

---

---

**LOW-DIMENSIONAL  
SYSTEMS**

---

---

# Threshold Behavior of the Formation of Nanometer Islands in a Ge/Si(100) System in the Presence of Sb

G. E. Cirlin<sup>\*^</sup>, V. G. Dubrovskii<sup>\*\*</sup>, A. A. Tonkikh<sup>\*</sup>, N. V. Sibirev,  
V. M. Ustinov<sup>\*\*</sup>, and P. Werner<sup>\*\*\*</sup>

<sup>\*</sup>*Institute for Analytical Instrumentation, Russian Academy of Sciences, Rzhskii pr. 26, St. Petersburg, 190103 Russia*  
<sup>^</sup>*e-mail: cirlin@beam.ioffe.ru*

<sup>\*\*</sup>*Ioffe Physicotechnical Institute, Russian Academy of Sciences, Politekhnicheskaya ul. 26, St. Petersburg, 194021 Russia*

<sup>\*\*\*</sup>*Max-Planck Institut für Mikrostrukturphysik, Weinberg 2, D-06120 Halle, Germany*

Submitted September 14, 2004; accepted for publication September 29, 2004

**Abstract**—Atomic-force microscopy is used to study the behavior of an array of Ge islands formed by molecular-beam epitaxy on an Si (100) surface in the presence of an antimony flux incident on the surface. It is shown that, as the Sb flux increases to a certain critical level, the surface density of the islands increases; however, if this critical level is exceeded, nucleation of the islands is suppressed and mesoscopic small-height clusters are observed on the surface. This effect is explained qualitatively in the context of a kinetic model of the islands' formation in heteroepitaxial systems mismatched with respect to their lattice parameters. © 2005 Pleiades Publishing, Inc.

## 1. INTRODUCTION

A large number of publications have been devoted to the physical properties and formation methods of nanodimensional Ge inclusions in an Si matrix. The interest of researchers in this field is caused, to a great extent, by the potential of using these inclusions as active elements of light-emitting and detecting devices based on silicon. For device applications, it is necessary to obtain a dense array of nanodimensional Ge islands on the Si surface, which can be accomplished, for example, using epitaxial technologies, in particular, molecular-beam epitaxy (MBE). An array of elastically stressed islands with nanometer-scale sizes is formed according to the Stranski–Krastanov mechanism as a result of the deposition of several Ge monolayers onto the surface of a single-crystal Si substrate using MBE. In general, the disadvantages of this method consist in a fairly large spread of the islands in relation to their shape and size. For example, in a temperature range from 550 to 600°C, two types of islands can be formed, i.e., multifaceted dome-shaped islands and pyramidal hut-shaped islands [1]. It has previously been shown [2] that, in growing the Ge islands on an Si substrate in a temperature range of 550–600°C, one can reduce the spread in the islands' sizes by exposing the surface simultaneously to fluxes of Sb<sub>4</sub> molecules and Ge atoms.

In this paper, we report the results of experiments with the growth of Ge islands at various Sb<sub>4</sub> fluxes incident on the substrate surface. The results obtained are discussed from the standpoint of the kinetic theory of formation of islands in systems that are mismatched with respect to their lattice parameters.

## 2. EXPERIMENT AND RESULTS

We used atomic-force microscopy (AFM) to experimentally study the effect of Sb surface concentration on the properties of an array of Ge islands on the Si (100) surface of the samples obtained as a result of growth experiments in an MBE system.

The samples under study were grown in a Riber SIVA-45 epitaxial system. A 100-nm-thick Si buffer layer was grown on the Si (100) surface for each sample. A Ge layer with an effective thickness of 0.8 nm was then deposited onto the Si buffer layer at a substrate temperature of 550°C; in all the cases, the deposition of Ge was accompanied by exposure of the surface to an antimony flux. The Ge growth rate was 0.016 nm/s. The Sb<sub>4</sub> flux was varied by adjusting the temperature of the antimony effusion source in a range from 450 to 550°C. In the course of the Ge deposition, the state of the surface was monitored using a system for reflection high-energy electron diffraction (RHEED). For samples 1–4 (see table), the RHEED pattern changed (the line reflections were replaced by point reflections) in the course of the formation of the Ge islands. This observation indicates that the elastically stressed Ge layer transforms into a system consisting of islands and a wetting layer. For sample 5, grown at the highest temperature of the antimony source, the RHEED pattern remained mainly linelike, and the lines corresponding to the most important reflections became thicker. Upon completion of the growth process, the samples were cooled to room temperature, removed from the growth chamber, and exposed to air. The samples' surfaces were then studied in a contactless mode using a Digital Instruments Inc. (USA) atomic-force microscope (AFM). NSC15/NoAl tips, produced by MicroMasch, were used in the AFM measurements.

The results of AFM measurements

Sample no.	Sb source temperature, °C	Multifaceted islands			Pyramidal islands		
		Base, nm	Height, nm	Density, cm <sup>-2</sup>	Base, nm	Height, nm	Density, 10 <sup>10</sup> cm <sup>-2</sup>
1	450	64.0	9.3	2.4 × 10 <sup>9</sup>	39.3	3.38	1.1
2	475				38.5	2.90	1.8
3	500				35.1	2.99	3.4
4	525				29.6	1.15	6.7
5	550	–	–	–	–	–	–

The main parameters of the growth experiments and the results of the AFM measurements are listed in the table.

In Fig. 1a, we show the AFM image of sample 1. It can be seen that pyramidal islands are present on the sample surface; the dome-shaped islands, which are not observed on other samples, are also present. This circumstance indicates that the effect of Sb on the formation of Ge islands is insignificant at a Sb source temperature of 450°C. Furthermore, the distributions in the shape and size of the islands are bimodal, as in the case of the deposition of pure Ge on the Si (100) surface [1]. Comparing this result with those reported in [2], we note that, in the case of the deposition of pure Ge on the Si surface at a substrate temperature of 450°C, the formation of the dome-shaped islands is accompanied by the formation of hut-shaped islands with rectangular or square bases; at the same time, the presence of even a small amount of Sb on the surface leads to the disappearance of the hut-shaped islands with the rectangular bases. In Fig. 1b, we show the AFM image of a surface area for sample 4. In this case, the size distribution of the islands is more uniform, their density is much higher, and their sizes are smaller than for sample 1. As the temperature of the Sb source is further increased to 550°C (sample 5), the structure changes radically. It follows from Fig. 1c that mesoscopic surface roughness with a characteristic height of less than 1 nm is observed for sample 5. This observation is consistent with the RHEED pattern obtained in situ. Thus, the nucleation of the islands at the surface becomes suppressed at a certain threshold value of the antimony flux. Experimental dependences of the surface density and the average lateral size of the islands on the temperature of the antimony source are shown in Fig. 2. As can be seen, the formation of islands in a Ge/Si(100) system exhibits threshold behavior in the presence of antimony; i.e., as the Sb concentration increases, the density of the islands' array first increases and then tends to zero as a certain threshold value of Sb concentration is exceeded. At the highest antimony flux used in this study, the suppression of the islands' formation and a transition to two-dimensional growth are observed.

This effect is typically related to a decrease in the system's surface energy (the surfactant-mediated growth) [3]. In order to clarify the origin of the observed effect, we undertook an additional theoretical study of Ge/Si growth processes with the involvement of Sb.

### 3. THEORETICAL MODEL AND DISCUSSION OF THE RESULTS

As was shown in [4–7], the kinetic stage of the formation of quantum dots, according to the Stranski–Krastanov mechanism in heteroepitaxial systems, can be described in terms of classical nucleation theory [8]. The following expression was derived for the critical layer thickness that corresponds to a transition from two-dimensional to three-dimensional growth on the basis of the model suggested by Dubrovskii *et al.* [5] for the free energy of the islands' formation:

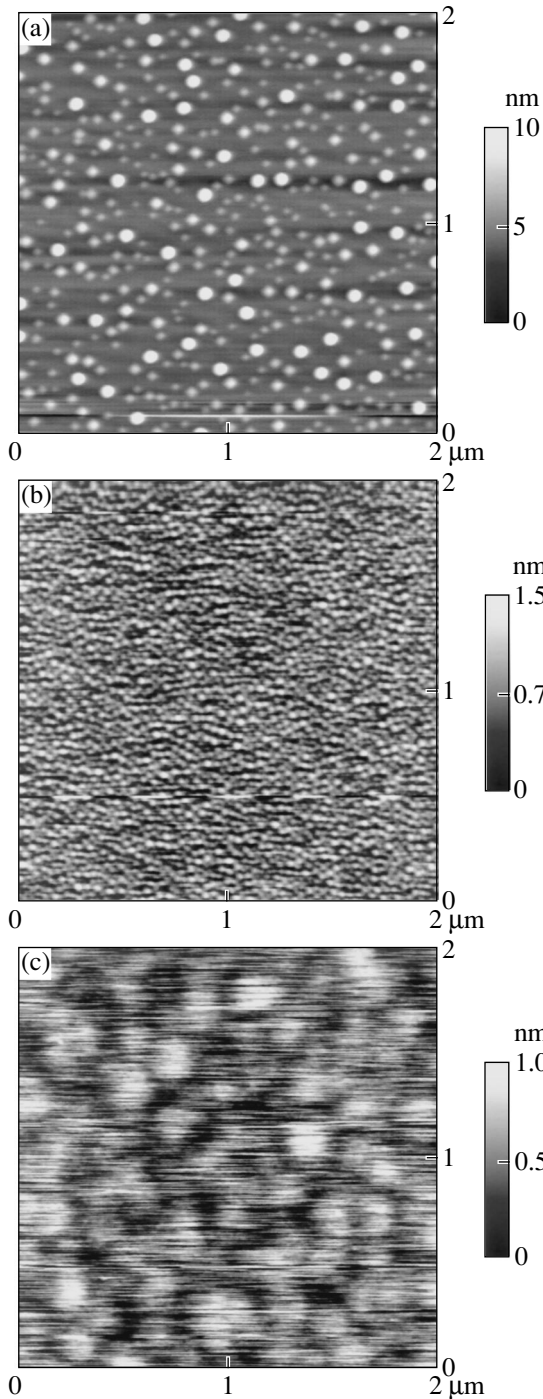
$$h_c = h_{eq} \left[ 1 + \left( \frac{2}{5} \frac{T_c}{T \ln Q} \right)^{1/2} \right]. \quad (1)$$

Here,  $h_{eq}$  is the equilibrium thickness of the wetting layer ( $h_{eq}$  is determined from the balance between the elastic and wetting forces [9] and is independent of the growth kinetics);  $T$  is the substrate temperature during the growth of the layer with quantum dots (this temperature is assumed to be constant);  $T_c$  is a quasi-equilibrium parameter that has the dimensions of temperature and is controlled by the surface energy, the islands' shape, and the lattice mismatch; and  $Q$  is a dimensionless kinetic parameter that depends on the conditions of epitaxial growth. As was shown in [5–7], the physical meaning of the parameter  $Q$  is the following:  $Q$  is the ratio between the characteristic time for the deposition of a material onto the surface and that for the growth of coherent islands from the atoms of the wetting layer. As a consequence, the dependence of  $Q$  on temperature  $T$  and the deposition rate  $V$  of the material is given by

$$Q \propto \frac{1}{V} \exp\left(-\frac{E_D}{k_B T}\right), \quad (2)$$

where  $k_B$  is the Boltzmann constant. The activation barrier  $E_D$  affects the rate at which the atom diffusion, caused by elastic stresses [4] and directed from the wetting layer to the islands, occurs.

We now consider the most important results of theoretical studies concerned with the formation kinetics of supercritical quantum dots (at an effective deposited-layer thickness  $H_0$  that appreciably exceeds  $h_c$ ). These results were reported in [5–7]. The nucleation of the islands occurs in the time period from  $t_c - \Delta t$  to  $t_c + \Delta t$ , where  $t_c = h_c/V$  is the time interval for growing a critical-thickness layer under the given conditions of heteroepitaxial growth. Upon completion of the nucleation

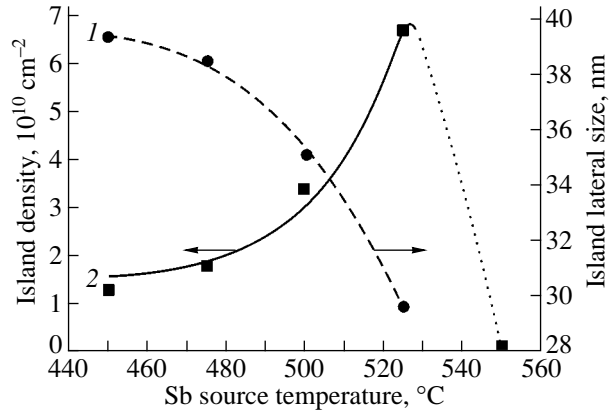


**Fig. 1.** AFM images of the surface for (a) sample 1, (b) sample 4, and (c) sample 5. The scanned area is  $2 \times 2 \mu\text{m}^2$  for all the samples.

stage (at  $t > t_c + \Delta t$ ), the surface density of the islands  $N$  attains the constant value

$$N = N_0 \frac{T}{T_c} \left( \frac{\ln Q}{Q} \right)^{3/2}. \quad (3)$$

Here,  $N_0$  is a known constant that is independent of the growth conditions. Upon completion of the nucleation



**Fig. 2.** Experimental dependences of (1) the average lateral size and (2) the density of islands on the Sb source temperature for samples 1–5.

stage, a longer stage sets in during which relaxation of the islands' sizes occurs. The average lateral size  $L$  of the islands increases to its quasi-stationary value  $L_R$  at  $t \approx t_c + 3t_R$ , where  $t_R$  is the characteristic time of the islands' size relaxation. The quasi-stationary average size of the islands depends on their surface density and also on the effective thickness of the deposited layer:

$$L_R = C_0 \left( \frac{H_0 - h_{eq}}{N} \right)^{1/3}. \quad (4)$$

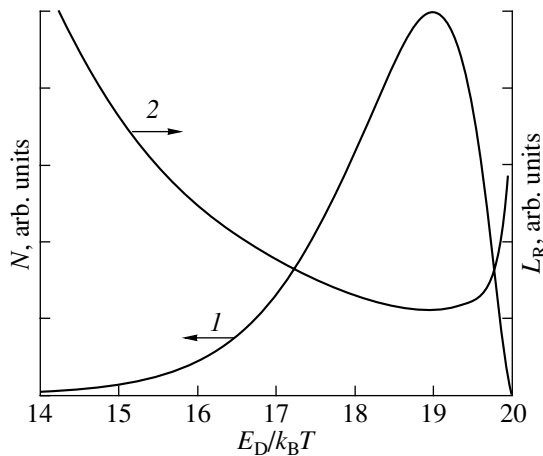
Here,  $C_0$  is a dimensionless constant controlled by the shape of the islands. This shape is assumed to be independent of the growth conditions in the kinetic stage of the islands' formation.

In the case where the structure was not exposed to the antimony flux (for example, if the surface was immediately cooled or the structure was overgrown at a low temperature after interruption of the growth of the layer with quantum dots), the experimental value of the islands' average size can be much smaller than  $L_R$ . The time dependence of the average size is given by  $L = L_R f[(t - t_c)/t_R]$ , where  $f(x)$  is an ascending function of  $x$  (this function was defined in [7]; it is important that  $f(0) = 0$  and  $f(3) \approx 1$ ). In the absence of exposure of the surface to the antimony flux, the islands' size  $L(t_0)$  at the instant ( $t_0 = H_0/V$ ) when the growth was interrupted after the deposition of the  $H_0$  Ge monolayers is given by

$$L(t_0) = L_R f \left( \frac{H_0 - h_c}{V t_R} \right). \quad (5)$$

An analysis of recent results [5–7] suggests that the dependences of the characteristic durations of the nucleation stage and the stage in which the size relaxation on  $Q$  occurs can be written as

$$\Delta t \propto \frac{1}{(\ln Q)^{3/2}}, \quad t_R \propto \frac{1}{(\ln Q)^{5/6}}. \quad (6)$$



**Fig. 3.** Dependences of (1) the surface density of islands  $N$  and (2) their quasi-stationary lateral size  $L_R$  on the parameter  $E_D/k_B T$ ; this parameter increases as the Sb flux increases.

Further evolution of the system requires a long-term exposure of the structure and occurs at time instants that appreciably exceed  $t_c + 3t_R$ .

The condition for the applicability of classical nucleation theory consists in the smallness of the thermodynamic fluctuation in the subcritical region:  $\exp(F) \gg 1$ , where  $F$  is the nucleation-activation barrier height expressed in thermal units [10]. In the model under consideration, it is this condition that makes it possible to derive a relation between the lowest activation barrier for the islands' nucleation at the largest thickness  $h = h_c$  of the wetting layer and the kinetic parameter  $Q$  [5]:

$$F(h_c) = (5/2) \ln Q. \quad (7)$$

Formula (1), describing the critical thickness, is a consequence of expression (7), which represents a specific form of the free energy for coherent-island formation. Evidently, the condition for the applicability of nucleation theory is satisfied with confidence in the case of  $Q \gg 1$ , which was analyzed in detail in [5–7].

However, as follows from expression (2), the value of the kinetic parameter  $Q$  decreases exponentially as the surface temperature  $T$  decreases and the height of the activation barrier  $E_D$  for the diffusion of atoms from the wetting layer to an island increases. The physical cause of this phenomenon is a retardation of the diffusion processes at the surface due to either a decrease in temperature or the use of impurities that restrict the diffusive motion. As has been shown recently (see, for example, [2]), one such diffusion-restricting impurity for a Ge/Si system is Sb. In the context of a simplified model, we assume that an increase in the Sb source temperature and the corresponding increases in the Sb concentration on the surface appreciably increase the effective barrier height  $E_D$  for the diffusion of Ge atoms from the wetting layer into an island (the quantity  $E_D$

appears in  $Q$  in formula (3) for  $N$ ) and affects, to a lesser extent, the surface energy of the system (this energy appears in  $T_c$  in the same formula). Considering  $N$  and  $L_R$  as functions of  $Q$  for the constants  $T$ ,  $T_c$ , and  $H_0$ , we ascertain that, in accordance with formulas (3) and (4), the density of the islands invariably exhibits a maximum, whereas their quasi-stationary size exhibits a minimum at  $Q = e$ . At the instant of growth interruption  $t_0$ , the islands' size  $L(t_0)$ , in accordance with formula (5), decreases progressively in comparison with  $L_R$ . This decrease is caused by both an increase in the critical thickness  $h_c$  (see formula (1)) and an increase in the size-relaxation time  $t_R$  (see formula (6)). Thus, as  $Q$  decreases to the threshold value  $Q \sim e$ , the suppression of nucleation in the heteroepitaxial system sets in. The height of the activation barrier for nucleation is small according to formula (7); consequently, there are no thermodynamic obstacles to the formation of islands. However, in this case, the nucleation rate and the islands' surface density are profoundly affected by the preexponential kinetic factor in the corresponding expression [8], which is proportional to the diffusion rate. The islands just cannot form, since the mechanism by which materials are transported from the wetting layer to an island is lacking under the conditions of an almost complete suppression of diffusion; at the same time, the probability of atoms arriving directly from the molecular flux is low. Theoretical dependences of the islands' surface density  $N$  and their lateral size  $L_R$  upon completion of the relaxation stage on the height of the diffusion-activation barrier, expressed in the thermal units  $E_D/k_B T$ , are shown in Fig. 3.

We should note the satisfactory qualitative agreement existing between the experimental data (Fig. 2) and the results of the theoretical calculations (Fig. 3) in the context of the application of the model under consideration to an interpretation of the reported experimental data on the dependences of the density and average size of quantum dots in a Ge/Si(100) system on a Sb flux. Figures 2 and 3 both indicate that the dependence of the islands' formation on Sb concentration is of a threshold type. However, owing to the following reasons, we should not expect good quantitative agreement between the theory and experiment. First, a quantitative relation between the Sb source temperature and the surface concentration of the adsorbed Sb atoms is not clear. The same is also true for the relation between the Sb concentration and the value of the activation-barrier height for the diffusion of Ge atoms. Second, an increase in the Sb concentration brings about an increase in the surface energy of the islands' lateral faces and, consequently, also affects the height of the activation barrier for nucleation. Finally, nucleation theory itself is on the verge of the applicability domain at small values of the parameter  $Q \sim e$ ; therefore, this theory holds only qualitatively in this case.

## 4. CONCLUSION

The results obtained in this study indicate unambiguously that the behavior of the structural characteristics of quantum dots in a heteroepitaxial Ge/Si(100) system is nonmonotonic and threshold-like as the antimony concentration on the surface increases. This effect can be qualitatively explained as follows. At first, as the Sb flux increases, the surface density of the Ge islands increases significantly while, simultaneously, their lateral sizes decrease. This behavior is completely consistent with the mechanism that was outlined in [10] and described theoretically in [5–7]. The presence of Sb retards the diffusive supply of Ge atoms to the growing islands; as a result, the size of the islands decreases. The height of the activation barrier for the islands' nucleation also decreases; consequently, the nucleation rate for the islands and their surface density increase. However, a further inhibition of diffusion leads to quenching of the islands' nucleation in the system; therefore, the islands' density decreases drastically after a certain maximum value of this density has been attained. The time required for the nucleation and growth of the islands increases appreciably, and, as a result, their lateral size cannot attain the corresponding quasi-equilibrium value. As was shown, the threshold effect of quenching for nucleation can be qualitatively explained in the context of the kinetic model of coherent-island formation in heteroepitaxial systems [5–7]. However, quantitative studies require further development of the theory; in addition, more detailed experiments are needed.

## ACKNOWLEDGMENTS

This study was supported in part by the scientific program Low-Dimensional Quantum Structures of the Russian Academy of Sciences.

G.E. Cirlin acknowledges the support of Alexander von Humboldt Stiftung. A.A. Tonkikh thanks the Deutsche Forschungsgemeinschaft.

## REFERENCES

1. O. P. Pchelyakov, Yu. B. Bolkhovityanov, A. V. Dvurechenskiĭ, *et al.*, *Fiz. Tekh. Poluprovodn.* (St. Petersburg) **34**, 1281 (2000) [*Semiconductors* **34**, 1229 (2000)].
2. A. A. Tonkikh, G. E. Cirlin, V. G. Dubrovskii, *et al.*, *Fiz. Tekh. Poluprovodn.* (St. Petersburg) **38**, 1239 (2004) [*Semiconductors* **38**, 1202 (2004)].
3. I. Berbezier, A. Ronda, A. Portavoce, and N. Motta, *Appl. Phys. Lett.* **83**, 4833 (2003).
4. A. V. Osipov, F. Schmitt, S. A. Kukushkin, and P. Hess, *Appl. Surf. Sci.* **188**, 156 (2002).
5. V. G. Dubrovskii, G. E. Cirlin, and V. M. Ustinov, *Phys. Rev. B* **68**, 075409 (2003).
6. V. G. Dubrovskii, Yu. G. Musikhin, G. E. Cirlin, *et al.*, *Fiz. Tekh. Poluprovodn.* (St. Petersburg) **38**, 342 (2004) [*Semiconductors* **38**, 329 (2004)].
7. V. G. Dubrovskii, G. E. Cirlin, Yu. G. Musikhin, *et al.*, *J. Cryst. Growth* **267**, 47 (2004).
8. D. Kashchiev, *Nucleation: Basic Theory with Applications* (Butterworth Heinemann, Oxford, 2000).
9. P. Müller and R. Kern, *Appl. Surf. Sci.* **102**, 6 (1996).
10. F. M. Kuni, Preprint No. 84-178.E (ITP, Kiev, 1984).

*Translated by A. Spitsyn*