INFLUENCE OF γ-IRRADIATION ON OPTICAL PROPERTIES OF NITROGEN-DOPED nc-Si/SiO$_2$ STRUCTURES

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Infra-red (IR) spectroscopy and photoluminescence (PL) methods have been used to study the radiation properties of nc-Si/SiO$_2$ and nc-Si/SiO$_2$:N (nitrogen-doped) structures subjected to γ-irradiation (^{60}Co) to expose doses ranging in the interval $10^3 - 10^7$ rad. In contrast to standard nc-Si/SiO$_2$ structures, where low doses ($5 \times 10^3 - 1.6 \times 10^4$ rad) of radiation give rise to an increase of the PL intensity, the irradiation of nitrogen-doped samples results in a usual monotonous PL decay. The analysis of the shape of IR-spectra shows that the irradiation does not change the content and structure of the oxide phase in the nc-Si/SiO$_2$ and nc-Si/SiO$_2$:N systems. At the same time, the doping with nitrogen substantially improves the structural state of the nc-Si–SiO$_2$ interface, so that the low-dose effect is absent in this case. The number of defects – in particular, dangling bonds – becomes reduced, and γ-quanta create only new defects, which results in a monotonous decay of the PL intensity, when the expose dose grows.

1. Introduction

Nanocrystalline silicon inclusions (nc-Si) that are built into a dielectric matrix (in particular, SiO$_2$) stimulate the emergence of PL in the visible and near-IR spectral ranges at room temperature [1]. This fact makes such structures promising as light-emitting elements in modern optoelectronic devices. Hence, the task to optimize luminescent properties of the nc-Si/SiO$_2$ system is challenging. An effective means to enhance the luminescence intensity is the doping of nanocomposites with various impurities: H$_2$, P, Au, N, and so on [2–7]. The effect of PL enhancement depends at that on the kind of dopants and their concentration, as well as on the conditions of heat treatment.

There are also other methods to reduce the density of recombination centers which give rise to photoluminescence quenching. In particular, in works [8, 9], the PL intensity of nc-Si/SiO$_2$ structures was shown to grow distinctly after the actions of small doses of ionizing radiation (γ-irradiations, the doses of about 10^4 rad); the composition and structure of oxide, as well as the dimension of nc-Si inclusions, having not changed at that. This effect was explained in such a way that γ-quanta removed surface defects of the P$_b$-center type which were located at the nanocrystal–matrix interface, so that the radiative recombination channel became strengthened. The efficiency of the "positive effect" given by small doses of ionizing radiation substantially depended on the technology of nanocrystalline silicon preparation and, in particular, on the structural-defective state of the nc-Si–SiO$_2$ interface. To elucidate the mechanism of how small exposure doses affect the PL properties of nanocomposites, it is pertinent to consider the influence of radiation on nc-Si/SiO$_2$ systems, in which surface defects are partially or completely passivated by previous treatments (for example, making use of nitrogen atoms). In this work, the influence of ionizing radiation on the PL properties of nc-Si/SiO$_2$ structures doped with nitrogen has been studied in detail.

2. Experimental Technique

SiO$_x$ films were produced on two-side polished silicon substrates by the method of thermal evaporation of SiO in vacuum (the pressure was about 10^{-4} Pa). The film thickness was determined with the help of a Dektak 3030

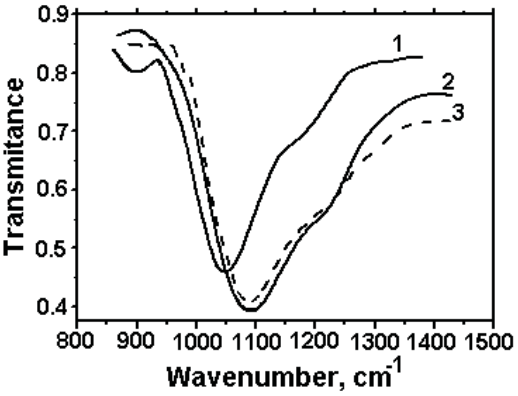

Fig. 1. IR transmission spectra of an as-deposited SiO_x film (*1*), an SiO_x film annealed for 15 min at 1150 °C (*2*), and an SiO_x film implanted with nitrogen and annealed for 15 min at 1150 °C (*3*)

profilometer and amounted to about 340 nm. Some SiO_x films were subjected to the implantation by nitrogen ions N^+ with energies of 70 and 140 keV to the total dose of 8.4×10^{15} cm^{-2}. A uniform distribution of nitrogen over the SiO_x film depth was confirmed by the SIMS method. Si–SiO_x specimens were annealed in the argon atmosphere for 15 min at a temperature of 1150 °C. As a result of thermally induced decomposition of the SiO_x phase, silicon nanoinclusions with crystalline structure and 3 ± 0.5 nm in dimensions were formed, which, as was demonstrated by us earlier [10] taking advantage of high-resolution transmission electron microscopy, were distributed rather regularly in the oxide matrix SiO_2. Specimens of nc-Si/SiO_2 and nc-Si/SiO_2:N (nitrogen-doped) were subjected to γ-irradiation (radiation from a ^{60}Co source with γ-quantum energies of 1.17 and 1.33 MeV); the irradiation intensity was 36.77 rad/s, and the exposure doses ranged in the interval from 10^3 to 10^7 rad.

PL spectra were measured in the spectral range 550 – 1000 nm at room temperature. PL was excited by the emission of a semiconductor laser with a wavelength of 473 nm. The laser radiation power was 50 mW. The PL spectra obtained were corrected taking the spectral sensitivity of the installation into account.

The IR transmittance spectra were measured in the range 700 – 1500 cm^{-1} with the help of an IKS-25M automated spectrometer. A silicon substrate without oxide film was used as a reference specimen. The details of the method used for the determination of a structural arrangement of oxygen in the silicon-oxygen phase were reported earlier [11].

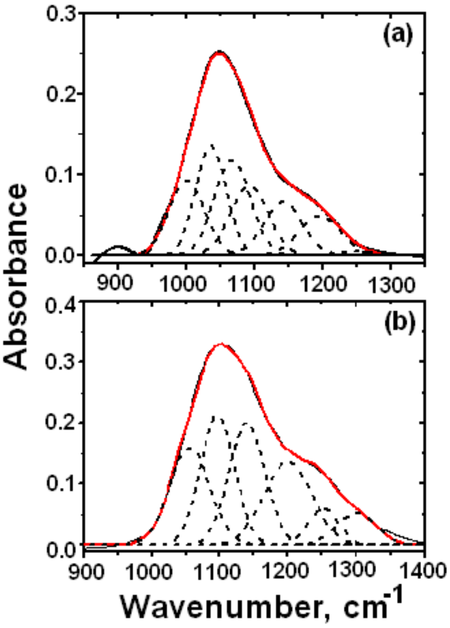

Fig. 2. Band of the Si–O bond absorption (solid curve) and its Gaussian components (dashed curves) for an as-deposited SiO_x film (*1*) and an SiO_x film annealed for 15 min at 1150 °C (*2*)

3. Results and Their Discussion

In Fig. 1, the IR transmission spectra of the films under investigation are depicted. The spectrum of an as-deposited film is well described by a sum of Gaussian components which are inherent to non-stoichiometric silicon oxides (Fig. 2,*a*). According to the position of the transmittance minimum (1049 cm^{-1}), the film content was determined as that corresponding to $x \approx 1.6$ [12,13].

High-temperature annealing gave rise to a shift of the IR spectra toward the high-frequency range (the transparency minimum position was at 1085 cm^{-1}) in both undoped and nitrogen-doped specimens. The spectral area increased considerably (by 58%), which means that the concentration of interstitial oxygen atoms in the film also grew substantially. The spectra did not contain components characteristic of the SiO_x phase (at 1000 and 1032 cm^{-1}), and the spectral curve shape was well described by a sum of Gaussian components inherent to the SiO_2 phase (see Fig. 2,*b*). Those facts prove that the high-temperature annealing gave rise to the thermally induced separation of the SiO_x phase into the SiO_2 and Si ones [10, 14]. In so doing, the presence of nitrogen almost did not influence the efficiency of the process indicated.

The fact of the formation of a Si nanocrystal due to annealing is confirmed by the manifestaion of a rather

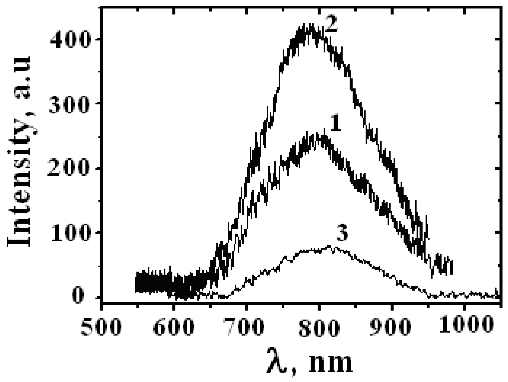

Fig. 3. Photoluminescence spectra of nc-Si/SiO$_2$ specimens: non-irradiated (*1*), and irradiated to the exposure doses of 1.6×10^4 (*2*) and 8×10^6 rad (*3*)

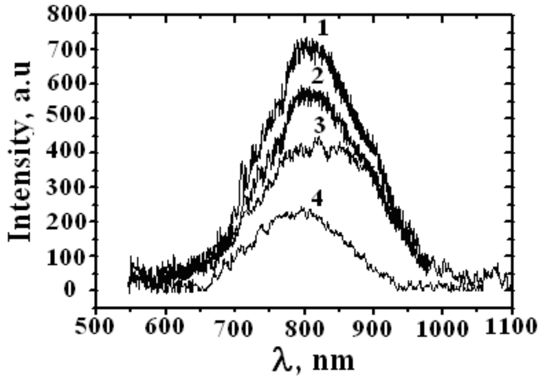

Fig. 4. Photoluminescence spectra of nc-Si/SiO$_2$:N films: non-irradiated (*1*), and irradiated to the exposure doses of 10^4 (*2*), 8×10^4 (*3*), and 8×10^6 rad (*4*)

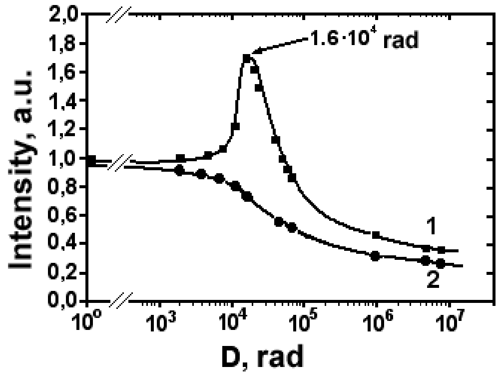

Fig. 5. Dose dependences of the PL intensity in nc-Si/SiO$_2$ (*1*) and nc-Si/SiO$_2$:N (*2*) structures

powerful photoluminescence in the initial nc-Si/SiO$_2$ and the annealed but not irradiated nc-Si/SiO$_2$:N specimens; in particular, the strong band with a peak at about 800 nm which corresponds to luminescence of silicon nanocrystals in the SiO$_2$ matrix was observed [16]. The PL intensity of the specimens doped with nitrogen was almost three times higher at that (Figs. 3 and 4), which is in good agreement with the results of other works [6, 7].

Additional irradiation of films did not influence their IR spectra; i.e. there was no further phase separation, and the concentration of silicon in the content of nanocrystals did not change. However, irradiation substantially affected the PL spectra of the films.

In Fig. 3, the PL spectra of some nc-Si/SiO$_2$ films subjected to various doses of γ-irradiation are shown. One can see that the PL band intensity demonstrates a noticeable growth (by about 70%) at small exposure doses (1.6×10^4 rad). Further irradiation is accompanied by a reduction of the PL band intensity which – at doses larger than 5×10^4 rad – becomes lower than that observed for the initial specimen. It is clearly seen in Fig. 5 (curve *1*), where the dose dependence of the PL band intensity is exhibited. This result confirms the data that were obtained by us earlier for the specimens of annealed SiO$_x$ films fabricated either following different CVC technologies [8] or by thermal sputtering of SiO powder in vacuum [9]. This fact testifies that the low-dose effect is most likely characteristic of the nc-Si/SiO$_2$ system in the initial state, irrespective of how it was fabricated. A somewhat different position of the PL band (the maximum position is at 930 nm), which was observed in work [9], is evidently associated with larger dimensions of silicon nanocrystals that are formed in the course of thermally induced phase separation of SiO$_x$ with $x \approx 1.3$ [15].

An absolutely different picture is observed, when nitrogen-doped films are subjected to irradiation. In Figs. 4 and 5 (curve *2*), the results of measurements of their PL spectra after irradiation are shown. One can see that the PL band intensity monotonously decreases with increasing the exposure dose. Hence, the positive effect of low doses does not manifest itself in nanocrystalline structures of nitrogen-doped silicon. In the whole range of doses, irradiation brings about a mere reduction of the PL band intensity, i.e. it generates structural defects which are the centers of radiationless recombination.

It is evident that the answer to the question "Why the behavior of the PL band is basically different in ordinary and nitrogen-doped nc-Si/SiO$_2$ structures subjected to irradiation?" should be searched for in the influence of nitrogen on the properties of such structures. Really, the authors of a number of works [2, 4, 6, 7, 18] found that the insertion of nitrogen can substantially influence

PL in silicon nanoclusters which are built into the SiO_2 matrix. High-temperature annealing (at 1100 °C) of nc-Si/SiO_2 specimens in a nitrogen-containing environment gave rise to a substantial (by a factor of about 2.5) growth of the PL intensity of the band at 800 nm [2, 18]. Implantation of silicon and nitrogen ions into a SiO_2 film followed by the annealing of the latter at 1000 °C demonstrates a non-monotonous character of the dependence of the 800-nm band intensity on the concentration of implanted nitrogen [4]. At implantation doses of about 10^{16} cm^{-2}, nitrogen enhances the radiation emission of light quanta by Si nanocrystals; at higher doses, a reduction of the PL intensity was observed. The effect of light emission enhancement in those cases can be explained by at least two factors. Nitrogen atoms can get to the nc-Si–SiO_2 interface and passivate the broken bonds of silicon (P_b-centers) [2, 7, 18]. Moreover, nitrogen can form precipitates of the Si_xN_y type with silicon, which become additional centers of nc-Si formation [6, 17]. The last effect favors the concentration growth of silicon nanocrystals and, accordingly, results in an increase of the intensity of the corresponding PL band. In addition, nanocrystals become smaller, which causes a shift of the PL band toward higher energies.

In our case, nc-Si/SiO_2:N specimens demonstrated only a substantial increase of the PL band intensity, whereas its maximum position practically did not change (in comparison with ordinary nc-Si/SiO_2 films). Hence, one can draw a conclusion that the doping of specimens with nitrogen results only in a considerable reduction of the defect concentration at the nc-Si–SiO_2 interface, and it is this effect that is responsible for the enhancement of the light emission by nanocrystals.

If usual (without nitrogen doping) nanocrystalline nc-Si/SiO_2 structures are irradiated, similar processes can take place [9]. The results obtained in this case can be explained in the framework of the model of “low doses”which was proposed for direct-band-gap semiconductors [19, 20]. One can suppose that there are two competitive processes of defect formation in the course of nc-Si/SiO_2 structure irradiation: those which enhance PL (passivation of P_b-centers) and those which quench it (the formation of centers of radiationless recombination). At low exposure doses, the passivation of P_b-centers is more effective in comparison with the formation of centers of radiationless recombination; therefore, we observe the growth of PL. At high exposure doses ($D > 1.6 \times 10^4$ rad), the process of formation of defects that quench PL becomes dominant. The exposure dose of 1.6×10^4 rad (Fig. 5, curve *1*) corresponds to the state of equilibrium between both the processes of defect formation, when the concentration of passivated P_b-centers becomes approximately equal to the concentration of generated centers of radiationless recombination.

It is worth noting that doping the specimens with nitrogen affects the PL enhancement more effectively than their γ-irradiation. In the case of nc-Si/SiO_2:N structures, the luminescence intensity was almost three times as high as that in nc-Si/SiO_2 films, whereas the irradiation of nc-Si/SiO_2 structures to low doses Si/SiO2 brought about the enhancement of the PL intensity by only 70%. Hence, nitrogen atoms make the defective state of the nc-Si–SiO_2 interface so improved (they passivate P_b-centers) that the following radiation treatment of nc-Si/SiO_2:N structures is no more effective with respect to the further improvement: γ-quanta mainly generate the centers of radiationless recombination, which gives rise to a monotonous diminishing of the PL intensity with the growth of the exposure dose, as was observed experimentally (Fig. 5, curve *2*).

4. Conclusions

As-deposited (initial) SiO_x films have been demonstrated to be a non-stoichiometric phase of silicon oxide ($x \approx 1.6$). High-temperature annealing of such films (undoped and doped with nitrogen) results in the formation of nanocrystalline silicon structures built into the SiO_2 matrix, which provides a rather powerful PL (the band with the peak position at about 800 nm). The intensity of this band is considerably (by a factor of about three) higher in the case of nitrogen-doped specimens. Irradiation of nc-Si/SiO_2 structures with γ-quanta to low exposure doses ($5 \times 10^3 - 2 \times 10^4$ rad) enhances the PL intensity in Si nanocrystals (by a factor of 2 at the optimal irradiation dose of 1.6×10^4 rad). In the case of nc-Si/SiO_2:N structures, γ-irradiation leads to a reduction of the PL intensity in the whole interval of exposure doses ($10^3 - 10^7$ rad).

1. L.T. Canham, Appl. Phys. Lett. **57**, 1046 (1990).
2. A.R. Wilkinson and R.G. Elliman, J. Appl. Phys. **96**, 4018 (2004).
3. K. Sato and K. Hirakuri, J. Appl. Phys. **97**, 104326 (2005).
4. D.I. Tetelbaum, O.N. Gorshkov, V.A. Burdov, S.A. Trushin, A.N. Mikhailov, D.M. Gaponova, S.V. Morozov, and A.I. Kovalev, Fiz. Tverd. Tela **46**, 21 (2004).
5. J. Kim, H.J. Woo, H.W. Choi, G.D. Kim, and W. Hong, Mater. Res. Soc. Symp. Proc. **792**, R9.20.1 (2004).

6. G.A. Kachurin, S.G. Yanovskaya, K.S. Zhuravlev, and M.O. Ruault, Fiz. Tekh. Poluprovodn. **35**, 1235 (2001).
7. M.S. Yang, K.S. Cho, J.H. Jhe, S.Y. Seo, J.H. Shin, K.J. Kim, and D.W. Moon, Appl. Phys. Lett. **85**, 3408 (2004).
8. I.P. Lisovskyy, V.G. Litovchenko, A.A. Evtukh, M.V. Muravska, V.V. Voitovych, and E.G. Manojlov, in *Materials of the 9-th International Conference PTTFN-XI* (Ivano-Frankivsk, Ukraine, 2007), p. 112.
9. I.P. Lisovskyy, I.Z. Indutnyi, M.V. Muravskaya, V.V. Voitovich, E.Ġ Gule, and P.E. Shepelyavyi, Semicond. **42**, 576 (2008).
10. A. Szekeres, T. Nikolova, A. Paneva, A. Cziraki, Gy.J. Kovacs, I. Lisovskyy, D. Mazunov, I. Indutnyy, and P. Shepeliavyi, Mater. Sci. Eng. B **124**–**125**, 504 (2005).
11. I.P. Lisovskyy, V.G. Litovchenko, V.B. Lozinskii, S.I. Frolov, H. Flietner, W. Fussel, and E.G. Schmidt, J. Non-Cryst. Solids **187**, 91 (1995).
12. A. Cachard, J.A. Roger, J. Pivot, and C.H.S. Dupuy, Phys. Status Solidi A **5**, 637 (1971).
13. H.R. Philipp, J. Phys. Chem. Solids **32**, 1935 (1971).
14. I.P. Lisovskyy, V.G. Litovchenko, I.Z. Indutnyy, D.O. Mazunov, and P.E. Shepelyavyi, Ukr. Fiz. Zh. **50**, 248 (2005).
15. T. Inokuma, Y. Wakayama, T. Muramoto, R. Aoki, Y. Kurata, and S. Hasegawa, J. Appl. Phys. **83**, 2228 (1998).
16. H. Takagi, H. Ogawa, Y. Yamazaki, A. Ishizaki, and T. Nakagiri, Appl. Phys. Lett. **56**, 2379 (1990).
17. V. Mulloni, P. Bellutti, and L. Vanzetti, Surf. Sci. **585**, 137 (2005).
18. M. Lopez, B. Garrido, C. Garcia, P. Pellegrino, A. Perez-Rodrigues, J.R. Morante, C. Bonafos, M. Carrada, and A. Claverie, Appl. Phys. Lett. **80**, 1637 (2002).
19. V.G. Litovchenko, Optoelektr. Poluprovodn. Tekhn. **1**, 27 (1982).
20. O.Yu. Borcovskaya, N.L. Dmitruk, R.V. Konakova, V.G. Litovchenko, and V.I. Shakhovtsov, Phys. Status Solidi A **58**, K25 (1980).

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ВПЛИВ γ-ОПРОМІНЕННЯ НА ОПТИЧНІ ВЛАСТИВОСТІ СТРУКТУР nc-Si/SiO$_2$, ЛЕГОВАНИХ АЗОТОМ

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Резюме

Методами інфрачервоної (ІЧ) спектроскопії та фотолюмінесценції (ФЛ) досліджено радіаційні властивості структур nc-Si/SiO$_2$ та nc-Si/SiO$_2$:N (леговані азотом), опромінених γ-квантами (^{60}Co) в діапазоні доз 10^3–10^7 рад. На відміну від звичайних nc-Si/SiO$_2$ структур, де малі дози ($5 \cdot 10^3$–$1,6 \cdot 10^4$ рад) радіаційної обробки приводять до зростання інтенсивності ФЛ, опромінення легованих азотом зразків nc-Si/SiO$_2$:N викликає звичайне монотонне спадання ФЛ. Аналіз форми ІЧ-спектрів показує, що під дією радіації не змінюється склад та структура оксидної фази систем nc-Si/SiO$_2$ та nc-Si/SiO$_2$:N. В той же час, легування азотом суттєво покращує структурний стан межі поділу nc-Si–SiO$_2$, тому ефект малих доз опромінення є відсутнім: дефектів, зокрема обірваних зв'язків, стає мало, і γ-кванти створюють тільки нові дефекти, що приводить до монотонного падіння інтенсивності ФЛ під час збільшення дози опромінення.