Available online at www.sciencedirect.com
SCIENCE DIRECT
ELSEVIER
Materials Science and Engineering C 23 (2003) 1027–1031
MATERIALS SCIENCE & ENGINEERING C
www.elsevier.com/locate/msec

Theoretical and experimental investigations of single- and multilayer structures with SiGe nanoislands

V.O. Yukhymchuk[a], A.M. Yaremko[a,*], M.Ya. Valakh[a], A.V. Novikov[b], E.V. Mozdor[b], P.M. Lytvyn[a], Z.F. Krasilnik[b], V.P. Klad'ko[a], V.M. Dzhagan[a], N. Mestres[c], J. Pascual[d]

[a] *Lashkaryov Institute of Semiconductor Physics, NAS of Ukraine, 45 Prospekt Nauki, Kiev, 03028, Ukraine*
[b] *Institute for Physics of Microstructures, RAS, 603950, Nizhny Novgorod, GSP-105, Russia*
[c] *Institut de Ciencia de Materials de Barcelona, CSIC, 08193 Bellaterra, Spain*
[d] *Departament de Fisica, Universitat Autonoma de Barcelona, 08193 Bellaterra, Spain*

Abstract

The influence of geometrical and physical parameters of self-assembled SiGe/Si nanoislands on their energy has been investigated theoretically. The island energy minimum was shown to depend on the growth temperature and Si content in the islands. The results of the theoretical calculations are compared with experimental data obtained by atomic force microscopy and Raman spectroscopy (RS).
© 2003 Elsevier B.V. All rights reserved.

PACS: 78.66
Keywords: , GeSi nanoislads; Elastic strain; Raman; AFM; X-ray

1. Introduction

A considerable progress in the production and investigation of self-assembled SiGe and Ge nanoislands on Si has recently been stimulated by their possible application in micro- and optoelectronics [1]. Ordered arrays of the islands having the same size and composition are very promising for efficient near-IR detectors and light emitters. Multilayer structures with nanoislands are of special significance because of a better size homogeneity and an extra vertical ordering of the islands. Such an ordering is due to the strain field in the spacer covering already formed islands. It is this strain that induces nucleation of the islands in the next layer right above those in the lower one.

It is known that silicon atoms diffuse from the substrate to the islands during the growth of a single Ge island layer, and also from the spacer in Ge/Si QD multilayers, resulting in a mixed SiGe composition of the islands. The diffusion process is strongly influenced by the temperature and duration of deposition, as well as by the field of elastic strain within the structure. Since the Si content increase in the island leads to its strain relaxation, this, in turn, changes the island energy and, thus, the resulting island size distribution. A reverse shape transition from dome-like to pyramidal was also observed [2]. In this connection, we have made an attempt to investigate theoretically the dependence of the island energy on its geometrical and physical parameters.

2. Experimental procedure

The structures investigated were obtained by MBE on Si(001) with a preliminarily deposited Si buffer layer, which was 250 nm thick. The samples were grown at different temperatures (550–750 °C) and thicknesses of deposited Ge (5.5–11 monolayers (ML)). The multilayer structures were obtained by deposition of 7.5 ML of Ge on the Si buffer at 600 °C followed by covering formed islands with 26 nm of Si. This procedure was repeated six times. The structures were studied by Raman spectroscopy (RS), high-resolution X-ray diffraction (HRXRD) and atomic force microscopy (AFM).

* Corresponding author. Tel.: +7-380-44-265-64-72; fax: +7-380-44-265-83-40.
E-mail address: Yaremko@isp.kiev.ua (A.M. Yaremko).

0928-4931/$ - see front matter © 2003 Elsevier B.V. All rights reserved.
doi:10.1016/j.msec.2003.09.156

3. Theoretical analysis and discussion

3.1. Energy of a strained island

In Refs. [3,4], an expression was derived for the energy of a dislocation-free Ge island. In deriving this equation, the island was assumed a rectangular truncated pyramid with height h, width s, and length t, and edges beveled at an angle θ to the substrate.

Then the island energy was

$$E = E_s + E_r, \tag{1}$$

where E_s is the extra surface and interface energy, and E_r is the energy change due to elastic relaxation. The extra surface energy is

$$E_s = st(\gamma_i + \gamma_t - \gamma_s) + 2(s+t)[h\gamma_e \csc\theta - h\cot\theta(\gamma_t + \gamma_s - \gamma_i)/2], \tag{2}$$

where γ_s, γ_t, and γ_e are the surface energies (per unit area) of the substrate and of the island's top and edge facets, respectively, and γ_i is the island–substrate interface energy. When the islands grow in Stranski–Krastanow mode, Eq. (2) can be simplified due to $\gamma_t = \gamma_s$, and $\gamma_i = 0$ [3].

The strain relaxation energy in quasi-two-dimensional approximation ($s \gg h$, $t \gg h$) is

$$E_r = -2ch^2[s\ln(te^{3/2}/h\cot\theta) + t\ln(se^{3/2}/h\cot\theta)], \tag{3}$$

where $c = \sigma_b^2(1-v)/2\pi\mu$, σ_b is strain tensor components of bulk Ge, and v and μ are the Poisson ratio and shear modulus of the silicon substrate, respectively.

In model developed in Ref. [3], the height h is assumed to grow slowly as compared to s and t and can thus be regarded as a constant. The energy of island edges and interaction between the islands was not taken into consideration in this model. In Ref. [4], minimization of the island energy was made at a fixed island volume. As a result of the calculations, the island energy minimum was found at $s = t = h\cot\theta$ and shown to depend on the size of the island, but not on the physical parameters c, γ_s, γ_e, etc., which is inconsistent with the experimental facts, since it was shown in Ref. [5] that the island shape must depend not only on the island energy, but on the growth kinetics as well. In this connection, we consider the problem defined in Refs. [3,4] taking into account all parameters s, t, h, γ_s, γ_e, and θ.

For convenience, Eqs. (1)–(3) can be written in terms of reduced values

$$\tilde{s} = s/h; \tilde{t} = t/h; \tilde{\gamma}_e = \gamma_e/ch; \tilde{\gamma}_s = \gamma_s/ch; \tag{4}$$

so that the island energy

$$E = 2ch^3\left\{(\tilde{s}+\tilde{t})(\tilde{\gamma}_e\csc\theta - \tilde{\gamma}_s\cot\theta) - \left(\tilde{s}\ln\left(\frac{\tilde{t}}{\alpha\cot\theta}\right) + \tilde{t}\ln\left(\frac{\tilde{s}}{\alpha\cot\theta}\right)\right)\right\},$$

where $\alpha = e^{-\frac{3}{2}}$.

In the model under consideration, h is a constant, and the product ch^3 is in energy units, all other values in braces in Eq. (5) are written in terms of reduced values. The function (5) is very complicated and its properties cannot be studied analytically. Therefore, a numerical analysis of the function has been performed. As a result, the minimum of the $E(\theta)$ dependency was found at $0 < \theta < \pi/2$, provided that $\tilde{\gamma}_s$ and $\tilde{\gamma}_e$ have close or equal values (Fig. 1). It should be noted that in this case, we have investigated only analytical properties of the $E(\theta)$ dependency, varying different parameters, without any physical limitation. Every physical conclusion must be concerned with the island energy minimum. The numerical analysis has shown (Fig. 1) that the minimum arises only at not very small values of $\tilde{\gamma}_s$ and $\tilde{\gamma}_e$, in particular, in this case, at $\tilde{\gamma}_s$ and $\tilde{\gamma}_e \geq 5$. On the other hand, when $\tilde{\gamma}_s < \tilde{\gamma}_e$ (curve 7, Fig. 1), E_{min} value corresponds to $\theta = \pi/2$, and the island must grow as a prism. It is worth noting that E_{min} and the corresponding value of the angle θ (Fig. 1) depend on a ratio between $\tilde{\gamma}_s$ and $\tilde{\gamma}_e$ (at constant ($\tilde{s}$, $\tilde{t}$)), which is, however, inconsistent with the results of Ref. [4]. It is seen in Fig. 1 that at given ($\tilde{s}$, $\tilde{t}$) and $\tilde{\gamma}_s$ = const, varying γ_e only shifts the curves $E(\theta)$, but does not lead to their intersection. These curves may, however, intersect with curves (are not presented) corresponding to another set of ($\tilde{s}$, $\tilde{t}$) and the same value of $\tilde{\gamma}_e$, which is evidence of a possibility of a transition from one local energy minimum to another corresponding to other angle ϑ.

3.2. The influence of the growth temperature and Si content in the islands on the island energy E

All above considerations are related to the islands of pure Ge. Experimental results of many groups, in particular, of Ref. [6], have shown that during the growth of Ge islands on

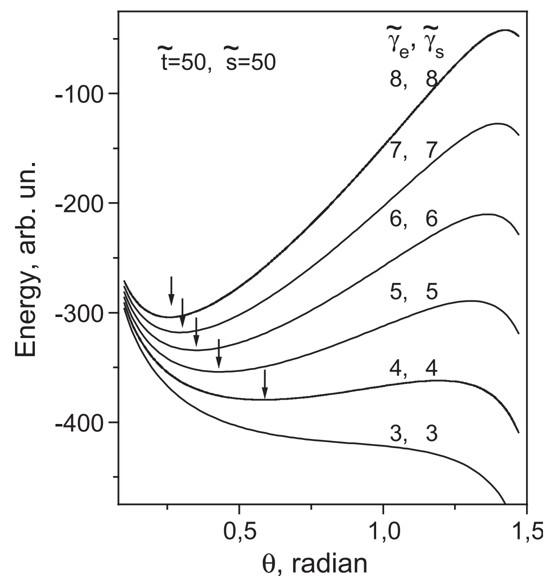

Fig. 1. The dependency of island energy on the angle θ at $\tilde{s} = \tilde{t} = 50$ and different $\gamma_e = \tilde{\gamma_s}$.

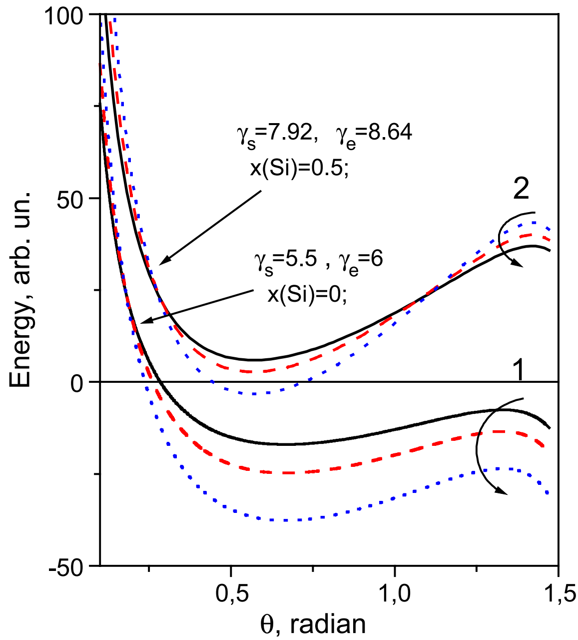

Fig. 2. The dependency of island energy on the angle θ for two sets of x, where x is Ge content in the island: (1) $x=1$; (2) $x=0.5$. Solid lines correspond to $\tilde{s}=\tilde{t}=10$, hatched lines to $\tilde{s}=\tilde{t}=12$, and dotted lines to $\tilde{s}=\tilde{t}=15$.

silicon, Si atom diffusion from the substrate to the island takes place. The silicon content in the islands increases with the growth temperature; this is confirmed by RS data [6]. The Si content increase in the islands leads to a decrease in lattice mismatch between the island and the substrate, and therefore to strain decrease. Shown in Fig. 2 is the dependency of $E(\theta)$ for two sets of ($\tilde{s}$, $\tilde{t}$) corresponding to $x=1$ and $x=0.5$, respectively. It is seen that for pure Ge islands ($x=1$, curve set 1), all curves have minimum, and $E_{\min}<0$. When Si content in the islands increases to 0.5, according to Eq. (4) and dependency of $c\sim(\sigma_b)^2$, the values of $\tilde{\gamma}_s$ and $\tilde{\gamma}_e$ change and cause an upward shift of the curve set (curve set 2), two of them having $E_{\min}>0$. From a physical point of view, $E_{\min}>0$ means that nucleated islands will dissociate at given parameters.

4. Experimental results

An analysis of the AFM data on the structures investigated has shown that depending on the growth temperature and thickness of deposited Ge, both bimodal and monomodal island size distribution can be observed, corresponding to the formation of two types of islands (Fig. 3): pyramids and

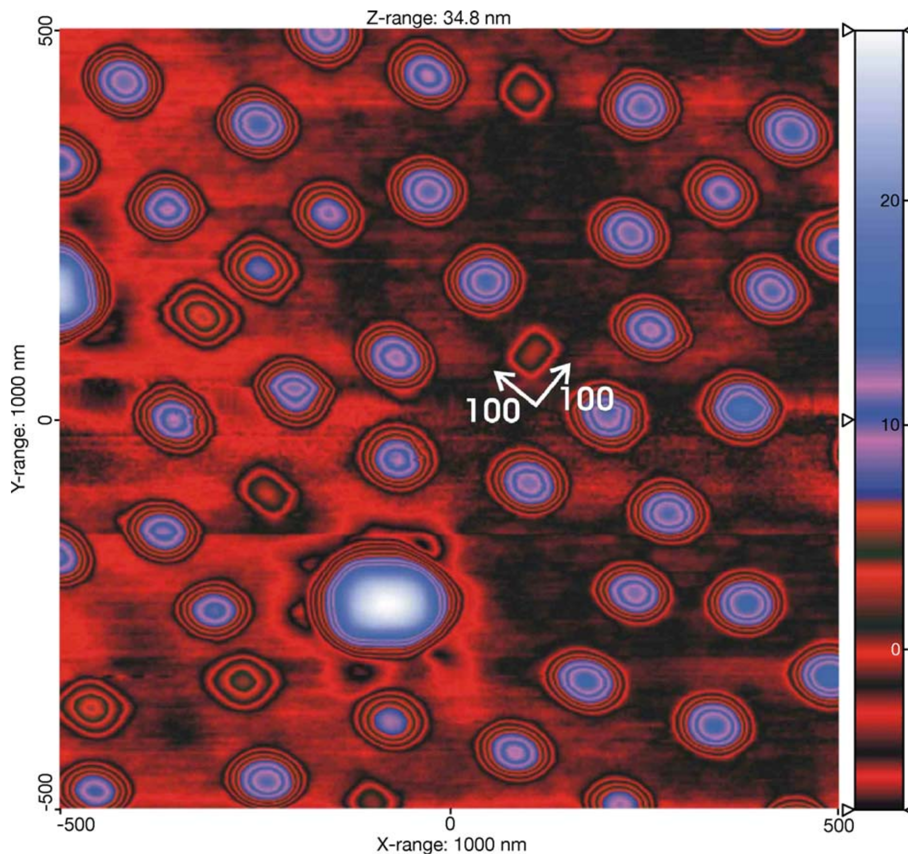

Fig.3. A plan-view AFM picture of the 8-ML sample grown at 600 °C.

domes, or only one type. Island size and shape depend on the growth temperature. An increase in growth temperature results in a change of the chemical potential of the structure and in enhanced Si atom diffusion from the substrate to the islands. The analysis of the AFM pictures has shown that the pyramids grow owing to a proportional increase of both their height and lateral dimensions. On achieving a critical volume, the pyramids gradually transform into domes with more steep side facets.

The values of composition x and mechanical strain ε in the nanoislands were determined using the data on Raman scattering by optic phonons (Fig. 4). The relations between the frequency of optical phonons and x and ε values are [7]:

$$\omega_{\mathrm{GeGe}} = 282.5 + 16x - 385\varepsilon \tag{6}$$

$$\omega_{\mathrm{GeSi}} = 400.4 + 14.2x - 575\varepsilon \tag{7}$$

$$\omega_{\mathrm{SiSi}} = 520.5 - 62x - 815\varepsilon \tag{8}$$

In order to determine the x and ε values correctly, we also have taken into account a contribution from the Si substrate and spacer, and Ge wetting layer into the Raman spectrum. By substituting the experimental values of the frequencies of Ge–Ge, Ge–Si, and Si–Si vibrations, and solving graphically the set of Eqs. (6)–(8), as shown in Ref. [7], we obtained $x = 0.6$, $\varepsilon = -0.015$.

An experimental low-frequency spectrum of Raman scattering on folded acoustical phonons was also recorded (Fig. 5). A small width of the lines is evidence of the high quality of the grown superlattices with nanoislands. We have used Rytov's [8] theory to describe the measured spectra theoretically. As the acoustical impedances of constituent layers were close, calculations could be performed using the simplified formula:

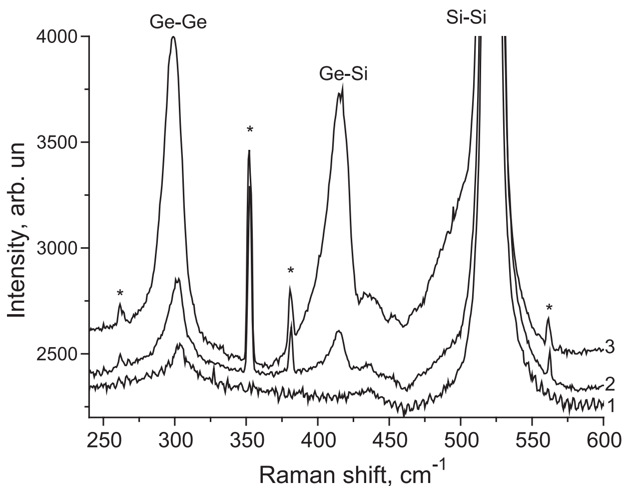

Fig.4. Raman spectra of Si substrate (1), single- (2), and multilayer structure (3) with $Si_{1-x}Ge_x$ nanoislands.

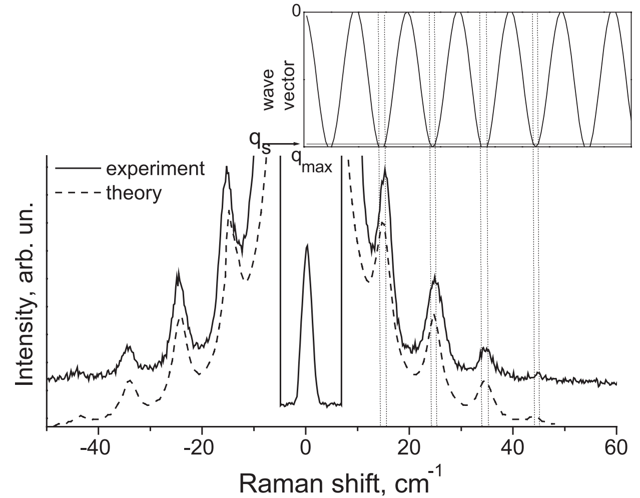

Fig.5. Stokes and antistokes Raman spectra due to scattering on the folded LA phonons in the sixfold stack with $Si_{1-x}Ge_x$ nanoislands. The inset shows the calculed theoretical dispersion dependence of the given phonon mode.

$$\omega = V_{\mathrm{SL}}\left(\frac{2\pi}{d}\right)m \pm V_{\mathrm{SL}}q_{\mathrm{s}},$$

where

$$V_{\mathrm{SL}} = d\left(\frac{d_1^2}{V_1^2} + \frac{d_2^2}{V_2^2} + \left(R + \frac{1}{R}\right)\frac{d_1 d_2}{V_1 V_2}\right)^{-1/2}, R = \frac{V_1\rho_1}{V_2\rho_2},$$

ρ_1, ρ_2 are layer densities, d_1, d_2 are layer thicknesses, v_1, v_2 are sound velocities, and ω is phonon frequency.

Theoretical spectra were simulated by a superposition of the scattering on two groups of phonons propagating perpendicular to the layers through (i) the islands and (ii) bare WLs between them. A good correlation between the calculated and measured frequencies (Table 1) confirms the values of island composition obtained from scattering on optical phonons.

Given in Fig. 6 are the results of HRXRD for the multilayer structure, where there are peaks caused by the layered structure. At the first stage of fitting, technological parameters of the structure were used, and an independent variation of all parameters of the structure—layer thicknesses, Debye–Waller static factor, and strain—was performed. The resulting values of composition and strain in

Table 1
The theoretical and experimental Raman frequencies of the folded LA phonons in the sixfold stack with $Si_{1-x}Ge_x$ nanoislands

m	+1	−2	+2	−3	+3	−4	+4	−5
	Raman shift, cm^{-1}							
Theory	14.8	15.1	24.5	24.8	34.4	34.7	44.2	44.7
Experiment	15		24.7		34.5		44.5	

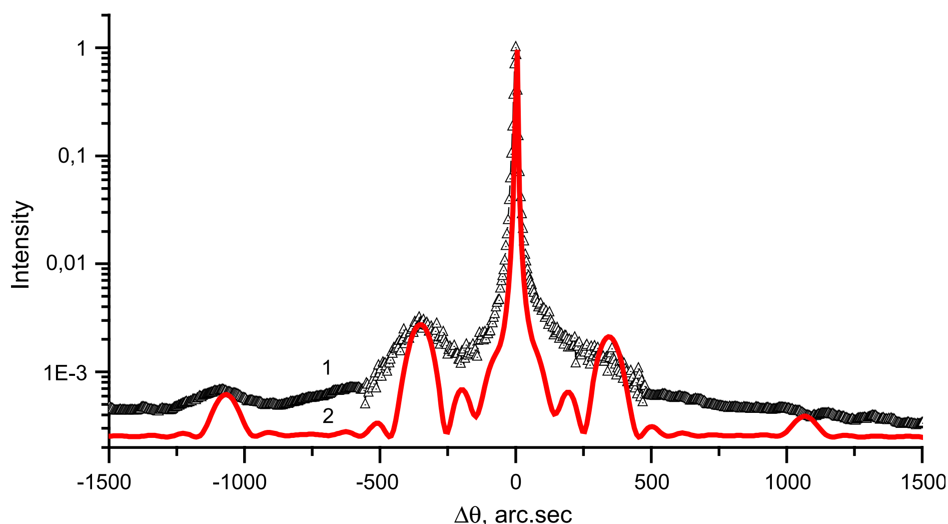

Fig.6. Experimental (1) and simulated (2) HRXRD rocking curves for multilayer structure with self-assembled $Si_{1-x}Ge_x$ nanoislands.

multilayers are in good agreement with those obtained by RS.

In order to investigate the influence of the silicon spacer on the $Si_{1-x}Ge_x$ island parameters, both the multilayer structure and a single layer of uncapped island were grown under the same conditions. We obtained $x=0.75$, $\varepsilon=-0.013$ and $x=0.6$, $\varepsilon=-0.015$ for single- and multilayer structures, respectively. The larger value of Si content in the island in multilayer structure is due to additional Si atom in-diffusion during overgrowth. As a result, these islands should be less strained than those with higher Ge content in single-layer structure. However, the strains are almost equal in both cases. The reason is that the islands in the multilayer structure are surrounded by silicon spacer and thus cannot relax completely.

5. Conclusion

We have shown that Si atom diffusion from the substrate and spacer is of great importance for island formation in both single- and multilayer structures. The diffusivity is strongly influenced by the temperature and duration of growth. The increase in Si content in the island leads to their strain relaxation, which, in turn, causes the island shape transition from domes to pyramids.

It was shown numerically that the temperature increase influences in a complicated manner the ratio between the surface and bulk physical characteristics of the islands, and at given temperature, Si content, and growth duration, a limiting ratio between the height and lateral dimensions has to exist, which defines the island shape.

Acknowledgements

The work was supported by INTAS-project N 01-444.

References

[1] K. Brunner, Rep. Prog. Phys. 65 (2002) 27.
[2] A. Rastelli, M. Kummer, H. von Kanal, Phys. Rev. Lett. 87 (N 25) (2001) 256101.
[3] J. Tersoff, R.M. Tromp, Phys. Rev. Lett. 70 (N 18) (1993) 2782.
[4] J. Tersoff, F.K. LeGoues, Phys. Rev. Lett. 72 (N 22) (1994) 3570.
[5] Y.W. Zhang, A.F. Bower, Appl. Phys. Lett. 78 (N 18) (2001) 2706.
[6] Z.F. Krasil'nik, P.M. Lytvyn, D.N. Lobanov, N. Mestres, A.V. Pascual, J. Pascual, M.Ya. Valakh, V.A. Yukhymchuk, Nanotechnology 13 (2002) 81.
[7] J. Groenen, R. Carles, S. Christiansen, M. Albrecht, W. Dorsch, H.P. Strunk, H. Wawra, G. Wagner, Appl. Phys. Lett. 71 (26) (1997) 3856.
[8] S.M. Rytov, Acoust. Zh. 2 (1) (1956) 71.