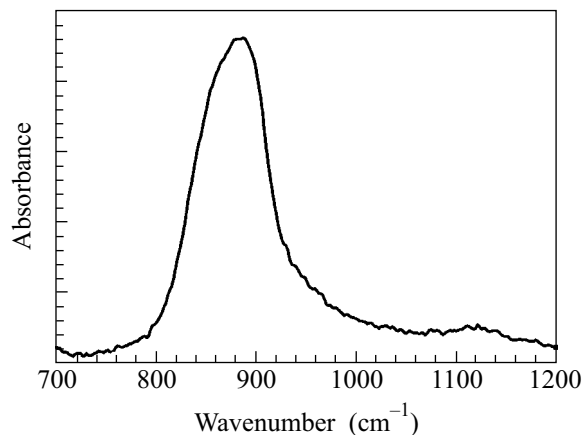


Fig.2. IR absorption spectrum of the initial Ge:GeO₂ film

1, so, one can assume, that even initial film (deposited from supersaturated GeO vapor at substrate temperature about 500–550 °C) is totally dissociated on Ge and GeO₂.

The Raman spectra of the initial and annealed films are shown in Fig.3. One can see the Raman peak due

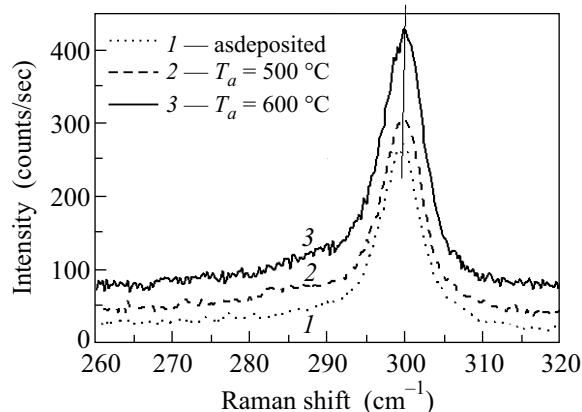


Fig.3. Raman spectra of as deposited Ge:GeO₂ film (covered by 50 nm thick SiO₂ cap layer) and films annealed at different temperatures (T_a)

to scattering on optical phonons confined in Ge NCs in Raman spectra. It is known, that Raman signal from amorphous Ge is a broad peak with maximum at 270–280 cm⁻¹. The Raman signal from crystalline Ge is narrower peak with position depending on NCs sizes. The confinement effect shifts the position of Raman peak to low frequencies from bulk-Ge Raman peak position (about 300.3–300.5 cm⁻¹). So, from Fig.3 one can see that in initial Ge:GeO₂ film practically all Ge clusters were crystalline. The NCs sizes can be estimated from position of Raman peaks [10, 17]. We use the model of efficient density of folded vibration states in NCs of

spherical shapes [18]. According to dependence of Raman peak position from NCs diameter [17], the diameter of Ge NCs is about 6–8 nm. It should be noted, that the Raman peak width is mainly defined by dispersion of NCs sizes, and the size dispersion in our case is relatively small, but we could not quantitatively define this dispersion. One can see very small shift of Raman peaks with annealing (thin line is drawn for convenient). It can be caused by some ordering of Ge-GeO₂ interface and also by annealing of defects in Ge NCs.

According to theoretical calculations of quantum confinement effects in Ge NCs with the sizes 6–8 nm, the maximum of PL signal should be in range 1.0–0.8 eV [19]. Our simple effective-mass approach model [10] also gives similar values. So, to study the PL signal we used IR-region PL setup with monochromator equipped with a 600 grooves/mm grating and InAs cooled photodiode as a detector. HeNe (633 nm) and HeCd (325 nm) cw lasers with power about 30 mW were used for excitation. For study PL in visible diapason we used other PL setups – one equipped by mercury lamp as an excitation source and silicon based CCD line as a detector and second with Ar⁺- and N₂-lasers for excitation and multi-alkaline photomultiplier tube as a detector.

The PL spectra in visible and IR diapason of the initial and annealed films are shown in Fig.4. In region

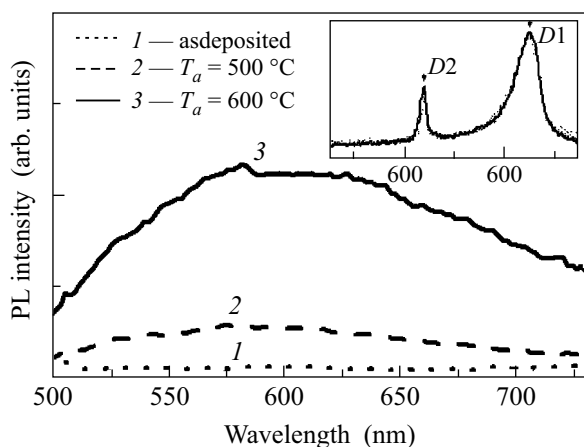


Fig.4. Room temperature PL spectra in visible diapason of as deposited Ge:GeO₂ film (covered by 50 nm thick SiO₂ cap layer) and films annealed at different temperatures (T_a). Inset – PL spectrum of the as deposited film in IR diapason measured at 4 K

near 1.1 eV at temperature 4 K we saw only peaks due to recombination in free and bound excitons in Si substrate, because our Ge:GeO₂ film with thickness about 50 nm was semi-transparent even in UV diapason. In diapason 0.8–1.0 eV we have observed two peaks (see insert in Fig.4). But intensity of this peaks increase

with decreasing of thickness of our initial films and also was more intensive in the case of HeNe laser excitation comparing with HeCd laser excitation. So, one can assume, that these peaks have origination from silicon substrate. And really, we ascertained that our silicon substrates contain dislocations, which can be irradiative recombination centers, and position of our peaks good coincide with well-known *D1* (1523 nm) and *D2* (1420 nm) peaks [20] (see inset in Fig.4, PL spectrum of initial Ge:GeO₂ film was excited by HeCd-laser). To grow our film on clear “fresh” surface we used silicon substrates with thick thermal silicon dioxide (used as a cap layer), which we had removed by HF acid immediately before the film deposition. Obviously, the thermal oxidation of silicon at very high temperatures had created the dislocations in our substrates. The PL signal from dislocation at low temperatures is relatively high, so we could not see PL signal from Ge NCs even if we had any. The PL peaks *D1* and *D2* have some different temperature dependence but both were diminished to zero at temperatures higher than 40 K. At temperatures 40 K and higher we had not observed PL signal (which can be associated with Ge NCs) in IR diapason.

According to theoretical calculations, radiative lifetime in Ge NCs of spherical shape with diameter 6–8 nm should be quite large – about 10⁻² second [19]. So, if we have nonradiative recombination centers with much shorter lifetime, the radiative recombination would be negligible. In Ge NCs such centers can be defects inside NCs, interface defects and molecules of water. It is known, that GeO₂ films and low temperature porous SiO₂ films can absorb H₂O molecules and evaporate it during thermal annealings [21]. Using the thermal annealing we have tried to anneal defects, to evaporate water and to order the Ge NCs – GeO₂ matrix interface. To avoid the evaporation of Ge:GeO₂ films its was covered by cap layer from 50 nm thick SiO₂. Using PL setup equipped with mercury lamp we have observed some weak PL signal in green region, but parasitic lines of mercury lamp do not allow us to study it accurately. So, we used Ar⁺ laser excitation and results are presented in Fig.4. After annealings the green-red PL signal appears (the blue-green 488 nm Ar⁺-laser line was used for excitation). The power of this cw Ar-laser line was 200 mW. The laser spot in the sample was about 200 micrometers, so the density of excitation was about 5 · 10¹² W/m². One can see in spectra small peak from 514.5 nm Ar⁺-laser line (marked by triangle). When we used the last line for excitation, similar PL signal was observed. It should be noted that the intensity of signal was 3–5 times lower comparing with PL signal from reference sample – 75 nm thick SiO₂ films with Si NCs with

sizes about 5 nm (similar samples were studied in work [5] – PL signal in 750-780 nm was observed). When we used for excitation UV pulse laser (N₂, wavelength 337 nm) the signals from Ge:GeO₂ films were very low, several orders less than signal from the reference sample. It is also important to mention, that we have reference Si/SiO₂ sample (the SiO₂ film was deposited on Si substrate without Ge:GeO₂ film in the same process – “side-by-side”) and we have no PL signal for this sample.

If the observed PL signal (2–2.4 eV) was from quasi-direct excitons in Ge NCs, the sizes of NCs should be about 2 nm [19]. As it was mentioned above, according to our Raman data and also according to direct electron microscopy data for samples grown in similar conditions [17], average diameter of Ge NCs in our case is 6–8 nm. So, one can assume, that we have PL assisted with some defects in GeO₂ matrix or Ge-GeO₂ interface, or some other excitations in Ge NCs. However, GeO₂ film obtained by Ge oxidation (without Ge NCs) has no PL in this region. Paying attention to band structure of bulk Ge (for example Fig.1 in work [19]), one can see that energy of direct transition between *L*-valleys for electrons and holes is about 2.1 eV. From this energy of photons the abrupt growth of light absorbance takes place. In the case excitation of bulk Ge, the holes relax very fast to Γ -valley emitting acoustical and optical phonons through continuous energy band states. In NCs electron (and phonon) states is discrete, not continuous, and such relaxation can be not very fast, and part of holes can radiative recombine with electrons through direct transitions in *L*-valleys. The similar effects of phonon “bottleneck” were theoretically studied in work [22]. Also, because the average quasi-pulse of electron and holes in NCs is zero (localized, standing waves), the 4 *L*-valleys is “folded” and electrons and holes from all that valleys can recombine, so probability of such processes can be compared with probabilities of nonradiative transitions. It can be presumable explanation of observed PL signal in our case. Some shift (compared to bulk Ge L_1-L_3' transition energy) can be due to quantum-size effects. The broad PL peak can be due to Ge NCs size dispersion, and also due to complex energy structure of discrete electron states in relatively big Ge NCs. In this approach, the Ge NCs can be the traps both for electrons and for holes and can be used in Ge based flash memory devices [23]. For accurateness' sake it should be mentioned, that blue-green PL (with maximum about 2.4 eV) in relatively similar hetero-system (Ge NCs in SiO₂ matrix) is usually associated with defect-related PL ([19] and references in it). In our case we have maximum PL about 2–2.1 eV, but, it should be noted, that at

temperature 600 °C and higher the intermixing of SiO₂ and GeO₂ films can begin with forming of Ge_{*x*}Si_(1-*x*)O₂ thin layer and origination of PL signal from this layer can be also possible. In further studies, the proposed mechanism of PL should be tested using the GeO₂ films with bigger and smaller Ge NCs.

So, the optical properties of GeO₂ films with Ge NCs with average sizes 6–8 nm (according to Raman data) were studied, the green-red PL was observed for samples annealed in high vacuum. The annealings can improve structure of the Ge NCs and its interface. The mechanism of direct radiative transitions for confined in the NCs electrons and holes (its wave functions are originated from *L* valleys of bulk Ge) is proposed for explanation of experimental effect. The GeO₂ films with Ge NCs can be perspective for using in opto-electronics and for quasi-non-volatile MOS memory.

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1. I. Sychugov, R. Juhasz, J. Valenta, and J. Linnros, Phys. Rev. Lett. **94**, 087405 (2005).
2. L. T. Canham, Appl. Phys. Lett. **57**, 1046 (1990).
3. T. Shimizu-Iwayama, S. Nakao, and K. Saitoh, Appl. Phys. Lett. **65**, 1814 (1994).
4. H. Rinnert, M. Vergnat, and A. Burneau, J. Appl. Phys. **89**, 237 (2001).
5. G. A. Kachurin, S. G. Yanovskaya, M.-O. Ruault et al., Semiconductors. **34**, 965 (2000).
6. O. Jambois, H. Rinnert, X. Devaux, and M. Vergnat, J. Appl. Phys. **100**, 123504 (2006).
7. E. B. Gorokhov, I. G. Kosulina, S. V. Pokrovskaya et al., Phys. Stat. Sol. (a) **101**, 451 (1987).
8. N. N. Ovsyuk and E. B. Gorokhov, JETP Letters **47**, 298 (1988).
9. V. A. Volodin, E. B. Gorokhov, D. V. Marin et al., JETP Letters **77**, 485 (2003).
10. E. B. Gorokhov, V. A. Volodin, D. V. Marin et al., Semiconductors **39**, 1210 (2005).
11. M. Ardyanian, H. Rinnert, X. Devaux, and M. Vergnat, Appl. Phys. Lett. **89**, 011902 (2006).
12. M. Ardyanian, H. Rinnert, and M. Vergnat, J. Appl. Phys. **100**, 113106 (2006).
13. M. Zacharias, P. M. Fauchet, J. Non-Cryst. Solids. **227–230**, 1058 (1998).
14. D. Riabinina, C. Durand, M. Chaker et al., Nanotechnology. **17**, 2152 (2006).
15. E. B. Gorokhov, V. A. Volodin, D. V. Marin et al., Proc. of SPIE **6260**, 626010 (2006).

16. G. Lucovsky, S. S. Chao, J. Yang et al., Phys. Rev. B **31**, 2190 (1985).
17. D. V. Marin, E. B. Gorokhov, A. G. Cherkov et al., *15th International Symposium "Nanostructures: Physics and Technology"*, Novosibirsk, Russia, 25–29 June, 2007, p. 126.
18. I. H. Campbell and P. M. Fauchet, Solid State Communications **58**, 739 (1986).
19. Y. M. Niquet, G. Allan, C. Delerue, and M. Lannoo, Appl. Phys. Lett. **77**, 1182 (2000).
20. N. A. Drozdov, A. A. Patrin, and V. D. Tkachev, JETP Letters. **23**, 597 (1976).
21. E. B. Gorokhov, A. G. Noskov, G. A. Sokolova et al., Poverxnost' (in Russian - Surface) **12**, 25 (1982).
22. H. Benisty, C. M. Sotomayor-Torres, and C. Weisbuch, Phys. Rev. B **44**, 10945 (1991).
23. I. B. Akca, A. Dana, A. Aydinli, and R. Turan, Appl. Phys. Lett. **92**, 052103 (2008).