Multimodal size distribution of Si nanoclusters in SiO$_2$ as manifestation of interaction in the space of sizes

I. V. Blonskiy, B. I. Lev
Institute of Physics, NAS Ukraine, 46 prospekt Nauki, Kyiv, 252028, Ukraine

M. Ya. Valakh
Institute of Semiconductor Physics, NAS Ukraine, 45 prospekt Nauki, Kyiv, 252028, Ukraine

Abstract. This paper summarizes the results of experimental studies revealing a multimodal character of the function of size distribution of Si nanoclusters in light-emitting SiO$_2$:Si structures. To explain the nature of this multimodality, a «liquid» approach to the description of the coalescence stage based on taking into account the correlation effects caused by particle-particle interactions in the space of sizes is proposed. This approach is justified by a high concentration of solutions where the nuclei of the new phase are described by a multimodal function of size distribution.

Keywords: nanoclusters; size distribution function; interaction in the space of sizes; silicon-based light-emitting devices.

1. One of the greatest challenges for the present-day IR optoelectronics is creation of silicon-based light-emiting devices. In the recent years, much hope was pinned on silicon nanoclusters acting as quantum dots. This line of work was inspired by the observation of quite bright luminescence in the visible spectral range, caused by silicon precipitates of nanometer sizes [1]. A correlation between the size of silicon nanoparticles and the spectral composition of the light emitted by them has already been reported [2–4]. As many researchers believe, this fact indicates that the nature of this emission is associated with quantum-dimensional effects. Renormalization of the electron bands in Si caused by the quantum-dimensional effect was analyzed [5, 6] and the results are indeed in good agreement with both the spectral composition of the luminescence and with the fact of its dramatic enhancement for the case of quantum dot-shaped structures. In view of the above, it is important to study the factors that under various conditions define the function of the size distribution of the quantum dots $F(R)$. The problem is that, as indicated by analysis of the experimental data available up to now [2, 3, 7], silicon nanoparticles in high-concentration solutions are formed according to a scenario which in some respects differs from that described by the well-known coalescence model [8, 9].

The objective of the present paper is to analyze those experimental data available for the SiO$_2$:Si system which do not fit into the existing views on the growth of the new phase nuclei in the process of a diffusion-controlled phase decomposition of supersaturated solid solutions at the stage of overcondensation, and to describe a theoretical model capable of explaining them.

2. There are several techniques used to create silicon quantum dots. One of the most promising technologies is based on a heavy-dose implantation of high-energy Si$^+$ ions into SiO$_2$ followed by isothermal annealing, which results in formation of silicon precipitates in SiO$_2$. The results obtained [2, 4] and other works have revealed the most favorable conditions for the formation of silicon nanoparticles with a high quantum efficiency and designated spectrum of emission. These conditions are: Si$^+$ ion beam energy of 200 to 250 KeV, implantation dose ranging from $6 \cdot 10^{16}$ to $6 \cdot 10^{17}$ cm^{-2}; annealing temperature from 1100 to 1300°C, annealing time ranging from 15 to 120 min, and nitrogen as a preferred annealing ambient. The initial samples subjected to ion implantation are silicon wafers with a thin (~500 nm) SiO$_2$ layer grown on them. With these technological parameters, implantation of SiO$_2$ with Si$^+$ ions followed by annealing creates in the SiO$_2$ layer silicon precipitates with

sizes ranging from 2 to 16 nm, which exhibit photoluminescence in the 650 to 1000 nm spectral range. As for the experimental data on the growth kinetics of these precipitates [2, 4, 7], they were explained in terms of the conventional coalescence model. According to this model, when the solution reaches a certain level of supersaturation at the first stage the fluctuations result in the emergence of nuclei of the new phase with the critical size R_0 inversely proportional to the supersaturation level $\Delta\mu_o$. Formation and the subsequent growth of these nuclei is accompanied with a reduction of the supersaturation to a level $\Delta\mu_1$, which allows new nuclei with a size $R_1 > R_0$ to emerge. The precipitated nuclei of R_1 size result in a further decrease of the supersaturation level, and so on until at a steady-state supersaturation level formation of nuclei of a new size R_K becomes unfavorable from the viewpoint of thermodynamics. At a steady-state supersaturation level $\Delta\mu_K$, any further growth of nuclei having «supercritical» sizes is possible only at the expense of consumption of smaller nuclei, i.e. due to dissolution of nuclei having «subcritical» sizes. In the framework of this scenario, well-known analytical expressions [8, 9] describe the evolution in time of the nuclei's size $R(t)$, number $M(t)$, and define the function $F(R)$. Let us compare the functions defined by these expressions with the dependences derived from the experimental data for the SiO_2:Si system [2].

Fig. 1 shows the $R(t)$ dependence deduced from the results presented in Fig. 4 of the paper [2]. To plot this dependence, we used the values R corresponding to the maximum of $F(R)$ at different annealing times t. In terms of the theory [8, 9], the $R(t)$ dependence should be fairly well described by the following function:

$$R = (4\alpha\Delta t/9)^{1/3}; \qquad (1)$$

where α is a coefficient associated with the interface tension between the two phases, and D is the diffusion coefficient of Si in SiO_2 at the temperature of annealing T.

As evident from Fig. 1, the experimental and theoretical data do not conform with each other. Several dependences $R = A \cdot t^{1/3}$ shown in Fig. 1 were computed for different values of A selected from the condition of best fit for the experimental $R(t)$ dependence at $t = 15$ min, 30 min, 60 min, and 120 min.

The total number of the new phase nuclei M, according to [8, 9], should decrease with time as

$$M = Q/(2D\omega t), \qquad (2)$$

where Q is the total initial level of supersaturation;

$$\omega = 2\alpha/(NkT)$$

N is the actual concentration of the «gaseous» Si component in SiO_2.

Furthermore, though no comprehensive data on the time dependence of M are available (since it is quite difficult to detect in the SiO_2 matrix silicon precipitates smaller than 2 nm), there are sufficient reasons to claim that description of the experimental dependence $M(t)$ with Eq. 2 also runs into problems. For example, it follows from the paper of Komoda et al. [2] that the number of smallest-size (2 nm) precipitates decreases with time more slowly than $1/t$, while the number of 16 nm precipitates is even growing. This type of time dependence of the number of nanoparticles of small (2 nm) and large (16 nm) sizes results in $F(R)$ transformation from the usual Gaussian function to a bimodal curve when the annealing time is increased from 15 to 120 min. This effect is accompanied with a spectral shift of the photoluminescence bands, which, in the opinion of the authors of some works [2, 3], was in a fair agreement with the time dependence of the size of light-emitting nanoclusters.

Spectral and temporal filtration of the signal performed by Blonskij et al. [10] has suppressed the background associated with the luminescence of defects in SiO_2, and thus revealed a finer structure of the photoluminescence bands in the spectral range of 650 to 1000 nm, which can be attributed to the emission from silicon nanoparticles. Using the results obtained by two groups of investigators [5, 6], one can estimate by the positions of the band maxima (660, 740, 870, and 1000 nm) the nanoparticle sizes corresponding to these discrete bands as 3.6, 4.1, 5.2, and 5.8 nm, respectively. This observation of the discrete band structure was ascribed [10] to a multimodal nature of $F(R)$. It should be noted that the experimental dependences [2], which illustrate the transformation of $F(R)$ from the Gaussian to a bimodal curve, are not smooth and allow an additional modulation of $F(R)$ in the domain of small R (2 to 6 nm).
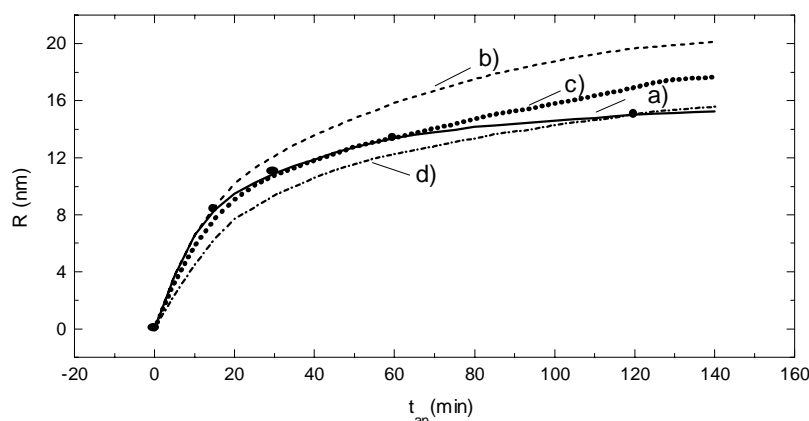
Fig. 1. Dependence of size R of Si nanoparticles in SiO_2 vs time t of annealing of the samples: (a) – experimental data; (b), (c), (d) – curves calculated for the fitting parameter values $A = 4$, 3.6, and 3 respectively.

A multimodal $F(R)$ dependence in a system of Si nanoclusters was revealed [7] also for deposited SiO_x films (x < 2) subjected to isothermal annealing in nitrogen ambient at 800°C. In the photoluminescence spectra of such samples, three intense and several weaker bands, which were also attributed to the nonuniform and strongly asymmetrical shape of $F(R)$, were detected [7].

Therefore, the above experimental data demonstrate a complex nature of the formation and evolution of Si nuclei in SiO_2. Their explanation requires a further development of the theory that should describe in more detail the processes of new phase nucleation in high-concentration solutions under the conditions of supersaturation.

3. It is well known from the kinetics of the phase transitions of first order that, when a solution reaches a certain level of supersaturation, nuclei of the new phase are starting to emerge. Spherical nuclei become stable when they exceed the critical size R_C, which is determined from the condition of free energy minimization and is described by the following expression:

$$R_C = 2\alpha/(\Delta\mu N_0), \qquad (3)$$

where $\Delta\mu = kT\ln(N/N_0)$ is the difference of chemical potentials for the atomic particle in different phases, N_0 is the concentration of defects in the case of thermodynamical equilibrium.

Precipitation of the new phase nuclei decreases the initial level of supersaturation, so that the nuclei formed at the subsequent stages can only be larger than R_C. The process of coalescence somewhat modifies the character of R evolution in time. However, as evident from [8, 9], it is quite difficult to explain the multimodality of $F(R)$ in the framework of the existing theoretical concepts of coalescence. The point is that, when considering the coalescence stage, the initial concentration of the solution is usually assumed to be insignificant, so that the emerging nuclei of the new phase are so distant from each other that their mutual influence can be neglected.

Let us try to lift this assumption and analyze the effect of particle-particle interactions on the shape of $F(R)$. This approach to interpretation of the experimental results appears to be reasonable in view of the very high initial concentration of the SiO_2:Si solution (for the case of ion-implanted samples under discussion, the concentration of Si in SiO_2 is as high as ${\sim}10^{22}$ cm^{-3}!). Therefore, for a system of this kind we will assume that a very high concentration of the dissolved substance and long annealing give rise to such a large number of Si nanoclusters of close sizes that one should take into account interactions between them in the space of sizes. The role of the field mediating in this interaction is played by variation of the supersaturation level. The process of interaction in the space of sizes can be qualitatively presented in such a way that dissolution of a «subcritical» nucleus and the growth of a «supercritical» nucleus at its expense depends on the presence in its vicinity of another nucleus with a similar size which would be its competitor in the growth process. Thus, we can speak about a repulsive interaction of nuclei with the same R in the space

of sizes. Obviously, the very fact of the presence in the solution of new phase nuclei with fixed sizes excludes the possibility of nuclei of the same size appearing in its vicinity, if only because of the local decrease of the initial supersaturation level. Therefore, the formal assumption about the interaction in the space of sizes makes it possible to describe a correlation between the possible sizes of the new phase nuclei. It means that we can speak about a generalized interpretation of a single-particle function of size distribution $F(R)$ as a conventional distribution described by the correlation function [12], when the zero count is taken at the zero size of an inclusion corresponding to the infinite supersaturation. A similar interpretation of the distribution function in the usual space is used to describe the liquid phase [12], when the concept of single-particle functions becomes incorrect because of a significant interaction.

Starting from this assumption, let us try to explain the nature of the experimentally observed $F(R)$ multimodality. For this purpose, one should write down and solve an equation for the correlation function of distribution, taking into account the interaction in the space of sizes. Using the superposition approximation in the theory of liquid [12], we can express the equation for the correlation function $g_2(R_{12})$ as

$$-kT\nabla_1 g_2(R_{12}) =$$
$$= \left[\nabla_2 V(R_{12}) + M\int dR_{13}\nabla_1 V(R_{13})g_2(R_{13})g_2(R_{23})\right]g_2(R_{13}), \quad (4)$$

where $\nabla_i V(R_{ij})$ is the derivative of the potential energy of the interaction between clusters sized R_i and R_j, while the operator ∇_i denotes the derivative with respect to the appropriate size.

The solution of this equation can be represented in the Boltzmannian form, in terms of the potential of two-particle interaction and a potential tail that arises because of its modification due to the role of indirect interactions [11]:

$$g_2(R_{12}) = exp\left(-\frac{V(R_{12})}{kT}\right)\tau(R_{12}), \qquad (5)$$

where $\tau(R_{12})$ is the component of the solution not accounted for by the direct interaction.

For many potentials of interaction, this solution is known and has an oscillating character similar to that exhibited by the experimental data on size distribution. The first maximum of the $g_2(R_{12})$ dependence for the interpretation proposed corresponds to such a size that smaller inclusions of the second phase are thermodynamically unfavorable. This size is determined by the maximum level of supersaturation and can be assessed using equation (3). If we assume that $\alpha \approx (4{\cdot}10^2 - 10^3)$ erg/cm^2, $T = 1150$°C, while $N \sim 10^{22}$ cm^{-3} and $N_0 \sim 2{\cdot}10^{16}$ cm^{-3}, which corresponds to typical experimental situations, we obtain $R_C \approx 3$ nm. One can see that this calculated value of the first maximum of the size distribution function is in reasonable agreement with the data obtained by structural analysis [2–4].

Therefore, it is logical to interpret the observed multimodality of $F(R)$ in the system of second-phase nanoclusters as a conjugation of cooperativity of their prop-

erties taking into account the interaction in the space of sizes. Effective interaction in the space of sizes, and thus transformation of the $F(R)$ dependence from the Gaussian to a multimodal shape, is facilitated by high concentration of Si in SiO_2, while the sharpness of the maxima increases with the annealing time.

Finally, we would like to conclude that the above discussion of the reasons for the appearance of $F(R)$ multimodality in the SiO_2:Si system is mostly qualitative. It has not yet explained a number of processes, such as the influence of the annealing ambient on the process of new phase nucleation and evolution in a supersaturated solution, though this influence is quite evident [2, 7]. Nevertheless, the «liquid» approach proposed in this work to explain the process of new phase nucleation in high-concentration solutions, such as those considered in the present paper, could be helpful for developing physical foundations for creation of a system of semiconductor quantum dots with designated properties, whatever the ultimate answer may be to the question about the nature of the radiative processes observed. This work was supported by the CRDF UP1-368 grant.

References

1. H. A. Atwater, K. V. Shcheglov, S. S. Wong, and K. J. Vahala, Mat. Res. Soc. Symp. Proc. **316**, 409 (1994).
2. T. Komoda, J. Kelly, F. Gristiano, A. Nejim, P. L. F. Hemment, K. P. Homewood, R. Gwilliam, S. E. Mynard, and B. J. Sealy, Nuclear Instruments and Methods in Physic Research, B **96**, 387 (1995).
3. T. Komoda, J. P. Kelly, R. M. Gwilliam, P. L. F. Hemment, and B. J. Sealy, Nuclear Instruments and Methods in Physic Research, B **112**, 219 (1996).
4. W. Skorupa, R. A. Yankov, I. E. Tyschenko, H. Frob, T. Bohme, and K. Leo, Appl. Phys. Lett. **68**, 2410 (1996).
5. T. Tahagahara and K. Takeda, Phys. Rev. B **46**, 15578 (1992).
6. C. Delerue, M. Lannoo, and G. Allan, J. Lumin. **57**, 247, (1993).
7. Qi Zhang and S. C. Bauliss, D. A. Hutt, Appl. Phys. Lett. **66**, 15, (1995).
8. I. M. Lifshyts and V. V. Slezov, JETP **35**, 475 (1958).
9. V. V. Slezov and Yu. Shmeltser, Fiz. Tv. Tel. (Sov.Phys. - Solid State), **39**, 2210 (1997).
10. I. V. Blonskij, M. S. Brodyn, B. I. Lev, P. M. Tomchuk, M.Ya.Valakh, and Yu. P. Piriatynski (unpublished).
11. J. M. Ziman, Models of disorder (Cambridge University Press, 1979).
12. C. A. Croxton, Liquid state physics a statistical mechanical information (Cambridge University Press, 1974).

БАГАТОМОДАЛЬНИЙ РОЗПОДІЛ РОЗМІРУ КРЕМНІЄВИХ НАНОКЛАСТЕРІВ В SiO₂ ЯК ПРОЯВ ВЗАЄМОДІЇ В ПРОСТОРІ РОЗМІРІВ

І. В. Блонський, Б. І. Лев, М. Я. Валах*

Інститут фізики НАН України
*Інститут фізики напівпровідників НАН України

Резюме. Узагальнені результати експериментальних досліджень, які засвідчують полімодальність функції розмірного розподілу кремнієвих наночасток в матриці SiO_2 в випадку сильного перенасичення розчину SiO_2:Si кремнійовою компонентою. Для пояснення природи полімодальності запропоновано «рідинний» підхід в описі стадії коалесценції, який оснований на врахуванні процесів міжчастинкової взаємодії в просторі розмірів. Запропонований підхід може виявитись перспективним для розвитку фізичних основ керування спектральним складом і інтенсивністю випромінювання кремнійових випромінювачів світла.

МНОГОМОДАЛЬНОЕ РАЗПРЕДЕЛЕНИЕ РАЗМЕРА КРЕМНИЕВЫХ НАНОКЛАСТЕРОВ В SiO₂ КАК ПРОЯВЛЕНИЕ ВЗАИМОДЕЙСТВИЯ В ПРОСТРАНСТВЕ РАЗМЕРОВ

И. В. Блонский, Б. И. Лев, М. Я. Валах*

Институт физики НАН Украины
*Институт физики полупроводников НАН Украины

Резюме. Обобщены результаты экспериментальных исследований, свидетельствующие о полимодальности функции размерного распределения кремниевых наночастиц в матрице SiO_2 в случае сильного пересыщения раствора SiO_2:Si кремниевой составляющей. Для объяснения природы полимодальности предложен «жидкостный» подход в описании стадии коалесценции, основанный на учете процессов межчастичного взаимодействия в пространстве размеров. Предложенный подход перспективен для развития физических принципов управления спектральным составом и интенсивностью излучения кремниевых излучателей света.