THE STRUCTURE AND PHOTOLUMINESCENCE OF SiO_2 FILMS WITH Ge NANOCRYSTALS OBTAINED BY PULSED LASER DEPOSITION

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UDC 621.15

We investigate the interrelation between the parameters of the laser pulse irradiation of a $Si_{1-x}Ge_x$ target under the deposition of quantum dots (QDs), their structure, and the time-resolved photoluminescence (PL) spectrum. We have obtained Ge QDs in the Ge nanocrystals/SiO_2 matrix system, whose PL spectra lie in the energy range 1.4–3.2 eV and the PL relaxation times are from 100 ns to 10 μs.

1. Introduction

Report [1] on the observation of PL in a visible region at room temperature in the layers of porous silicon (por-Si), which is related to the quantum-confinement effect, has stimulated the investigation of the visible PL in $Si_{1-x}Ge_xO_z$ films containing Si and Ge nanocrystals which don't have the drawbacks of por-Si such as the structure fragility, instability of properties, and "wet" chemical methods of their formation. An actuality of the studies of low-dimensional Si and Ge nanocrystals in a dielectric matrix of their oxides (the Si and Ge QDs) is conditioned by the possibilities of a manifestation of zero-dimensional quantum phenomena and their utilization for the creation of light emitters, structures with energy-independent memory, and other novel optoelectronic devices on the base of a silicon technology.

The Ge QDs has attracted less attention in comparison with the Si ones, and only several works have been devoted to the fabrication of Ge QDs with controlled dimensions and PL spectra (see review [2]). As compared to the monocrystalline Si (c-Si), however, the monocrystalline Ge (c-Ge) is characterized by a smaller band gap width (0.67 eV), a greater dielectric permittivity (16.5), smaller values of the effective masses of electrons and holes, and greater exciton radii (24—30 nm). Thus, the quantum-dimensional effects are expected to be stronger expressed in Ge nanocrystals. A great experience in the formation of Ge nanocrystals in $Si_xGe_yO_z$ films and in the study of their structure and PL properties has been accumulated up to date. Such fabrication methods as the magnetron co-sputtering of Ge and SiO_2, the reduction from $Si_{1-x}Ge_xO_2$ oxides, the implantation of Ge^+ ions into SiO_2 layers, etc. have been mostly used.

Only a few works [3,4] dealt with Ge QDs obtained by the method of pulsed laser deposition which has advantages on the composite formation due to the congruence of the process, the versatility of a control over deposition parameters, vacuum purity, and others. For the films obtained in work [3], the PL spectrum was in a high-energy region (with energies higher than 2.5 eV). It was reported in work [4] that, as the pulse deposition duration was changed from 1 s to 3 min, the size of Ge nanocrystals was increased from 5 to 20 nm, the PL spectrum was in a low-energy region, and a position of its maximum was shifted from 0.8 to 0.74 eV. Whereas work [4] dealt with the Ge nanocrystals embedded in a SiO_2 matrix, work [3] studied Ge nanocrystals embedded in a GeO_2 film.

An advantage of semiconducting nanocrystals embedded in a SiO_2 matrix is the stronger manifestation of the dielectric amplification effect, as compared to the case of nanocrystals in a GeO_2 matrix. The wave functions of the charge carriers of nanocrystals penetrate deeper into the GeO_2 matrix, than into a SiO_2 one. The PL efficiency decreases due to the fact that the oscillation intensity depends on a degree of the quantum confinement of carriers in a nanocrystal, as well as due to an increase in the probability of nonradiation recombination on the nanocrystal/matrix boundary and within the barrier layer itself.

The aim of the present paper is to fabricate the PL films of SiO_2 with Ge nanocrystals by the pulsed laser deposition method and to study the influence of deposition conditions on the structure and time-resolved PL spectra.

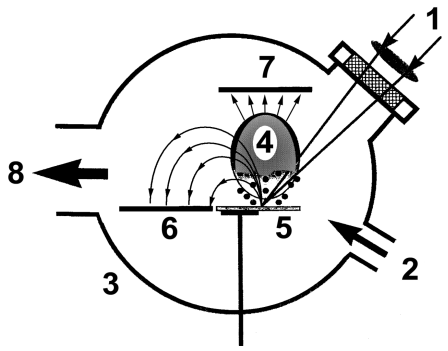

Fig. 1. Scheme of a vacuum chamber for the fabrication of SiO_2 films containing Ge QDs: *1* — laser beam, *2* — gas jet, *3* — vacuum chamber, *4* — erosive torch, *5* — target, *6,7* — substrates, *8* — to a vacuum pump

2. Experimental Technique

The SiO_2 films with Ge nanocrystals were deposited in a vacuum chamber *3* with a working gas under the pressures: oxygen — 6.5 Pa and argon — from 13.5 to 200 Pa (Fig. 1). The beam of a YAG:Nd^{3+} laser *1* operating in the modulated Q-factor mode (a pulse duration was 10 ns, a pulse frequency — 25 Hz, and a pulse energy — 0.2 J) scanned target *5* consisting of c-Ge and c-Si. When the deposition was carried out from the forward flow of an erosive torch *4*, the c-Si substrate *7* of the KDB-10 type was placed at a distance of several tens of millimeters from the target (film I). In the case of the film formation from a backward flow of particles, the c-Si substrate *6* lay in the target plane (film II).

The irradiation of a target gives rise to the appearance of a luminescent torch containing Ge and Si particles (atoms, ions, and clusters). After the adiabatic expansion of the torch, the particles are dispersed by the atoms of a working gas, cooled, partially oxidized, and deposited on a substrate. Some of the films were doped by gold during the film formation. To do this, a gold layer was preliminary deposited on the target. The deposition time did not exceed 60 min. The thickness of the films was changed from a few tens to hundreds of nanometers [5, 6].

The scanning atomic force microscopy (AFM) was employed to perform the topometric studies of the surfaces of films. The investigations were carried out with the use of a NanoScope IIIa microscope (Digital Instruments, USA) with the silicon probes (NT-MDT, Russia) operating in the tapping mode. The radius of a probe tip was examined before and after the measurements by means of a TGT-1 test grating (NT-MDT, Russia) and did not exceed 5—10 nm. A grain height was regarded as a characteristic size since, even after the surface reconstruction carried out according to the known algorithms [7], the diameter measured near a grain base doesn't correspond to the actual grain size, because it is impossible to obtain the negative angles in an AFM image of spherical particles. It is worth to note that the grain sizes obtained from the AFM images of Ge nanocrystals are greater that the actual ones, since the grains consist of Ge nanocrystals covered with oxide shells.

Both the phase composition and crystal structure of the films were controlled by means of the X-ray diffraction carried out with the use of a DRON-3M installation operating with the Cu K_α radiation. To improve the instrument sensitivity, a focusing monochromator (LiF) was placed in front of a detector.

For the films obtained, the time-resolved measurements of PL spectra were performed using a nitrogen laser (λ = 337 nm, τ = 8 ns) as a PL excitation source. The stroboscopic signal detection was performed in the photon counting mode. The minimal strobe duration was 250 ns.

3. Results and Their Discussion

The enthalpy of the SiO_2 formation equals 203.4 kcal/mol, which is higher than that of the GeO_2 formation (128 kcal/mol). What is more, the stability of GeO_2 is worse. Therefore, even under conditions when the equal numbers of Si and Ge atoms are sputtered, the silicon atoms become predominantly oxidized, by forming a SiO_2 matrix [2]. The thermodynamic estimations show that Ge is stable in the SiO_2 environment, and the reaction of substitution of GeO_2 by SiO_2 with the separation of pure Ge can spontaneously occur at the GeO_2/Si boundary even at 300 °C, but it demands the presence of Si atoms. The $Si_{1-x}Ge_xO_2$ metastable oxides are reduced to Ge with the help of not only hydrogen, but also silicon, according to the substitution reaction

$$GeO_2 + Si = SiO_2 + Ge.$$

In fact, according to the X-ray phase analysis, films I, which were obtained from the forward flow of particles of the erosive torch, contain the phases of polycrystalline c-Ge, silicon oxide, and a small amount of polycrystalline c-Si (Fig. 2). It is likely that they also contain the

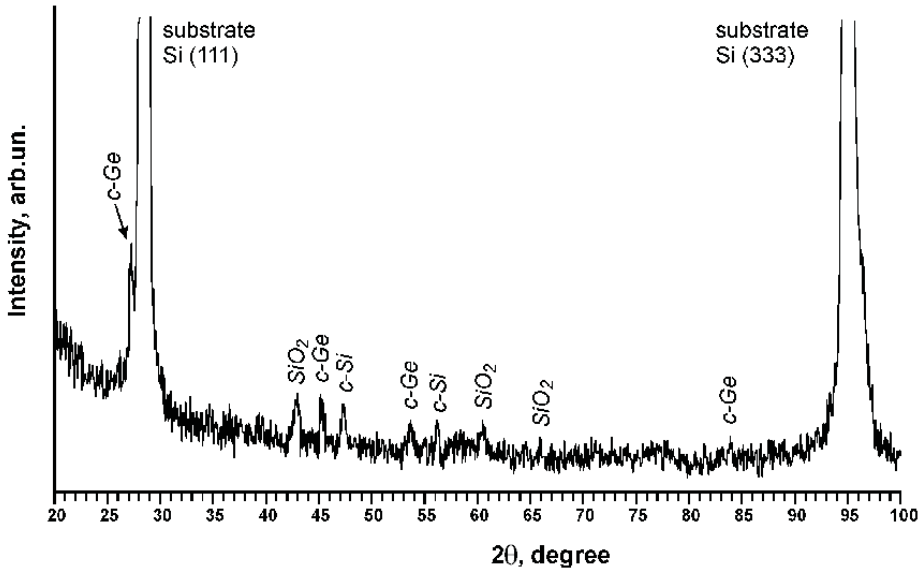

Fig. 2. X-ray diffractogram for a SiO_2 film with Ge nanocrystals, deposited from the forward flow of particles of a torch. The radiation dose was equal to $j = 20$ J/cm^2 and the oxygen pressure $p_{O_2} = 6.5$ Pa

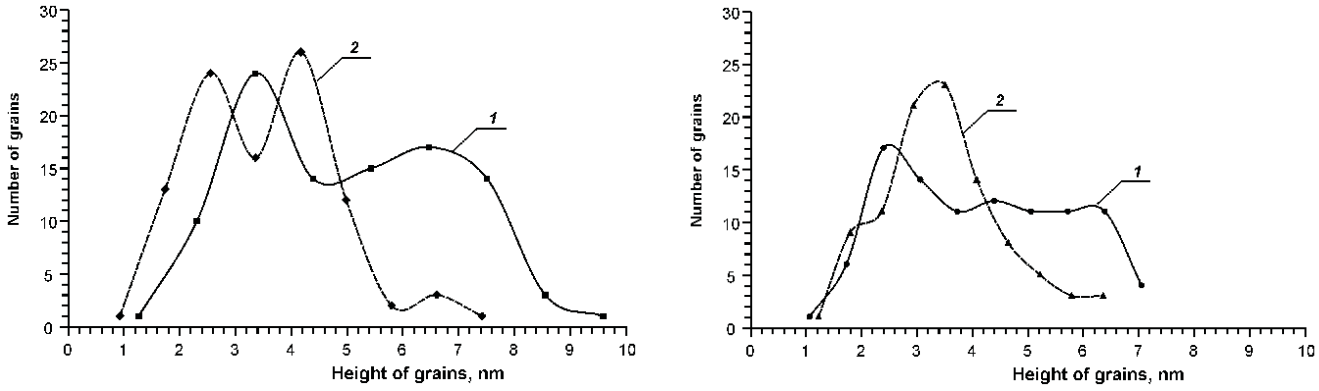

Fig. 3. Histogram of the grain height distribution for the undoped (*a*) and gold doped (*b*) films with the Ge QDs, formed from a backward flow of particles of the erosive torch: *1* — near the torch axis; *2* — at a distance of 12 cm from the torch axis

amorphous (with regard to the x-ray diffraction measurements) c-Ge phase with a crystallite size less than 5 nm. It should be noted that the diffraction peaks are shifted, which testifies to a stressed state of the structures. The fact that c-Si is not revealed in films II indicates that Si becomes completely oxidized under such deposition conditions.

For films II undoped and doped with gold, the surface consists of the grains with sharp boundaries and pores of 15—30 nm in diameter between them (Fig. 3). The surface of the undoped films contains the grains with a bimodal distribution of heights. In this case, the approach of a substrate to the axis of the erosive torch results in a slight shift of the maxima toward the larger sizes, practically not changing the limit values: 1—9.5 nm (Fig. 3,*a*, curve *1*) and 1—7.5 nm for the case where a substrate is moved away from the torch axis by 12 cm (Fig. 3,*a*, curve *2*).

In the gold-doped films, the grain height values lie between 1 and 7.5 nm independently of the distance to the torch axis. However, contrary to the case of a remote substrate where the histogram of the height distribution is Gaussian-like (Fig. 3,*b*, curve *2*), in the case where a substrate is near the axis, we observe a small maximum at 2.4 nm and a plateau ranging from 3 to 6.4 nm (Fig. 3,*b*, curve *1*).

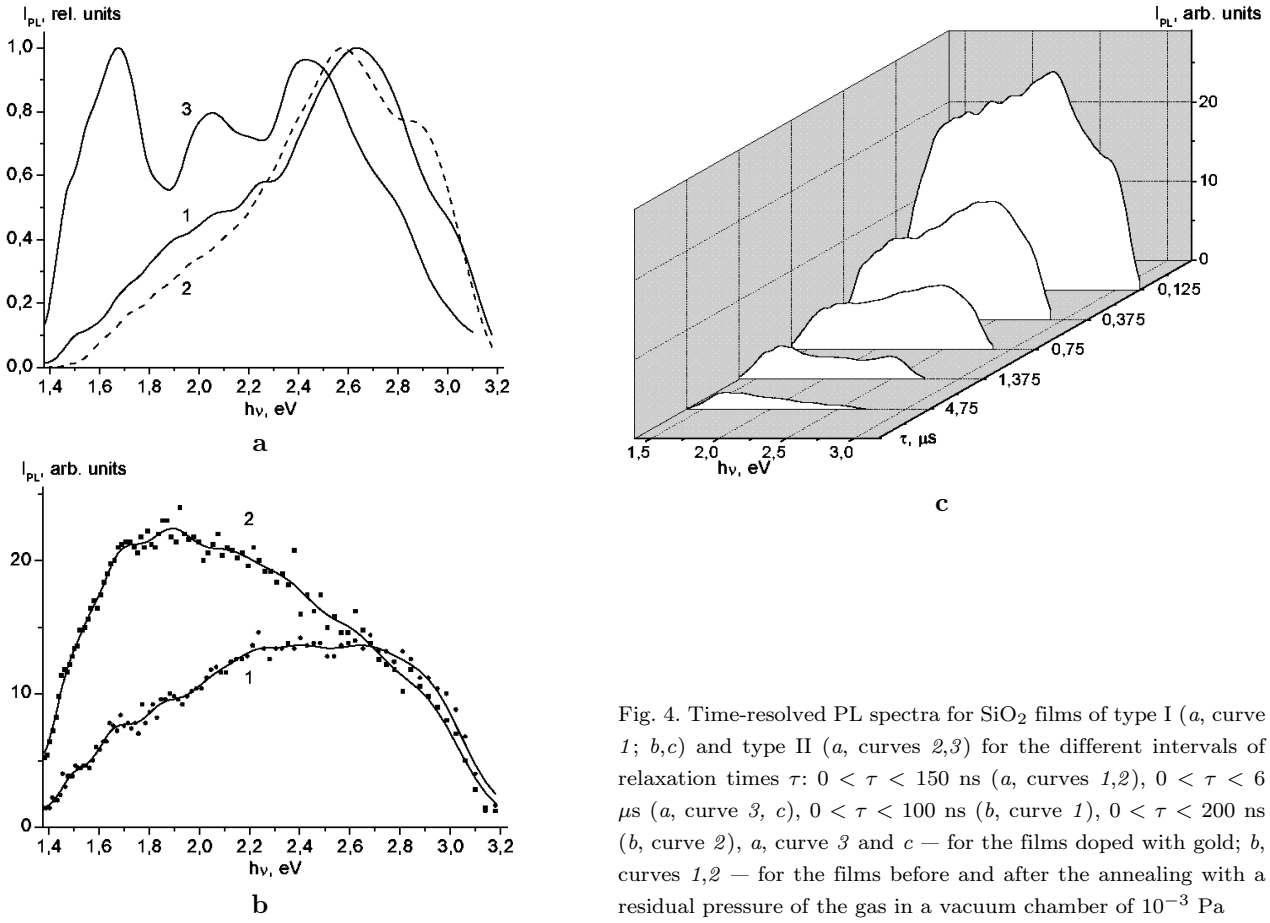

Fig. 4. Time-resolved PL spectra for SiO_2 films of type I (*a*, curve *1*; *b*,*c*) and type II (*a*, curves *2*,*3*) for the different intervals of relaxation times τ: $0 < \tau < 150$ ns (*a*, curves *1*,*2*), $0 < \tau < 6$ μs (*a*, curve *3*, *c*), $0 < \tau < 100$ ns (*b*, curve *1*), $0 < \tau < 200$ ns (*b*, curve *2*), *a*, curve *3* and *c* — for the films doped with gold; *b*, curves *1*,*2* — for the films before and after the annealing with a residual pressure of the gas in a vacuum chamber of 10^{-3} Pa

For the films of both types, the time-resolved PL spectra cover the energy range 1.4—3.2 eV and the PL relaxation times from tens of nanoseconds to a few tens of microseconds (Fig. 4). The PL spectra for the undoped films (Fig. 4,*a*, curves *1*, *2* and Fig. 4,*b*, curve *1*) exhibit maxima in the high-energy spectral region. They are characterized by the small values of PL relaxation times lying in the nanosecond region. The gold doped films (Fig. 4,*a*, curve *3* and Fig. 4,*c*) show the more intense PL. The values of the PL relaxation times reach an order of 10 μs, and, as a rule, a stationary PL spectrum has a noticeable intensity in the low-energy region. The low-energy intensity can be enhanced even at a slight degree of the oxidation of films carried out by means of a low-vacuum (10^{-3} Pa) annealing (see Fig. 4,*b*, curve *2*).

It is known that the neutral oxygen vacancies in SiO_2 containing Ge atoms or two-coordinated G̈e atoms are responsible for the ultraviolet and violet PL bands with energies of 4.3 and 3.1 eV, respectively [8]. As regards the nature of the PL bands ranging from 2.1 to 2.6 eV, there is no consistent view on it. The researchers associate the appearance of these bands not only with the radiative annihilation of excitons in the quantum-dimensional Ge nanocrystals [9], but also with the recombination of the quantum-confined charge carriers inside Ge nanocrystals [10], on their surface states [11], or even on the defects of the SiO_2 matrix [12]. There are also convincing proofs that the red and infrared PL bands ranging from 0.7 to 1.5 eV originate from the recombination of charge carriers in the larger-scale quantum-dimensional Ge nanocrystals [13]. Though the mechanisms of visible PL for the Ge nanocrystals in SiO_2 are under discussion yet, the important role of the quantum-dimensional effect is widely recognized [2].

For the films obtained in this work, we associate the nature of PL with the exciton PL of the Ge nanocrystals embedded in a SiO_2 matrix. The arguments in favour of this point follow from the calculations of both the binding energies for excitons, which predict a large amount of such excitons, and the energies of radiated

photons [14,15]. The spectrum of the exciton PL for Ge nanocrystals is determined by a nanocrystal dimension, the effect of a dielectric enhancement associated with the SiO_2 matrix, the height of a potential barrier at the Ge nanocrystal/SiO_2 boundary, and by the different contributions to PL from nanocrystals of different sizes. Whereas the smaller nanocrystals radiate in a high-energy spectral region, the larger ones do in a region of lower energies. The oscillator strength is greater for the nanocrystals smaller in size. The nanocrystals greater in size have a greater quantity of the Ge broken bonds, which are a principal channel of a nonradiation recombination. Radiationless centers are also the Si broken bonds in the SiO_2 matrix. They all should be passivated for a decrease of the nonradiation recombination. The oxygen, nitrogen, and gold atoms saturate these bonds. That's why the films, doped with gold or processed in oxygen, are characterized by an intense PL in a low-energy spectral region.

Thus, the results of the present work give the evidence for that it is possible to obtain, by means of the pulsed laser deposition method, Ge nanocrystals in a SiO_2 matrix, which radiate at room temperature in the energy region of 1.4—3.2 eV with the PL relaxation times from 100 ns to 10 μs.

1. L.T. Canham, Appl. Phys. Lett. **57**, 1046 (1990).
2. E.B. Kaganovich, E.G. Manoilov, E.V. Begun, and S.V. Svechnikov, Optoelektr. Poluprov. Tekhn. **42**, 1 (2007).
3. L. Patrone, D. Nelson, V.I. Safarov *et al,* Appl. Phys. A **69**, S217 (1999).
4. X. Ma, W. Shi, B. Li, Semicond. Sci. and Technol. **21**, 713 (2006).
5. E.B. Kaganovich, I.M. Kizyak, E.G. Manoilov, V.E. Primachenko, and S.V. Svechnikov, Ukr. J. Phys. **47** (**7**), 680 (2002).
6. E.B. Kaganovich, I.M. Kizyak, E.G. Manoilov, V.E. Primachenko, and S.V. Svechnikov, Ukr. J. Phys. **47** (**8**), 760 (2002).
7. P.M. Lytvyn, O.S. Lytvyn, I.V. Prokopenko *et al*, Nanosist., Nanomater., Nanotekhn. **1**, 601 (2004).
8. R. Rebohle, J. von Borany, H. Fröb, W. Scorupa, Appl. Phys. B **70**, 1 (2000).
9. J.Y. Jeong, S.I. Im, M.S. Oh et al., J. Korean Phys. Soc. **35**, S591 (1999).
10. Y. Maeda, Phys. Rev. B **51**, 1658 (1995).
11. V.Ya. Bratus', M.Ya. Valakh, E.G. Gule, S.M. Okulov, and V.O. Yukhymchuk, Ukr. J. Phys. **50** (**6**), 610 (2005).
12. M. Zacharias, P.M. Fauchet, J. Non-Cryst. Solids **227—230**, 1058 (1998).
13. T. Gao, S. Tong, X. Wu *et al*, Phys. Lett. A **253**, 234 (1999).
14. T. Takagahara, K. Takeda, Phys. Rev. B **46**, 15578 (1992).
15. Y.M. Niquet, G. Allan, C. Delerue, M. Lannoo, Appl. Phys. Lett. **77**, 1182 (2000).

Received 26.07.06.
Translated from Ukrainian by A.I. Tovstolytkin

СТРУКТУРА ТА ФОТОЛЮМІНЕСЦЕНЦІЯ ПЛІВОК SiO_2 З Ge-НАНОКРИСТАЛАМИ, ОДЕРЖАНИХ ІМПУЛЬСНИМ ЛАЗЕРНИМ ОСАДЖЕННЯМ

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Р е з ю м е

Досліджується взаємозв'язок між умовами імпульсного лазерного опромінення $Si_{1-x}Ge_x$-мішені для осадження квантових точок, їхньою структурою та спектрами фотолюмінесценції (ФЛ) з часовим розділенням. Одержано Ge квантові точки системи Ge-нанокристали/SiO_2-матриця, спектри фотолюмінесценції яких лежать у діапазоні енергій 1,4–3,2 еВ, а часи релаксації ФЛ становлять 100 нс–10 мкс.