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GROWTH OF GERMANIUM QUANTUM DOTS ON OXIDIZED SILICON SURFACE

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Epitaxial growth of germanium quantum dots on an oxidized silicon surface is considered. A kinetic model of the nucleation and growth of three-dimensional islands by the Volmer–Weber mechanism in this system is proposed. The dependences of the average size and surface density of quantum dots on the parameters of their synthesis are obtained. The proposed theoretical model can easily be extended to other material systems in which island growth by the Volmer–Weber mechanism is realized.

Keywords: quantum dots, silicon, germanium, silicon oxide, nanoheterostructures, molecular beam epitaxy, critical thickness, Volmer–Weber mechanism, surface density, size distribution function.

INTRODUCTION

The germanium/silicon material system is currently one of the most promising for the development of semiconductor electronics and photonics. Structures with quantum dots of germanium in silicon are of interest from the point of view of creating high-speed transistors, photodetectors, and solar cells [1, 2]. The main way to create nanoislands is their self-organization during molecular beam epitaxy (MBE) of germanium on a silicon substrate [3]. Despite the fact that the processes of the epitaxial formation of quantum dots in this system have been studied for a long time, there are still many blank spots in this problem, especially concerning the theoretical description of the processes occurring at various stages of the nanoislands growth. New experimental works constantly appear that reveal unexpected effects during epitaxy in the germanium/silicon system [4, 5].

Of particular interest is the growth of germanium on the oxidized silicon surface [6–8]. It is in this system that islands with a record (extremely) high density of up to 10^{12}–10^{13} cm^{-2} and sizes less than 10 nm were obtained [8]. However, until now, the laws of the formation and subsequent growth of germanium nanoislands on the surface of silicon oxide have been poorly studied. There are no physical and mathematical models to calculate the surface density, average size, and size distribution function of islands in this material system. Only ordinal estimates of the surface density of quantum dots obtained in the framework of phenomenological theories of reaction rates are given [8]. Nevertheless, for the successful use of structures with high-density quantum dots, it is necessary to be able to predict the dependences of all the listed parameters of the nanoisland array on the conditions of their synthesis by the MBE method: temperature, growth rate, and amount of deposited material.

Difficulties in modeling the germanium quantum dots formation on an oxidized silicon surface are associated primarily with the fact that on this surface, a growth mechanism is realized that is fundamentally different from the case of a clean silicon surface. On an oxidized silicon surface, the Volmer–Weber growth mechanism without the formation of a wetting layer is realized. The second feature of the germanium islands formation on the silicon oxide surface is

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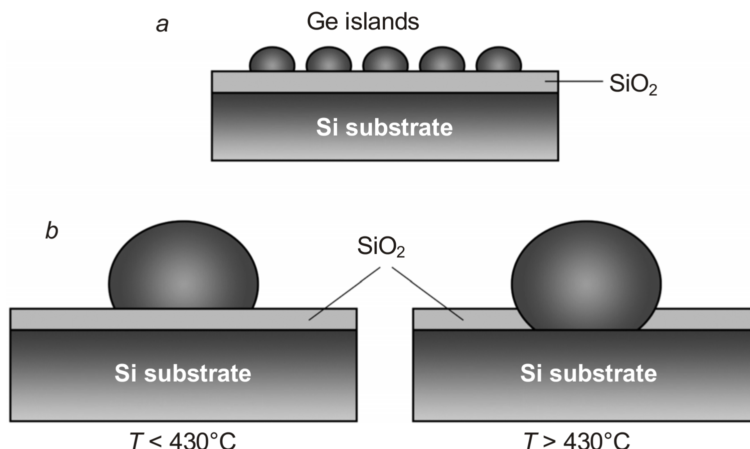


Fig. 1. Mechanisms of nucleation (*a*) and growth (*b*) of germanium islands on an oxidized silicon substrate, depending on the synthesis temperature.

another shape of the island – a hemispherical instead of the pyramidal one. Finally, depending on the growth temperature, germanium islands can form on the surface of silicon oxide (at low temperatures) or in pits formed due to the desorption of atoms denuding the clean surface of the silicon substrate (at high temperatures) [6–8].

The aim of this work is to construct a kinetic model of the nucleation and growth of three-dimensional germanium islands on the surface of silicon oxide by the Volmer–Weber mechanism.

THEORETICAL MODEL

We consider growth by the Volmer–Weber mechanism as the limiting case of growth by the Stransky–Krastanov mechanism when the critical thickness of the wetting layer tends to zero. Such a change in the growth regimes and the formation of islands practically without the formation of an intermediate two-dimensional layer occurs with an increase in the mismatch between the lattice constants of the deposited material and the substrate (Fig. 1). The lattice mismatch for germanium on a clean silicon surface is 4.2%, and for the germanium/silicon oxide system, it is 15.2%, which causes the implementation of the Volmer–Weber growth regime on the oxidized surface.

Similar to the formation of germanium islands on a clean silicon surface [9, 10], to construct a theoretical model of the germanium quantum dots growth on the silicon oxide surface, we find the change in the free energy of the system upon island formation.

Let us consider islands in the form of a spherical segment, since it is precisely such a shape that is observed experimentally in the $Ge/SiO_2/Si$ system [6–8].

We write the expression for the change in free energy upon nucleation of an island containing *i* atoms in the following form:

$$\Delta F(i) = \Delta F_{\mathrm{surf}}(i) + \Delta F_{\mathrm{elas}}(i) + \Delta F_{\mathrm{attr}}(i) . \quad (1)$$

This expression takes into account three competing factors affecting island formation: a change in the surface energy ΔF_{surf}, relaxation of elastic stresses ΔF_{elas}, and a decrease in the attraction of atoms to the substrate ΔF_{attr}.

The change in the surface energy ΔF_{surf} is the difference between the surface energy of the island boundary and the surface energy of the two-dimensional layer over an area equal to the area of the island base [10, 11].

The surface area *S* of the island in the form of a spherical segment with a base diameter *L* and a height *H* is

$$S = \pi\left(a^2 + H^2\right) = \frac{\pi L^2}{4}\left(4\kappa^2 + 1\right), \quad (2)$$

where $a = L/2$ is the radius of the island base, $\kappa = H/L$ is the ratio of the island height to the diameter of the island base. The base area S_0 of the spherical segment is

$$S_0 = \frac{\pi L^2}{4}. \quad (3)$$

Then, the change in the surface energy ΔF_{surf} during the island formation is

$$\Delta F_{\text{surf}} = \gamma S - \gamma_0 S_0 = \frac{\pi L^2}{4}\left[\gamma\left(4\kappa^2 + 1\right) - \gamma_0\right], \quad (4)$$

where γ_0 and γ are the specific surface energies of the base and free surface of the island, respectively.

The dependence of ΔF_{surf} on the number of atoms in an island can be determined using the relationship between the number of atoms in an island i and its characteristic size L. The number of atoms in an island is defined as the ratio of the island volume V_{isl} to the volume occupied by one atom Ω_0: $i = V_{\text{isl}} / \Omega_0$. The volume per atom in the island can be estimated as the product of the square of the distance between the atoms on the substrate surface l_0 and the height of one monolayer of the deposited material d_0: $\Omega_0 = l_0^2 d_0$. In turn, the volume V_{isl} of a spherical segment with the base diameter L and height H is

$$V_{\text{isl}} = \frac{\pi h}{6}\left(3a^2 + H^2\right) = \frac{\pi\kappa L}{6}\left(\frac{3L^2}{4} + \kappa^2 L^2\right) = \frac{\pi\kappa L^3}{24}\left(4\kappa^2 + 3\right). \quad (5)$$

Therefore, the relationship between the number of atoms i in an island and its lateral size L can be written as

$$i = \frac{V_{\text{isl}}}{\Omega_0} = \frac{\pi\kappa L^3}{24 l_0^2 d_0}\left(4\kappa^2 + 3\right) = \left(\frac{L}{\alpha l_0}\right)^3, \quad (6)$$

where α is the geometric factor determined by the shape of the island:

$$\alpha = \left[\frac{24 d_0}{\pi\kappa l_0\left(4\kappa^2 + 3\right)}\right]^{1/3}. \quad (7)$$

Using expressions (4) and (6), we obtain the change in the surface energy ΔF_{surf} during the island formation as a function of the number of atoms in it:

$$\Delta F_{\text{surf}}(i) = \frac{\pi}{4}\left[\gamma\left(4\kappa^2 + 1\right) - \gamma_0\right]\alpha^2 l_0^2 i^{2/3}. \quad (8)$$

Now, expression (1) can be written as

$$\Delta F(i) = A i^{2/3} - B\zeta i, \quad (9)$$

where

$$A = \frac{\pi}{4}\left[\gamma\left(4\kappa^2 + 1\right) - \gamma_0\right]\frac{\alpha^2 l_0^2}{k_B T}, \quad (10)$$

$$B = \frac{\left(1 - Z\right)\lambda\varepsilon_0^2 l_0^{\,2} d_0}{k_B T}\ln\left\{\frac{\Psi_0}{d_0\left(1 - Z\right)\lambda\varepsilon_0^2}\right\}, \quad (11)$$

Z is the elastic energy relaxation coefficient [12], λ is the elastic modulus of the deposited material, ε_0 is the lattice mismatch of the deposited material and the substrate, Ψ_0 is the density of the wetting energy on the substrate surface, h is the two-dimensional layer thickness, k_0 is the relaxation coefficient [13, 14], k_B is the Boltzmann constant, T is the substrate temperature, $\zeta = (h / h_{eq} - 1)$ is the overstress of the two-dimensional layer, and h_{eq} is the equilibrium thickness of the two-dimensional layer.

Then, the critical number of atoms in the island i_c is calculated, at which the function $\Delta F(i)$ reaches its maximum and the activation barrier of nucleation is $\Delta F(i_c)$. Further, according to the Zeldovich formula, the nucleation rate of coherent islands is determined [14]. The critical thickness h_c of the transition from the two-dimensional growth to the three-dimensional one is determined by solving the following transcendental equation for critical overstress

$\zeta_c = (h_c / h_{eq} - 1)$ [10, 11]:
$$\frac{4}{3\sqrt{\pi}}\frac{h_{eq}}{d_0}\frac{\zeta_c}{2a\left(\zeta_c + 1\right)F\left(\zeta_c\right)}\left[\frac{2F\left(\zeta_c\right)}{\zeta_c^{\,2}}\frac{\tau}{t_{eq}}\right]^{\frac{5}{2}}\exp\left[F\left(\zeta_c\right)\right] = 1, \quad (12)$$

where $t_{eq} = h_{eq} / V$ is the growth time of a layer of equilibrium thickness and V is the growth rate. All further calculations of the kinetics of the quantum dots formation by the Volmer–Weber mechanism are carried out similarly to the case of growth according to the Stransky–Krastanov model [11, 15], but with parameters recalculated according to the above formulas.

RESULTS AND DISCUSSION

When calculating the characteristics of the array of germanium quantum dots on the oxidized silicon surface, the following values were used for the parameters of the theoretical model [6, 8, 11, 14]: $l_0 = 0.3$ nm, $d_0 = 0.145$ nm, $\gamma = \gamma_0 = 800$ erg/cm^2, $\lambda = 1.27\cdot10^{12}$ dyn/cm^2, $\varepsilon_0 = 0.152$, $\Psi_0 = 450$ erg/cm^2, $\kappa = 0.1$, $Z = 0.7$, $k_0 = 0.8$, $\nu = 10$, and $D(T) = 2\cdot10^{-8}\exp(-0.67 / k_B T)$ cm^2/s.

First of all, the equilibrium thickness of the two-dimensional layer h_{eq} was found for the growth of quantum dots in the $Ge/SiO_2/Si(001)$ system according to the Volmer–Weber mechanism. In accordance with the Muller–Kern criterion [13], for a layer thickness of $h < h_{eq}$, layer-by-layer growth of one material on the surface of another is realized. With an increase in $h > h_{eq}$, a transition from a two-dimensional growth to the island growth is observed, which leads to a decrease in the total energy of the system due to the relaxation of elastic stresses [14]. As a result, using the above parameters, for the equilibrium thickness of the two-dimensional layer, we obtained the value of $h_{eq} = 0.92$ ML (monolayers), i.e., less, than one monolayer, as it should be for the Volmer–Weber mechanism.

Figure 2 shows the dependence of the change in free energy upon island nucleation on the number of atoms i in it at a deposited germanium layer thickness $h = 1.1$ ML and temperature $T = 400$°C.

For thicknesses of a two-dimensional layer greater than h_{eq}, the free energy function is limited. There is a critical number of atoms in the island i_c, after which the free energy of the system decreases with the attachment of new atoms to the island. This maximum corresponds to the potential barrier for nucleation, which must be overcome by a three-dimensional island for further growth. For example, at a thickness of the deposited germanium layer of $h = 1.1$ ML, a maximum is reached when the number of atoms in the nucleus is $i_c \approx 21$, and its value is $\Delta F(i_c) \approx 3\ k_B T$. With an increase in the thickness of the deposited layer of the material and the growth temperature, the probability of

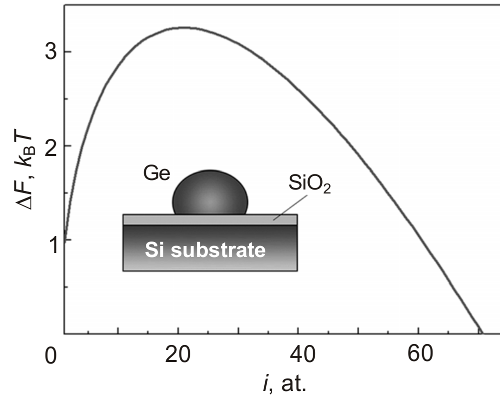


Fig. 2. Function of the free energy change at a thickness of the deposited germanium layer $h = 1.1$ ML and a temperature $T = 400°C$.

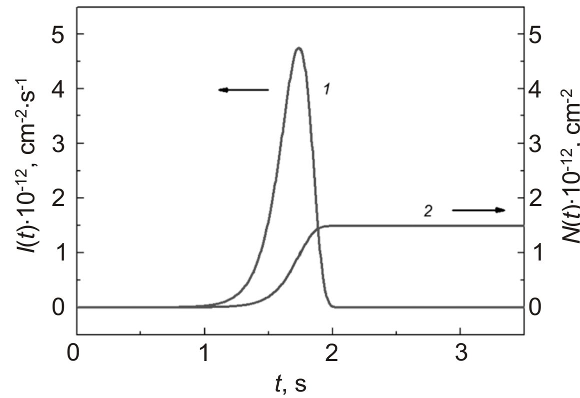


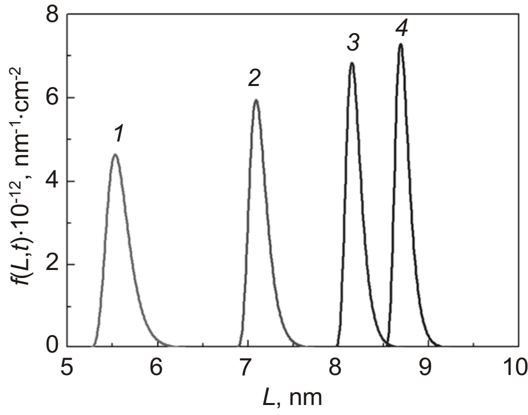
Fig. 3. Time dependence of the nucleation rate (*1*) and surface density (*2*) of islands for the growth temperature $T = 400°C$ and the deposition rate of germanium of $V = 0.07$ ML/s.

overcoming the thermodynamic nucleation barrier increases. Thus, at a wetting layer thickness of $h > 0.92$ ML, the transition from the two-dimensional growth to the three-dimensional one becomes thermodynamically possible.

The non-monotonous nature of the free energy function behavior is explained by an initial increase in the surface energy of the island boundary and a subsequent decrease in the elastic stress energy. Thus, the physical mechanism of the transition from the two-dimensional growth to the island growth is determined by the balance between the increase in the surface energy and relaxation of elastic stresses caused by the mismatch of the crystal lattice parameters of the deposited material and the substrate [16]. For the growth according to the Volmer–Weber mechanism, the process of the quantum dots formation on the substrate surface without growth of a two-dimensional layer is realized.

The critical thickness of the two-dimensional layer is found from equation (12). For example, for a growth temperature of $T = 400°C$ and a germanium deposition rate of $V = 0.07$ ML/s, it is $h_c = 1.04$ ML. That is, the formation of three-dimensional islands occurs almost immediately with the formation of the first monolayer. The obtained value of the critical thickness fully corresponds to experiments on the growth of the germanium quantum dots on the surface of silicon oxide [6–8].

Figure 3 shows the time dependences of the nucleation rate and surface density of islands for the growth temperature $T = 400°C$ and the germanium deposition rate $V = 0.07$ ML/s. According to Fig. 3, as in case of growth



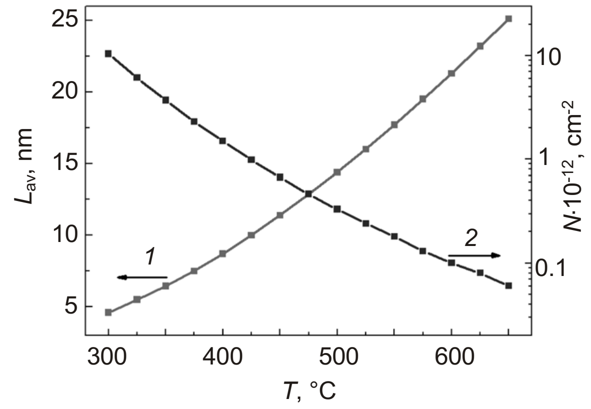


Fig. 4

Fig. 5

Fig. 4. Size distribution function of islands $f(L, t)$ for a growth temperature T = 400°C and germanium deposition rate V = 0.07 ML/s at different instants of time t: 20 s (*1*), 40 s (*2*), 60 s (*3*), and 80 s (*4*).

Fig. 5. Dependences of the average size (*1*) and surface density (*2*) of islands on the Si(111) surface on the synthesis temperature at a growth rate of V = 0.07 ML/s.

according to the Stransky–Krastanov mechanism [17], the fastest process is the nucleation of islands. The duration of this stage is about 1 s. The surface density of islands for these conditions is $N = 1.5 \cdot 10^{12}$ cm^{-2}. At the same time, further growth of the islands to their stationary size is much slower, and the average size of the islands at the end of growth is L_{av} = 8.7 nm. These values of the surface density and average size of the islands are in good agreement with experimental data on the growth of germanium islands on the oxidized silicon surface [6–8].

The time evolution of island sizes is shown in Fig. 4, which shows the size distribution function of islands $f(L, t)$ at different instants of time.

According to Fig. 4, the average size of nanoclusters increases with time, while the relative size variation of the islands decreases slightly.

From the point of view of practical applications, the dependences of the parameters of the formed quantum dots arrays on the conditions of their synthesis are of interest. Figure 5 shows the dependences of the average size and surface density of germanium quantum dots on the oxidized silicon surface on the growth temperature.

As in case of the germanium islands growth on a clean silicon surface, the average size of nanoclusters on the surface of silicon oxide decreases with an increase in the deposition rate and a decrease in the growth temperature. The surface density of the islands, on the contrary, increases with an increase in the deposition rate and a decrease in temperature. It should be noted that the surface density of islands on the oxidized silicon surface increases almost linearly with the deposition rate ($N \sim V$), in contrast to the case of a clean silicon surface, which is characterized by a steeper power law dependence: $N \sim V^{3/2}$ [11]. From the theory of reaction rates, it is known that the exponent p in the dependence $N \sim V^p$ is the larger, the larger the critical nucleus size [8]. This means that for the Ge/SiO_2/Si system, the critical atom size and critical thickness are much smaller than those for the Ge/Si system, which is confirmed by the previous consideration and the results of experimental studies.

CONCLUSIONS

Thus, in the Ge/SiO_2/Si(001) material system, growth by the Volmer–Weber mechanism is really realized with the formation of islands directly on the substrate surface without the formation of a wetting layer. The approximation of the Volmer–Weber mechanism consideration as the limiting case of growth according to the Stransky–Krastanov model

is valid. The proposed theoretical model can easily be extended to other material systems in which islands growth by the Volmer–Weber mechanism is realized.

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REFERENCES

1. R. M. H. Douhan, A. P. Kokhanenko, and K. A. Lozovoy, Russ. Phys. J., **61**, No. 7, 1194–1201 (2018).
2. I. I. Izhnin, O. I. Fitsych, A. V. Voitsekhovskii, *et al*., Opto-Electron. Rev., **26**, 195–200 (2018).
3. K. A. Lozovoy, A. P. Kokhanenko, and A. V. Voitsekhovskii, Nanotechnology, **29**, 054002 (1–7) (2018).
4. T. David, J.-N. Aqua, K. Liu, *et al*., Sci. Rep., **8**, 2891 (1–10) (2018).
5. K. Liu, I. Berbezier, L. Favre, *et al*., Phys. Rev. Mater., **3**, 023403 (1–7) (2019).
6. A. I. Nikiforov, V. V. Ul'yanov, O. P. Pchelyakov, *et al.,* Phys. Solid State, **46**, 77–79 (2004).
7. N. L. Rowell, D. J. Lockwood, A. Karmous, *et al*., Superlattices and Microstructures, **44**, 305–314 (2008).
8. A. A. Shklyaev and M. Ichikava, Phys.-Usp., **51**, 133–161 (2008).
9. K. A. Lozovoy, A. P. Kokhanenko, and A. V. Voitsekhovskii, Phys. Chem. Chem. Phys., **17**, No. 44, 30052–30056 (2015).
10. V. G. Dubrovskii, G. E. Cirlin, and V. M. Ustinov, Phys. Rev. B, **68**, P, 075409 (1–9) (2003).
11. V. G. Dubrovskii, Nucleation Theory and Growth of Nanostructures, Springer, Berlin (2014).
12. X. Zhang, V. G. Dubrovskii, N. V. Sibirev, and X. Ren, Crystal Growth & Design., **11**, 5441–5448 (2011).
13. P. Muller and R. Kern, Appl. Surf. Sci., **102**, 6–11 (1996).
14. S. A. Kukushkin and A. V. Osipov, Phys.-Usp., **41**, 983–1014 (1998).
15. K. A. Lozovoy, A. P. Kokhanenko, and A. V. Voitsekhovskii, Crystal Growth & Design, **15**, No. 3, 1055–1059 (2015).
16. O. P. Pchelyakov, Yu. B. Bolkhovityanov, A. V. Dvurechenskii, *et. al*., Semiconductors, **34**, 1229–1247 (2000).
17. A. P. Kokhanenko, K. A. Lozovoy, and A. V. Voitsekhovskii, Russ. Phys. J., **60**, No. 11, 1871–1879 (2018).