STUDY OF RADIATION DEFECT ANNEALING IN nc-Si/SiO$_2$ FILM STRUCTURES

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PACS 61.80.Ed,73.63.Bd,
78.55.Ap,78.67.Bf,78.67.Hc

The nc-Si/SiO$_2$ structures irradiated with γ-quanta to a dose of 2×10^7 rad and annealed in the temperature range 50–450 °C have been studied. The process of radiation defect annealing was shown to be characterized by a distribution of activation energy rather than a unique value. By analyzing the isothermal annealing curves, the frequency factor $A = 10^7$ s^{-1} was determined. Using the data on isothermal and isochronal annealing, the distribution function for the activation energy $n(E_a)$ was calculated. This quantity is distributed within the range of 0.85–1.05 eV and has a peak at 0.96 eV. The calculated annealing parameters make it possible to conclude that radiation-induced defects, which lead to a partial quenching of photoluminescence, emerge at the Si nanocrystal–oxide matrix interface. Their nature and the mechanism of their generation are most likely similar to those which are inherent to surface states formed by ionizing irradiation at the Si–SiO$_2$ interface in planar metal–oxide–semiconductor structures.

1. Introduction

Recently [1, 2], γ-irradiation of SiO$_2$ films containing silicon nanocrystals (nc-Si) has been demonstrated to substantially affect the photoluminescence (PL) band intensity with the peak at about 810 ± 5 nm , giving rise to its considerable reduction at high exposure doses (up to 2 times at a dose of 10^7 rad). Bearing in mind that this band is associated with the luminescence of nc-Si [3], this effect was explained as a result of the generation of radiation-induced defects which are the centers of radiationless recombination.

The elucidation of the nature of those defects demands further researches, in particular, the study of thermal annealing processes. It is known that the analysis of the latter makes it possible to classify defect types, makes their identification easier, and also gives the necessary information concerning the stability of radiation-induced centers [4, 5]. Therefore, this work aims at the detailed research of characteristics of the thermal instability of radiation-induced defects in nc-Si/SiO$_2$ structures and the determination of parameters of the annealing of defects.

2. Experimental Technique

SiO$_x$ films on silicon substrates polished from both sides were produced by thermal evaporation of silicon monooxide in vacuum (a pressure of about 10^{-4} Pa). After the deposition, the thickness of SiO$_x$ films ($x \approx 1.3$) measured using an MII-4 microinterferometer was 450 nm. Si-SiO$_x$ specimens were annealed at a temperature of 1100 °C in an argon atmosphere for 15 min. As a result of the thermally induced decomposition of the SiO$_x$ phase, there emerged crystalline nanoinclusions of silicon 3 ± 0.5 nm in dimensions, which were distributed rather regularly over the SiO$_2$ oxide matrix (it was demonstrated by us earlier [6], making use of high-resolution antireflection electron microscopy). Specimens of nc-Si/SiO$_2$ obtained in such a way were subjected to γ-irradiation (a ^{60}Co source with γ-quantum energies of 1.17 and 1.33 MeV) to an exposure dose of 2×10^7 rad.

Specimens (irradiated ones and the reference one) were annealed in the temperature range $50 - 450$ °C in an argon environment. The temperature was monitored with the help of a chromel–alumel thermocouple. The temperature stabilization was carried out with an accuracy of ±1 °C using an industrial high-precision temperature regulator VRT-3.

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

After the specimens had been annealed, we measured the parameters of their PL bands, determined the peak intensity values for three specimens (the initial, $I^i_{\rm PL}$, irra-

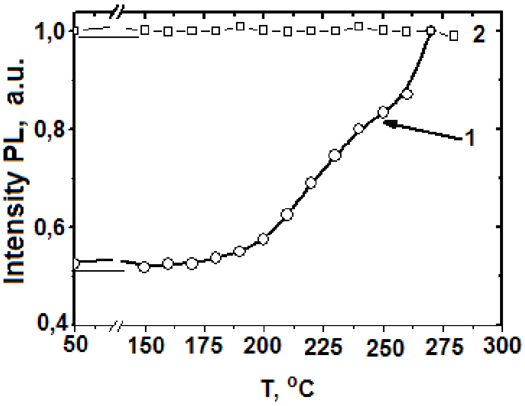

Fig. 1. Dependences of the PL intensity on the annealing temperature for irradiated (*1*) and initial (*2*) nc-Si/SiO$_2$ structures

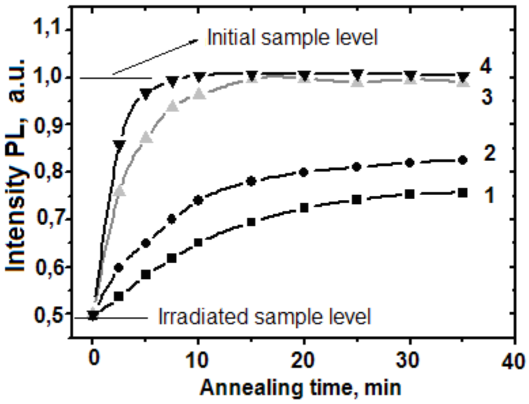

Fig. 2. Dependences of the PL intensity on the annealing time for irradiated nc-Si/SiO$_2$ structures. The anneaing temperatures: 230 (*1*), 280 (*2*), 330 (*3*), and 450 °C (*4*)

diated, $I_{\rm PL}^R$, and annealed, $I_{\rm PL}^a$, ones), and calculated the fraction of non-annealed radiation-induced variations [4]:

$$N = \frac{I_{\rm PL}^a - I_{\rm PL}^i}{I_{\rm PL}^R - I_{\rm PL}^i}. \qquad (1)$$

The dependences of N on the time (at isothermal annealing) or the temperature (at isochronal annealing) were used to calculate the annealing activation energy and the frequency factor of radiation-induced defects in the nc-Si/SiO$_2$ structures under investigation.

3. Experimental Results and Their Discussion

The non-irradiated nc-Si/SiO$_2$ specimens revealed the presence of a rather intensive PL band peaked at about 850 nm, which was associated with the luminescence of nc-Si nanocrystals in the SiO$_2$ matrix [3]. After the specimens had been subjected to γ-irradiation, the PL intensity $I_{\rm PL}$ became half as large as that given by the non-irradiated specimen. Such a deterioration of light-emitting properties of the structures concerned was persistent enough and practically did not change after the two-year storage of irradiated specimens at room temperature.

The annealing of radiation-induced defects in such structures starts only at temperatures higher than 200 °C. This fact is illustrated in Fig. 1, where the results of the isochronal annealing (the temperature step is 10 °C, and the annealing duration at every temperature is 10 min) of irradiated (curve *1*) and non-irradiated (curve *2*) specimens are depicted. The heat treatment of the non-irradiated specimen did not affect the PL intensity (curve *2*).

In Fig. 2, the results of isothermal annealings applied to irradiated specimens are shown. The annealing curves have the exponential profile. This means that the disappearance kinetics of radiation damages is simple (the reaction of the first order) [7]. One can also see that, at relatively high temperatures of the heat treatment (curves *3* and *4*), when the defect annealing is complete, the annealing temperature affects only the rate of radiation-induced damage annealing. At lower temperatures ($200\ ^\circ{\rm C} < T < 300\ ^\circ{\rm C}$), defects are annealed only partially; here, the temperature is responsible not only for the annealing rate, but also for the fraction of non-annealed defective states. This result is quite important, because it means [5, 8] that the radiation-stimulated defect formation in nc-Si/SiO$_2$ structures is not characterized by a single value of the annealing activation energy, but its certain distribution within a definite interval. Note that such a feature is also inherent to radiation-induced defects in usual planar systems Si-SiO$_2$ [5, 9, 10].

Taking the last fact into account, we analyzed the annealing curves and determined the activation energy making allowance for the activation energy distribution. Our purpose was to describe the distribution function and to determine the position of the activation energy peak on the corresponding axis following the general theoretical approach which was proposed in work [8] and widely used in the researches of annealing processes of radiation-induced defects [5, 9, 10].

In the case of isothermal annealing, the distribution function of the activation energy is connected with the curve parameters as follows:

$$n(E_a) = -(t/\tau)(dN/dt), \qquad (2)$$

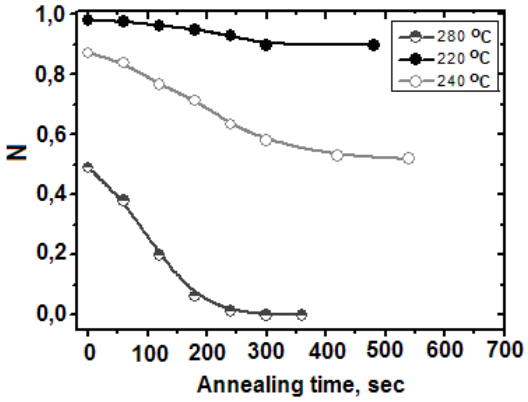

Fig. 3. Dependences of the fraction of non-annealed radiation-induced defects in irradiated nc-Si/SiO$_2$ structures on the annealing time for various annealing temperatures

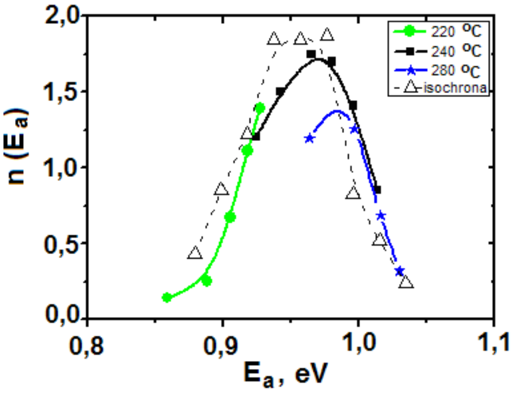

Fig. 4. Distributions of the activation energy of radiation defect annealing in nc-Si/SiO$_2$ structures calculated from the data for isothermal (■, •, ∗) and isochronal (△) annealing. The frequency factor $A = 10^7$ s^{-1}

$$E_a = \tau \ln(At). \qquad (3)$$

Here, $\tau = kT$, T is the annealing temperature, $k = 8.62 \times 10^{-5}$ eV/K is the Boltzmann constant, t is the time of heat treatment, and A is the frequency factor. According to the results of works [5, 9], for the frequency factor and the activation energy to be determined correctly, the specimen was subjected sequentially to three cycles of isothermal annealing at different temperatures (220, 240, and 280 °C, as is shown in Fig. 3). Using expressions (2) and (3), we plotted the distribution functions of the activation energy for every annealing cycle at various, arbitrary chosen values of the frequency factor within the interval from 10^3 to 10^{10} s^{-1}. The value of the parameter A was considered as satisfactory, when the distribution function became continuous from segment to segment (every segment corresponded to a definite isotherm). This circumstance allowed us to determine $A = 10^7$ s^{-1} and the corresponding spectrum of the annealing activation energy (Fig. 4).

In the case of isochronal annealing (Fig. 1) under the conditions of our experiment, we have $E_a/\tau \gg 1$. Then, in view of the results of work [8], we can write

$$E_a/\tau + \ln(E_a/\tau) = \ln A\Delta t, \qquad (4)$$

$$n(E_a) = -(dN/d\tau)(E_a/\tau)^{-1}, \qquad (5)$$

where $\Delta t = 10$ min. In the calculations of $n(E_a)$, we used the value of frequency factor found when analyzing isothermal curves, $A = 10^7$ s^{-1}. The results of calculations are presented in Fig. 4. One can see that the distribution functions calculated from the data of different experiments (either at isothermal or isochronal annealing) are in good agreement with one another. The results obtained show that the activation energy of annealing of radiation-induced defects, which are responsible for a partial quenching of PL in nc-Si/SiO$_2$ structures, is distributed in the interval 0.85–1.05 eV and has a peak at 0.96 eV.

It is expedient to compare the obtained E_a-value with the known values of annealing energy of radiation-induced defects in both single-crystalline silicon and planar Si-SiO$_2$ systems. The annealing energy of primary radiation defects in silicon crystals is rather low (for instance, it amounts to 0.18 and 0.33 eV for vacancies in n- and p-Si, respectively [11]). The majority of secondary radiation-induced defects (i.e. the associations of primary defects with one another or with impurities or other imperfections in the crystal lattice) have the annealing activation energies which are either substantially larger (complexes vacancy–oxygen atoms) or substantially lower (complexes vacancy–donor impurity atoms) than that determined in work [11]. Only definite secondary radiation-induced defects in silicon crystals can be annealed in a corresponding temperature range and possess the activation energy close to the calculated value. In particular, defect Si-P6, which includes interstitial silicon atoms, has the activation energy $E_a = 0.92$ eV, but it is observed only after the silicon irradiation with neutrons [11]. Complexes vacancy–donor impurity atom (E-centers) in the neutral state can have $E_a = 0.95$ eV [11]; however, first, the corresponding frequency factor of the annealing process substantially exceeds the value found for the structures concerned, and, second, the presence of the indicated impurities in silicon nanocrystals can hardly be expected, taking into account the conditions of fabrication and treatment of nc-Si/SiO$_2$ structures. In our opinion, it is important that, in all cases of the annealing of radiation-induced defects in silicon crystals, the activation energy is characterized by a single value rather than a distribution.

The presented data concern the defects located in the silicon bulk. The presence of a surface can affect the thermal stability of radiation-induced defects. It is known, in particular, that a near-surface (up to 2 μm in thickness) layer in oxidized silicon single crystals differs from the silicon bulk by both a higher sensitivity to ionizing radiation, and the characteristics of radiation damage annealing [10]. From this point of view, silicon nanocrystals with an average dimension of 3 nm, which are built into the SiO$_2$ matrix, owing to the emergence of significant mechanical stresses caused by mismatches between the Si and SiO$_2$ structures, are more likely similar by their properties to such a near-surface layer of silicon than to its bulk. For this reason, it is more correct to compare the parameters of the radiation-induced defect annealing in nc-Si/SiO$_2$ systems with those determined for the near-surface layer of oxidized silicon subjected to γ-irradiation. The study of the generation lifetime of minority charge carriers in the space charge region of silicon under γ-irradiation (to a dose of 10^6 rad) allowed us to determine the activation energy for the annealing of corresponding near-surface radiation-induced defects: in the maximum of its distribution, it amounted to 1.1–1.2 eV depending on the technology of silicon oxidation [10]. This magnitude appreciably differs from the E_a-value calculated in this work. A conclusion can be drawn that, in irradiated nc-Si/SiO$_2$ structures, there emerge radiation-induced defects which are not located in the bulk of silicon nanocrystals. Moreover, it is easy to demonstrate that, in our case, the radiation damages that arise in silicon nanocrystals cannot affect the PL intensity appreciably. In particular, it is known [12] that one γ-quantum generates about 10^{-3} primary defects per cubic centimeter in silicon. Hence, the concentration of point-like radiation-induced defects, which were formed in the bulk of silicon nanocrystals in the structures under investigation (the exposure dose was 2×10^7 or 3.38×10^{16} γ-quanta), is of the order of 10^{13} cm^{-3}. On the other hand, it is known [13] that the PL quenching occurs in nc-Si/SiO$_2$ structures, when the concentration of radiationless recombination centers (P_b-centers) reaches $10^{16} - 10^{18}$ cm^{-3}. Hence, the number of defects, which arose in the bulk of silicon nanocrystals owing to the irradiation of our specimens, was obviously insufficient to affect their optical properties.

Some time ago, the researches concerning the processes of radiation damage generation and annealing in planar structures at the Si–SiO$_2$ interface were carried on rather intensively. In particular, the annealing activation energies were found for the centers in the oxide bulk and the fast surface states that were generated under the action of various kinds of irradiation, such as fast electrons [5], ultra-violet light, and γ-radiation [9, 10]. In every case, the annealing activation energy was distributed over the energy axis with a peak located at 0.92 ± 0.5 eV, and the frequency factor was 10^7 s^{-1}. These values coincide with those calculated in this work. A conclusion can be drawn that, if nc-Si/SiO$_2$ systems are γ-irradiated to exposure doses below 2×10^7 rad, the radiation-induced defects responsible for a partial PL quenching are generated at the nc-Si/SiO$_2$ interface. These defects are the centers of radiationless recombination and can be of the same origin as fast surface states which are generated by the radiation at the interface of planar Si–SiO$_2$ structures. Evidently, the generation mechanism for those defects has to be similar to that taking place in planar Si–SiO$_2$ systems.

When studying the influence of ionizing radiation on metal–insulator–semiconductor structures, a number of alternative models for the mechanism of fast surface state generation were proposed [9, 14, 15]. Being different in details, they have three key common features: (i) the process of recombination center generation at the Si–SiO$_2$ interface is multistage; (ii) irradiation produces damages in the oxide bulk (broken Si–O–Si bonds, oxygen vacancies, hydrogen, and protons); (iii) the indicated defects migrate to the Si–SiO$_2$ interface, where they play the role of surface states or take part in their formation. It is easy to show that, in the case of Si–SiO$_2$ structures as well, the oxide matrix bulk is the most probable region, where plenty of damages can be formed under irradiation. First, in our case of silicon nanocrystals 3 ± 0.5 nm in dimension, the volume fraction of crystalline silicon in the oxide matrix constitutes not more than 3%, even if the concentration of nanocrystals is maximally possible (of about 10^{18} cm^{-3} [13]). The fraction of the volume occupied by the nc-Si/SiO$_2$ interface is even smaller. Second, the efficiency of the defect generation in SiO$_2$ is considerably (by 2–3 orders of magnitude) higher than that in silicon; for instance, the γ-irradiation of a SiO$_2$ matrix to a dose of 2×10^7 rad can generate E'-centers (oxygen vacancies) with a concentration of $10^{15} - 10^{16}$ cm^{-3} [11]. This magnitude is rather close to that necessary for quenching the PL of nanocrystals [13].

By summarizing our results, a conclusion can be drawn that ionizing radiation invokes the processes of generation of defects in the oxide matrix, and, as a result of the multistage reaction at the Si–SiO_2 interface, there appear the recombination centers which are responsible for a partial PL quenching.

4. Conclusions

Irradiation of nc-Si/SiO_2 structures with γ-quanta brings about the generation of defects which substantially (by up to a factor of two at an exposure dose of 2×10^7 rad) quench the photoluminescence. These defects are annealed in the temperature interval from 200 to 300 °C. The annealing activation energy is distributed over the energy axis within the interval $0.85 - 1.05$ eV with a peak at 0.96 eV, and the frequency factor amounts to 10^7 s^{-1}. Such parameters allow a conclusion to be made that radiation-induced defects, which give rise to a partial PL quenching, are generated at the interface between Si nanocrystals and the oxide matrix. The nature of those defects and the mechanism of their formation are most likely similar to mechanisms inherent to surface states, which are generated by ionizing radiation at the interface of planar structures Si–SiO_2.

The work was supported in the framework of project 1.1.5/9 of the State target scientific and engineering program of development and creation of high-technology sensor products for 2008–2012.

1. I.P. Lisovskyy, I.Z. Indutnyi, M.V. Muravskaya, V.V. Voitovich, E.G. Gule, and P.E. Shepelyavyi, Fiz. Tekh. Poluprovodn. **42**, 591 (2008).
2. I.P. Lisovskyi, V.G. Litovchenko, M.V. Voitovych, V.P. Mel'nyk, I.M. Khatsevych, V.V. Voitovych, V.Yu. Povarchuk, M.V. Mezhrennyi, and D.I. Smirnov, Ukr. Fiz. Zh. **53**, 1001 (2008).
3. Y. Kanzawa, T. Kageyama, S. Takeoka, M. Fujii, S. Hayashi, and K. Yamamoto, Solid State Commun. **102**, 533 (1997).
4. V.S. Vavilov and H.A. Ukhin, *Radiation Effects in Semiconductors and Semiconductor Devices* (Consultants Bureau, New York, 1977).
5. V. Danchenco, U.D. Desai, and S.S. Brashears, J. Appl. Phys. **39**, 2417 (1968).
6. 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).
7. E.N. Eremin, *Fundamentals of Chemical Kinetics* (Vysshaya Shkola, Moscow, 1976) (in Russian).
8. W. Primak, Phys. Rev. **100**, 1677 (1955).
9. V.G. Litovchenko, I.P. Lisovskii, and R.O. Litvinov, Appl. Surf. Sci. **6**, 15 (1980).
10. V.Ya. Kiblik, Ph.D. thesis (Kyiv, 1982) (in Russian).
11. V.S. Vavilov, V.F. Kiselev, and B.N. Mukashev, *Defects in Silicon and on Its Surface* (Nauka, Moscow, 1990) (in Russian).
12. V.M. Kulakov, V.I. Shakhovtsov, and S.I. Shakhovtsova, in *Physical Principles of Radiation Technology of Solid-State Electronic Devices* (Naukova Dumka, Kyiv, 1978) (in Russian).
13. K. Sato and K. Hirakuri, J. Appl. Phys. **100**, 114303 (2006).
14. F.J. Grunthaner and P.J. Grunthaner, Mater. Sci. Rep. **1**, 65 (1986).
15. *Defects in Microelectronic Materials and Devices*, edited by D.M. Fleetwood, S.T. Pantelides, and R.D. Schrimps (CRC Press, Boca Raton, Fl., 2008).

Received 15.06.09
Translated from Ukrainian by O.I. Voitenko

ДОСЛІДЖЕННЯ ПРОЦЕСУ ВІДПАЛУ РАДІАЦІЙНИХ ДЕФЕКТІВ У ПЛІВКОВИХ СТРУКТУРАХ nc-Si/SiO_2

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Резюме

Досліджено структури nc-Si/SiO_2, опромінені γ-квантами дозою $2{\cdot}10^7$ рад і відпалені в діапазоні температур 50–450 °C. Показано, що процес відпалу радіаційних дефектів характеризується не єдиним, а розподіленим значенням енергії активації. З аналізу ізотермічних кривих знайдено значення частотного фактора процесів відпалу $A = 10^7$ $с^{-1}$. Використовуючи методи ізохронного та ізотермічного відпалів, побудовано функцію розподілу енергії активації $n(E_а)$. Ця величина розподілена в інтервалі 0,85–1,05 еВ з піком при 0,96 еВ. Наведені характеристики відпалу дозволяють зробити висновок, що радіаційні дефекти, які приводять до часткового гасіння фотолюмінесценції, утворюються на межі поділу Si нанокристал–оксидна матриця. Природа цих дефектів і механізм їх утворення, скоріш за все, подібні таким, що притаманні поверхневим станам, які утворюються іонізуючим опроміненням на межі поділу планарних структур Si – SiO_2.