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Experimental and theoretical study of the influence of growth temperature on composition in self-assembled SiGe QD's

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Abstract

A detailed study of self-induced SiGe nanoislands on Si substrate formed at different substrate temperatures is presented. As a result of AFM investigations, the dependencies of the density, volume and shape of the islands on the growth temperature are established. Using Raman spectroscopy and HRXRD, the dependences of average values of strain and composition in the islands on the growth temperature are determined. Based on the experimental results and theoretical calculations, the dependence of SiGe island volume on Si content is established.

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1. Introduction

As the dimensions of semiconductor structures are reduced to tens of nanometers, their physical properties are strongly influenced by the confinement effect. In this connection, desirable parameters of electron and phonon energy spectra of nanostructures can be obtained by varying their size and shape. One of the most promising ways of producing nanostructures, in particular Ge/Si ones, is their self-induced growth in Stranski–Krastanov mode [1–4]. A physical background of this phenomenon is a significant reduction of the total energy of a strained heterosystem due to 2D–3D transition. Both shape and size of islands are strongly dependent on the growth temperature, T_g, nominal thickness of deposited Ge, d_{Ge}, and deposition rate. For $T_g \geq 600$ °C both pyramidal and dome-shaped islands are formed. Deposition of a small quantity of Ge (~8 ML) at temperatures below 600 °C results in appearance of small (<2 nm high and 20...60 nm wide) rectangular-based islands, called as "huts". Due to their small height-to-diameter ratio, huts may be more strained as compared with square-based pyramids and domes.

It is known [5] that Si content in islands increases significantly with the growth temperature. As we have shown in [6] and other authors in [7], the islands grown at 700 °C can contain up to 60% of Si. Such a significant value cannot be taken into account for by bulk Si diffusion from the substrate, because it needs much higher diffusion coefficient than that for bulk Si/Ge. A most probable is a surface diffusion from the region near the island base due to highly non-uniform strain fields in this region. The strain gradient drives Ge atoms from the wetting layer (WL) from the vicinity of the island base, where the strain is maximal, upwards onto the growing island [8], resulting in a partial strain relaxation of the near-base region. After the very thin (3–4 ML) WL is completely removed, Si substrate atoms start to diffuse into the islands. As the strain in the substrate around islands depends on the islands size, its value varies during the island growth. Under certain deposition conditions, at least two island types (pyramids and domes) with different sizes are formed. Therefore, the size-related

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dependence of the diffusivity on strain becomes still more complicated. As a result, a general problem of finding the dependence of Si content in the islands on their size is very complex. In order to establish such dependence, in this work, we first studied experimentally the variation of Si content in the islands with the growth temperature. Afterwards, using the obtained experimental dependence and calculated relation between the island volume and growth temperature, we finally obtained the dependence of the islands volume on Si content in them.

This work was aimed at determination of composition and strain variation in self-induced SiGe islands grown at different temperatures using Raman spectroscopy, high resolution X-ray diffraction (HRXRD), AFM and SIMS.

2. Experimental technique

The structures under investigation were grown by molecular beam epitaxy (MBE) on Si (001) substrate. The islands were formed from 8 to 9 monolayers (ML) of Ge deposited on 200 nm Si buffer. A series of samples were grown in the temperature range from 500 up to 750 °C. To avoid the oxidation of very small hut clusters grown at 500 °C with height of only 1–2 nm, they were capped with Si except those assigned for AFM measurements. Raman spectra were excited in back-scattering geometry at the room temperature using 488 nm Ar^+-laser line. The known frequencies of Ar^+-laser plasma lines were used for an accurate determination of the Raman peak frequencies.

HRXRD measurements were performed for 400 and 113 reflexes using double-crystal spectrometer with GaAs(100) monochromator. The samples were scanned within 5° near the exact Bragg angle value in both $\omega / 2\vartheta$ and ω modes. For analysis of the experimental data χ^2-technique was used which allows one to find both the average values of parameters and their deviations [9].

A morphology of the uncapped island layers was investigated by atomic force microscopy (AFM) using NanoScope IIIa operating in the tapping mode. Tip testing was performed before and after measurements in order to control the tip shape. The tips were highly symmetrical with a radius less than 6 nm at 10 nm distance from their ends. This allowed us to neglect the effect of convolution of the tip shape with the surface investigated via the nanoislands shape and size.

3. Results and discussion

Fig. 1 shows AFM images of SiGe nanoislands grown at different substrate temperatures (500, 600, 700, 750 °C) by deposition of the same $d_{Ge} \approx 9$ ML. The largest density of islands per unit area ($3 \cdot 10^{11}$ cm^{-2}) is observed for $T_g = 500$ °C, at which all islands are hut clusters with more or less elongated rectangular base. At 600 °C, the island density drops down to $1.2 \cdot 10^{10}$ cm^{-2}, only ~11% of them retaining pyramidal shape and other being dome-shaped. As the growth temperature increases to 700 °C, the total island density further decreases to $2.5 \cdot 10^{9}$ cm^{-2} with the

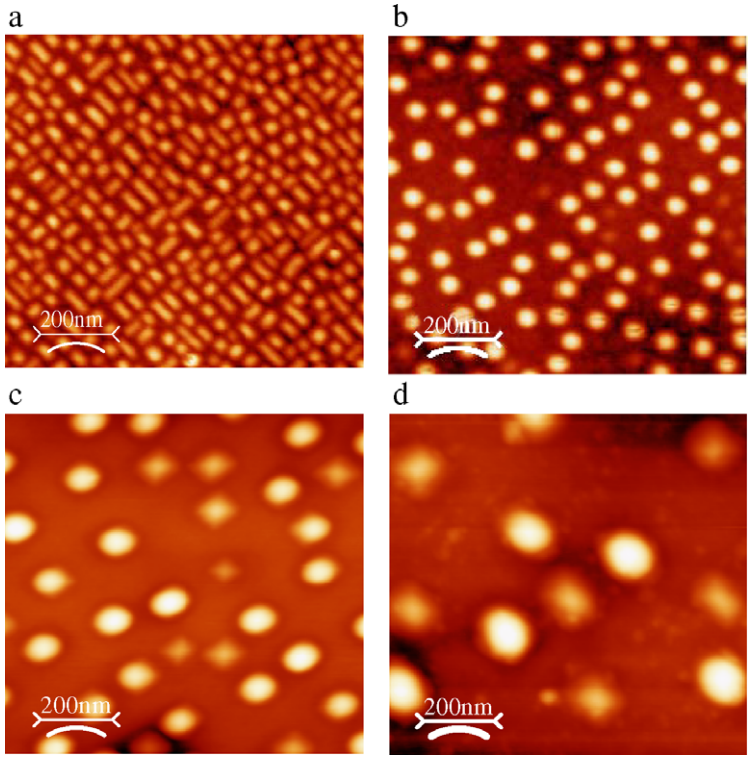

Fig. 1. AFM-image (top view) of self-assembled nanoislands grown at $d_{Ge} = 9$ ML and T_g of (a) 500 °C; (b) 600 °C, (c) 700 °C, (d) 750 °C.

portion of pyramids of 37%. This tendency is still more pronounced for T_g=750 °C, when the discussed values are $1\cdot10^9$ cm^{-2} and 58%, respectively.

The Raman spectra of $Si_{1-x}Ge_x$-nanoislands grown at different temperatures are shown in Fig. 2. Along with a very strong band from the substrate, there are peaks related to vibrations of Ge–Ge, Ge–Si and Si–Si bonds in $Si_{1-x}Ge_x$-alloy [10]. It should be noted that the substrate spectrum was subtracted when deriving frequency and intensity of island-related peaks, as was shown in Ref. [5], for more exact determination of these values. Raman peak frequencies of a strained $Si_{1-x}Ge_x$ alloy depend on composition x and elastic strain ε as follows [11,12]:

$$\omega_{SiSi} = 520.5 - 62x - 815\varepsilon \quad (1)$$

$$\omega_{GeSi} = 387 + 81(1-x) - 78(1-x)^2 - 575\varepsilon \quad (2)$$

$$\omega_{GeGe} = 282.5 + 19.37x - 400\varepsilon. \quad (3)$$

Substituting experimentally found ω_{SiSi}, ω_{GeSi} and ω_{GeGe} values and solving any pair of the Eqs. (1)–(3) gives values of x and ε in the islands, summarized in Table 1. Of course, all values are averaged over a large ensemble of islands with a certain distribution of sizes and volumes. However, as we have shown in Ref. [5], composition of islands grown at the same T_g only slightly depends on d_{Ge}. At the same time, Si content in the islands increases significantly with rising growth temperature due to increasing diffusivity of substrate atoms to the islands. As the diffusion is strongly enhanced by highly non-uniform strain field in the substrate around the islands, this process is of crucial importance in the stage of nucleation and growth of pyramids. The increase of Si content in pyramids allows them to preserve their pyramidal form to higher volumes without transformation to domes [5].

A direct determination of the island composition using SIMS was performed on the sample grown at 700 °C and

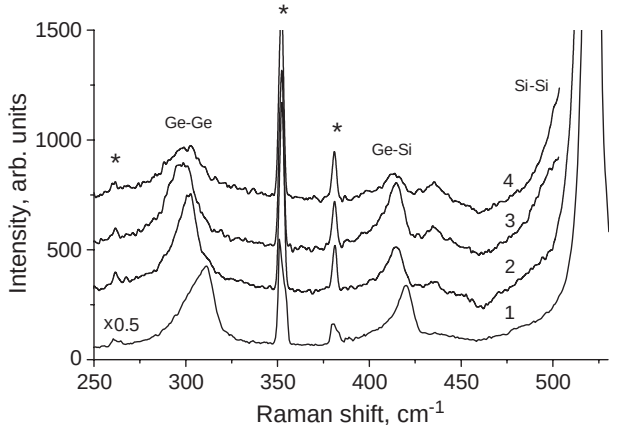

Fig. 2. Raman spectra of self-assembled nanoislands grown at d_{Ge}=9 ML and T_g of 1) 500°C; 2) 600 °C; 3) 700 °C, 4) 750 °C.

Table 1
The values of strain and composition in nanoislands grown at different temperatures as deduced from HRXRD and Raman data

Growth T, °C	Si cap	HRXRD		Raman	
		Strain $\varepsilon_\perp$ (%)	Strain $\varepsilon_\parallel$ (%)	Strain $\varepsilon_\parallel$ (%)	Ge content x
500	+			3.9±0.2	0.86±0.04
600	–	2.01	1.4	1.3±0.3	0.73±0.04
700	–	2.6	0.95	0.9±0.1	0.63±0.01
750	–	2.62	0.69	0.8±0.2	0.43±0.02

d_{Ge}=11 ML. As was shown in Ref. [5], under such growth conditions only dome-shaped islands are formed with a very narrow size distribution. In order to ensure uniform sputtering the sample surface during SIMS measurements, the islands were caped with Si. The obtained distribution of Ge atoms (in at.%) within the islands is presented in Fig. 3. Having taken into account the area island density and variation of the section area of the island with its height, we obtained the maximum Ge content in the islands of 55% at height of 20 nm from the island base. An average Ge content in the islands of ~30% is in a good agreement with that obtained from the Raman spectra. Some higher value as compared to uncapped domes is accounted for by an additional Si in-diffusion during their overgrowth [6].

Based on the known values of x in the islands obtained by SIMS, we used high-resolution X-ray diffraction for determination of residual strains in the islands. The variation of inter-plane distance $\Delta d = d_f - d_s$ (f and s relate to the film and substrate, respectively) in the epitaxial film depends on the crystal plane and strain value in the film. Both components of strain—perpendicular $\varepsilon_\perp$ and parallel $\varepsilon\|$ to diffraction plane—are determined by the relative change of inter-plane distance in the film as compared to bulk:

$$\Delta d/d_s = \varepsilon_\perp \cos^2\Psi + \varepsilon_\parallel \sin^2\Psi \quad (4)$$

where ψ is the angle between the crystallographic plane and the sample surface. The diffraction peak from the region of

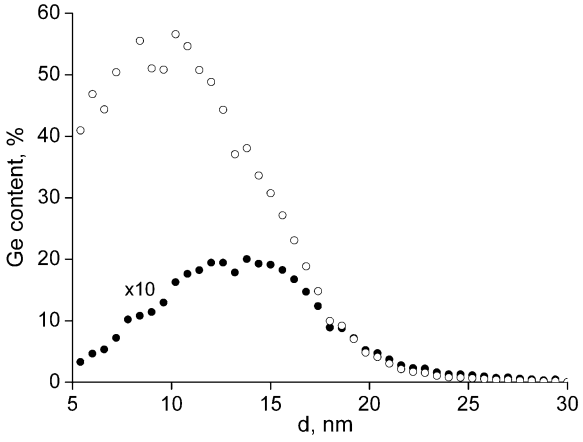

Fig. 3. SIMS profile of Ge within the Si layer containing islands grown at 700 °C (filled circles) and Ge profile within a single island calculated from the SIMS profile (open circles).

the lattice constant different from that of the substrate is shifted from the substrate peak by the angle $\Delta\vartheta_0$:

$$-\Delta\vartheta_0 = k_1 < \varepsilon_\perp > + k_2 < \varepsilon_{\|} > ,$$

where

$$k_1 = \cos^2\Psi tg\vartheta_B \pm \sin\Psi\cos\Psi$$

and

$$k_2 = \sin^2\Psi tg\vartheta_B \pm \sin\Psi\cos\Psi. \quad (5)$$

Here the brackets denote averaging over the film thickness, ϑ_B is the Bragg angle, "+" or "−" depends on the geometry of experiment for the asymmetrical case of diffraction. Experimental spectra were fitted using semi-cinematic theory of X-rays scattering given in detail in Refs. [13,14].

The picture of lattice distortion related to the island formation is very non-uniform. Therefore, modeling the single structure with islands is a very complicated problem not solved up to date even theoretically. Hence, for obtaining strain characteristics of the structures investigated here, we have used the approach based on measuring both symmetric and sharply asymmetric diffraction curves. From HRXRD spectra ([Fig. 4) taken for 400 reflexes, strain values in the islands perpendicular to the growth plane ($\varepsilon_\perp$) was obtained using Eqs. (4) and (5). The strain component $\varepsilon\|$ was derived from asymmetric 113 scans. All results are summarized in Table 1.

From the oscillating structure of the asymmetric 113 reflection (Fig. 4, curve 1) on Si caped samples, the thickness of the capping layer was also obtained. The weaker strain relaxation in the capped islands, as compared to uncapped ones (Table 1), was attributed to the presence of Si lattice around the islands, which does not allow them to relax as much as uncapped.

The conclusions derived from Raman and XRXRD studies about the influence of Si atoms diffusion into the islands on their strain and composition are further confirmed by a detailed examination of AFM pictures. The diffusion of Si atoms from the substrate, which is strongly enhanced by highly non-uniform strain around the islands, results in formation of trenches around the islands. The depth of the trenches is much larger than the thickness of Ge wetting layer. When after formation islands are cooled down to the room temperature, the different thermal expansion coefficients of the islands and the substrate result in additional residual strains near the islands base that is added to those caused by the lattice mismatch [15]. Si atoms driven by strain gradient from the substrate to the islands thus account for the trenches in the substrate around the islands, which are most deep at growth temperatures of 700 and 750 °C (Fig. 1c,d).

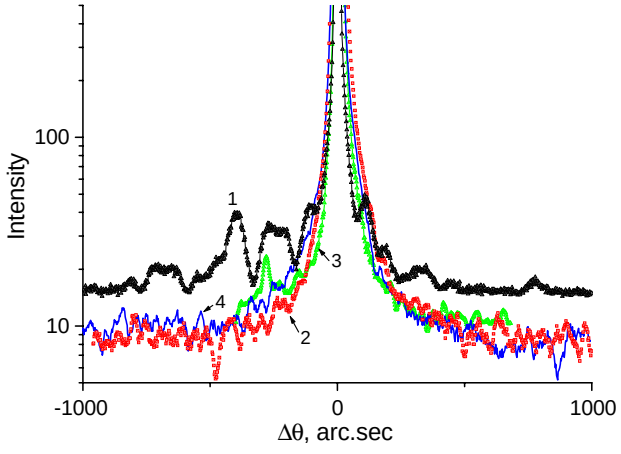

Fig. 4. Experimental HRXRD spectra for structures with self-assembled nanoislands grown at d_{Ge}=9 ML and T_g of (1) 500 °C; (2) 600 °C; (3) 700 °C; (4) 750 °C.

In what follows, we have used the obtained experimentally variation of Si content in islands with the growth temperature to establish the dependence of the nanoisland volume on Si content in it.

The growth of Ge islands on Si is related to a diffusion flux of Ge atoms in the points of island nucleation. This flux can be described by the diffusion equation

$$\frac{\partial\tilde{c}}{\partial t} = D\nabla^2\tilde{c} \quad (6)$$

where $D=\eta T$ (Einstein equation) is a diffusion coefficient, η is a constant, T is the temperature, $\hat{c}$ is the concentration. A fundamental solution of Eq. (6) is

$$\tilde{c}(x,t) = (4\pi Dt)^{-\frac{3}{2}} e^{-\frac{(x_0-x)^2+(y_0-y)^2+(z_0-z)^2}{4Dt}}. \quad (7)$$

Dependence Eq. (7) gives a probability to find a particle at a given temperature in a point (x, y, z, t), if it begins moving from point (x_0, y_0, z_0, t_0).

An important characteristics of the systems under consideration is a standard deviation $\overline{(x-x_0)^2}$. For 2D case, which takes place experimentally at $x_0=y_0=0$,

$$\overline{r^2} = 4Dt = 4\eta Tt \quad (8)$$

where r is a distance at which the particle diffuses with the probability close to unity.

The formation of an islands on the surface of Ge WL leads to an energy decrease in this point and an increase of chemical potential, which results in enlargement of the diffusion flux of particles. A dome-shaped island can be well described by a cone with a volume V_c:

$$V_c = \frac{\pi}{3} r^3 tg\theta \quad (9)$$

where θ is the angle between the island facet and substrate. Assuming $r = \sqrt{r^{-2}} = \sqrt{4\eta Tt}$, we obtain:

$$V_c = \frac{\pi(4\eta^2)^{\frac{3}{2}}}{3}(Tt)^{\frac{3}{2}} tg\theta = \frac{\pi(4\eta t_0)^{\frac{3}{2}}}{3}(TL)^{\frac{3}{2}} tg\theta. \quad (10)$$

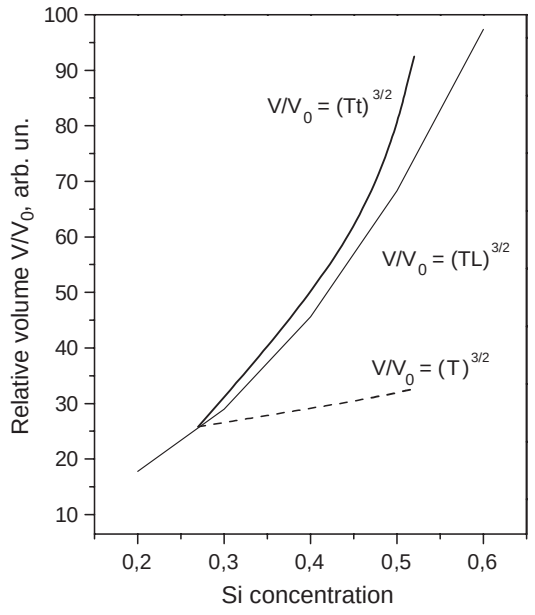

Fig. 5. Experimental (thick solid line) and calculated (thin solid line) dependencies of island volume vs. Si content. Dotted line corresponds to $t=t_0$ (the same time for all structures).

Therefore, the island volume is an ultralinear function of temperature (T) and duration (t) of growth. As the deposition of L Ge layers requires more time, we can assume $t=L\cdot t_0$, where t_0 is the time needed for deposition of one Ge monolayer. Using the experimental data from Refs. [5,12], we can relate T and the concentration, and compare experimental results of Ref. [16] and those obtained by the Eq. (10). In Fig. 5, experimental data are depicted by a thick solid line, dotted line correspond to $t=t_0$ (the same time for all structures), and the theoretical curve is drawn by a thin solid. Notice that deposition time of 11 MLs is approximately two times longer as that for 5.5 MLs. A qualitative correlation between theory and experiment is obvious.

4. Conclusions

The dependence of the density, volume and shape of the islands on the growth temperature was ascertained using AFM. Raman spectroscopy and HRXRD provided data about average values of strain and composition of the islands for different growth temperatures. The mixed SiGe content of the islands was found to be due to Si diffusion from the substrate to the islands during growth. The diffusion is strongly increased with the rising growth temperature, which results in broadening the stability region of the pyramidal islands with different volumes. The theoretically predicted temperature dependence of the island composition is in a qualitative agreement with experimental data.

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References

[1] K. Bruner, Rep. Prog. Phys. 65 (2002) 27.
[2] V.A. Shchukin, N.N. Ledentsov, P.S. Kop'ev, D. Bimberg, Phys. Rev. Lett. 75 (1995) 2968.
[3] F.M. Ross, J. Tersoff, R.M. Tromp, Phys. Rev. Lett. 80 (1998) 984.
[4] V.A. Markov, O.P. Pchelyakov, L.V. Sokolov, et al., Surf. Sci. 250 (1991) 229.
[5] Z.F. Krasil'nik, P.M. Lytvyn, D.N. Lobanov, N. Mestres, A.V. Novikov, J. Pascual, M.Ya. Valakh, V.A. Yukhymchuk, Nanotechnology 13 (2002) 81.
[6] V.O. Yukhymchuk, A.M. Yaremko, M.Ya. Valakh, et al., Mater. Sci. Eng., C, Biomim. Mater., Sens. Syst. 23 (2003) 1027.
[7] M. Floyd, Y. Zhang, K.P. Driver, J. Drucker, P.A. Crozier, D.J. Smith, Appl. Phys. Lett. 82 (9) (2003) 1473.
[8] A.L. Barabasi, Appl. Phys. Lett. 70 (19) (1997) 2565.
[9] A.M. Afanas'ev, M.A. Chuev, R.M. Imamov, A.A. Lomov, V.G. Mokerov, Yu.V. Fedorov, A.V. Tuk, Krystallogphy 42 (1997) 514.
[10] M.A. Renucci, J.B. Renucci, M. Cardona, Proceed., II Inter. Conf. "Light Scattering in Solids", (Flammarion), 1971, p. 326.
[11] J. Groenen, R. Carles, S. Christiansen, M. Albrecht, W. Dorsch, H.P. Strunk, H. Wawra, G. Wagner, Appl. Phys. Lett. 71 (1997) 3856.
[12] M.Ya. Valakh, V.M. Dzhagan, P.M. Lytvyn, V.A. Yukhymchuk, Z.F. Krasil'nik, A.V. Novikov, D.N. Lobanov, Phys. Solid State 46 (2004) 85.
[13] I. Tapfer, K. Ploog, Phys. Rev., B 40 (14) (1989) 9802.
[14] F.F. Sizov, Yu.M. Kozyrev, V.P. Klad'ko, S.V. Plyatsko, S.I. Shevlyakov, Phys. Solid State 31 (8) (1997) 920.
[15] A.M. Yaremko, V.M. Dzhagan, P.M. Lytvyn, V.O. Yukhymchuk, M.Ya. Valakh, Phys. Stat. Sol. (b), (in press).
[16] A. Rastelli, M. Kummer, H. von Kanel, Phys. Rev. Lett. 87 (25) (2001) 256101.