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Optical and acoustical phonon modes in superlattices with SiGe QDs

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Abstract. Multilayers with SiGe nanoislands grown in a broad temperature range (300-600 °C) are studied using Raman spectroscopy, HRXRD and AFM. It is shown that the islands are fully strained when obtained at 300 ºC and gradually relax with the growth temperature increase. The main contribution to the Raman peaks caused by scattering on folded acoustic phonons in multilayers ($n \le 10$) with nanoislands is due to the islands themselves. The enhancement of the scattering intensity due to resonance of the exciting light with the electronic transitions inside the islands is shown to play a significant role.

Keywords: SiGe quantum dots, Raman scattering, X-ray diffraction, phonon folding, strain.

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1. Introduction

Reduction of a semiconducting structure dimensions down to ~ 10 nm results in a quantum confinement effect changing abruptly the physical properties of the system. Hence, a desirable variation of the parameters of electron and phonon energy spectra of nanostructures can be obtained by varying their size and shape. One of the most promising ways for producing nanostructures is their self-induced growth in Stranski – Krastanow mode [1]. A physical background of this phenomenon is a significant reduction of the total energy of a strained heterosystem due to the 2D–3D transition during the epitaxial growth.

Among the structures with self-induced semiconductor quantum dots (QD), the arrays of Ge and SiGe QDs on Si substrate are of special significance [2]. Because of being fully compatible with a well-developed silicon technology, they are very attractable for application in opto- and nanoelectronics. A production of high-quality devices requires a precise knowledge about optical and electrical properties of Ge (SiGe) QDs which depend on size, shape, composition and strain in the islands as well as on their area density. The average values of composition and strain in SiGe QDs can be evaluated by Raman spectroscopy (RS) when using the strain and compositional dependences of Ge–Ge, Ge–Si and Si–Si optical vibration modes [3, 4]. The information on the superlattice (SL) periodicity as well as on the interface quality can be derived from the acoustic confined phonon modes. In most of preceding papers, RS was used to study the Ge (SiGe) QDs grown on Si substrate predominantly at high temperatures (600…750 °C) [5-8]. In this work, we have studied QDs grown at lower temperatures – from 300 to 600 °C.

2. Experimental technique

The structures under investigation were tenfold multilayers grown by molecular beam epitaxy (MBE) on Si (001) substrate with 200 nm Si-buffer within the range of the growth temperatures (T_g) from 300 °C up to 600 °C. The islands in every layer were formed from 8 monolayers (ML) of deposited Ge and capped with Si to form a spacer layer. The spacer thickness was varied from 10 to 50 nm for different samples. The islands in the top layer were not capped with Si. Raman spectra were excited at room temperature by different Ar^+- and Kr^+-lasers lines and analyzed by Jobin Yvon T6400 and DFS-24 spectrometers. In order to avoid the contribution of air molecular vibrations to the spectrum, the samples were kept in vacuum during the measurements. The known frequencies of Ar^+- laser plasma lines were used for accurate determination of the Raman peak frequencies. The morphology of the uncapped island

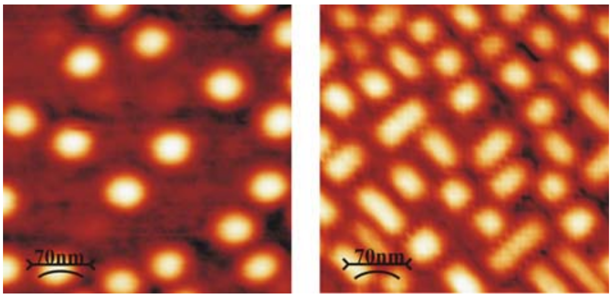

Fig. 1. A plan-view AFM pictures of self-induced $Si_{1-x}Ge_x$ nanoislands grown at 500 °C (a) and 600 °C (b).

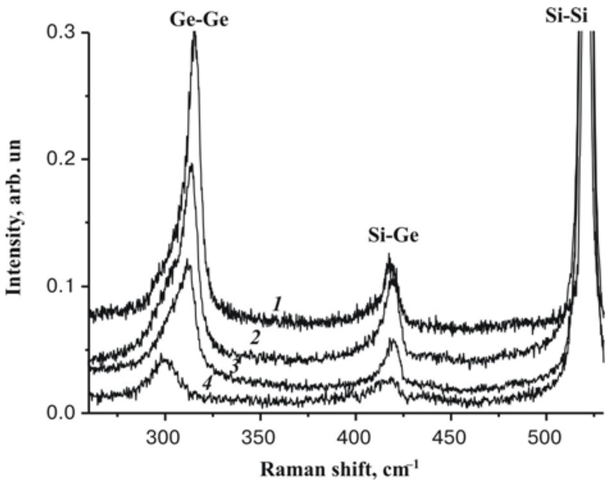

Fig. 2. Raman spectra of SiGe nanoislands obtained from 8 ML Ge grown at 300 °C (1); 400 (2); 500 (3); 600 (4).

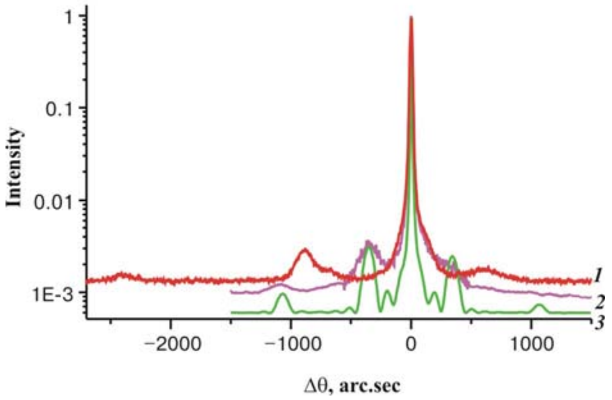

Fig. 3. Experimental HRXRD rocking curves for multilayer structures with self-assembled $Si_{1-x}Ge_x$ islands grown at 300 °C (1), 600 (2) and simulated (3) for T_g = 600 °C.

layers was investigated by atomic force microscopy (AFM) using NanoScope IIIa operating in the tapping mode. High resolution X-ray diffraction (HRXRD) measurements were performed for 400 and 113 reflexes by double-crystal spectrometer with GaAs (100) monochromator.

The samples were scanned within 5° near the exact Bragg angle value in both $\omega/2\theta$ and ω modes. For the analysis of the experimental data χ^2-technique was used, which allows one to find both the average values of the parameters and their deviations [5].

3. Results and discussion

Epitaxially deposited thin Ge layers (8 ML) on Si substrate at temperatures below 550 °C self-assemble into hut-clusters with the height ≤ 2 nm. As the growth temperature increases up to T_g = 600 °C, square-based pyramids and multifaceted domes with larger height-to-lateral size ratio arise. The distinct difference between the shape, size and area density of the islands grown at 500 and 600 °C are clearly seen from their AFM-images (Fig. 1). The T_g-induced change of composition and strain in the islands manifests itself in the change of Raman spectra shown in Fig. 2. There are some distinctive features in the spectra of islands grown at 300…500 °C as compared to those corresponding to T_g = 600 °C. First, it is a low-frequency shoulder of Ge–Ge mode whose origin is discussed elsewhere [9, 10]. Second, a different relative intensities caused by a resonant enhancement of both Ge–Ge and Ge–Si peaks is observed, which is evidenced additionally by the intensity variation for Ge–Ge and Ge–Si peaks under excitation with different laser wavelengths [11]. The reason is that the T_g increase enhances Si diffusion from the substrate into the islands, changing the energy of the direct optical transition $E_1(Si_{1-x}Ge_x)$ that gives the main contribution to the observed resonance. Third, the Ge–Ge mode frequency (315…312 cm^{-1}) is the evidence for the large strain in the low-temperature islands. The estimation of the strain and composition values from the frequency positions of the Ge–Ge and Ge–Si peaks [7] gives x = 0.98 and ε = – 0.041 for the islands grown at 300 °C while x = 0.56 and ε = – 0.021 for T_g = 600 °C. These significant differences in x and ε values are due to the increase of both Si content in the islands and their height-to-lateral size ratio with T_g.

The HRXRD spectra for the multilayer structures (Fig. 3) show equidistant peaks caused by the layered structure. At the first stage of fitting the experimental curves, the technological parameters of the structure were used, and independent variation of all parameters of the structure – layer thickness, Debye – Waller static factor and strain – was performed. The resulting values of composition and strain in the multilayers are in a good agreement with those obtained by Raman spectroscopy. The periodicity of the SLs was also derived from HRXRD spectra and used for the interpretation of the Raman scattering by acoustic phonons.

It is known [12] that the frequencies of low-frequency peaks in the Raman spectrum of planar SLs are very precisely described by the model of folding the acoustic phonons (FAP) developed in Refs [13, 14]. The peak intensities are commonly calculated using the photoelastic mechanism [14] and are determined by the difference in photoelastic constants of the SL layers. Recently, a theory was developed [15] which describes the low-frequency Raman peaks in SLs with QDs irrespective of the number of layers. This model is based on the interference between the acoustic phonons and localized electronic states. As was shown in [15], when the number of periods is five and more, the phonon frequencies obtained in the interference model coincides with those derived from the consideration of phonon folding. Taking into account this fact as well as simplicity of the phonon folding model, we used it for the interpretation of our experimental low-frequency spectra.

The following should be stressed before the further consideration. All the known Raman measurements on FAP in planar SLs without QDs were made on samples containing tens of periods. If the number of periods N is reduced to less then ten, the folded modes are usually not observed. The linear chain model calculations made in Ref. [16] for a real finite structure with N periods (as opposed to the idealized phonon folding model that requires $N = \infty$) showed that for $N \leq 5$ almost homogenous distribution of low-frequency vibrational modes is observed, and their slight accumulation at the expected FAP frequencies is not enough to be observed experimentally. The possibility of observation of FAP appears only for $N > 10…15$, as follows both from the theory and experiment. Simultaneously, for the layered structures with QDs sufficiently strong low-frequency peaks are observed already for $N < 5$. It should be stressed that for the experimental observation of the phonon folding, besides large N, a good interface quality is required. Deterioration of the interface, e.g. during the annealing, leads to a significant decrease of the FAP peaks intensity. As to the QD multilayers, the interfaces are modulated by the islands and smeared by interdiffusion enhanced by non-uniform strain fields around the islands. In spite of this, distinct low-frequency peaks are observed even for the structures grown at high temperatures (~ 600 °C), for which the above modulation by the islands and interdiffusion is the most pronounced.

In order to elucidate the influence of the QD formation on the appearance of the low-frequency peaks in the Raman spectra, we studied a series of samples with the QDs and without them (i.e., containing only wetting layers (WL)). Islands are known to cause the strain distribution in the Si spacer resulting in the fact that the island formation in the subsequent layers starts at a smaller WL thickness [17]. In order to obtain islands of equal size, the thickness of the deposited Ge was gradually reduced from 8 ML in the first layer to 6.8 ML in the latter one. The WLs without QDs were 3 ML thick. About half of all the deposited Ge is used to form the wetting layers ($d_{WL} \approx 3…4$ ML). The rest of the material forms islands which cover 20…30 % of the WL. Thus, the volume of pure (uncovered) WL that appears in the calculations is only 2…3 times less than

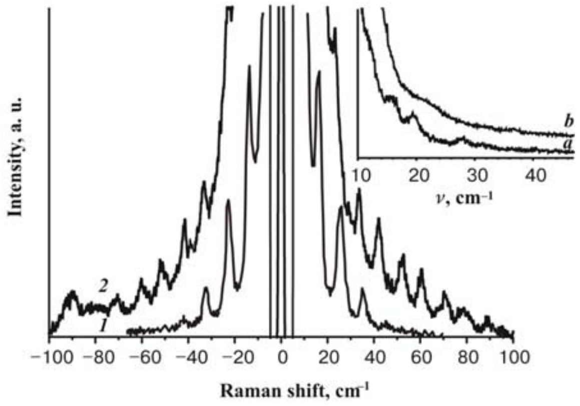

Fig. 4. Stokes and anti-Stokes Raman spectra due to scattering by folded LA phonons in the multilayers with $Si_{1-x}Ge_x$ nanoislands grown at 600 °C (1) and 300 °C (2). Inset: Raman spectra in the acoustic phonon frequency range for tenfold SL with the nanoislands (a) and with the WLs only (b).

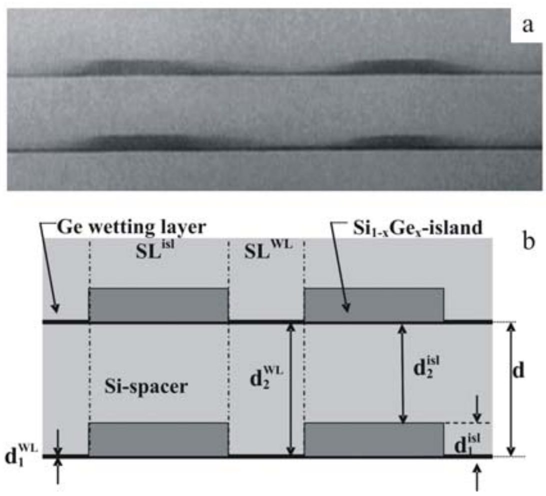

Fig. 5. TEM image (a) and schematic cross-section (b) of the stack with $Si_{1-x}Ge_x$ nanoislands grown at 600 °C.

the volume of the islands. It was shown in [18] for planar SLs that phonon folding is readily observed for the layer thickness equal to those of our QDs and WLs. Taking into account comparable effective volumes of the QDs and WLs, as stated above, it is not obvious which of them, QDs or WLs, manifest themselves in the low-frequency Raman spectra. The inset to Fig. 4 shows Raman spectra for two such 10-fold structures grown at 600 °C. It is seen that the FAP-related features are observed only for multilayer structures with QDs. The same pattern was observed for other pairs of structures, as well as in Ref. [19]. Based on these experimental data, we conclude that the main contribution to the observed low-frequency peaks in the Raman spectrum for the layered structures with small N is paid by the phonons within the islands. Therefore, for the description of phonon folding in QD multilayers the real structure of the dot layer should be considered.

We have studied in detail five-layer QD structure grown by MBE at 600 °C. The islands were formed from 7…8 ML of Ge and capped with 26 nm of Si to form the spacer layer. The spacer thickness is small enough to allow almost 100 % vertical correlation of the islands. Raman spectra were excited by 488.0 and 514.5 nm lines of Ar^+-laser.

Due to the shape of the capped islands, the structure under consideration depicted in Fig. 5a can be described by two planar SLs: SL^{isl} and SL^{WL} (Fig. 5b) with the same period d. SL^{isl} contains the nanoislands (d_1^{isl}) and the spacer area above them (d_2^{isl}), and SL^{WL} contains the WL between the islands (d_1^{WL}) and the spacer region above the WL (d_2^{WL}). This simple model allowed us to apply the theory of phonon folding to SL^{isl} and SL^{WL} separately.

Using the structural parameters obtained by HRXRD and TEM, $d = 27$ nm, $d_1^{isl} = 5$ nm, $d_2^{isl} = 22$ nm, $d_1^{WL} = 0.8$ nm, $d_2^{WL} = 26.2$ nm, we calculated FAP frequencies separately for SL^{isl} and SL^{WL} (Table). In the calculation, we used the average Ge content in the islands $x = 0.6$, obtained from the Raman frequencies of the optical phonons. Since the acoustic impedances of constituent layers were close, calculations were performed using the formula:

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

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

ρ_1, ρ_2 are layer densities, d_1, d_2 are layer thicknesses; V_1, V_2 are sound velocities, ω is the phonon frequency.

It is seen from Table that the doublet splitting is very small for $\lambda_{exc} = 488$ nm and cannot be resolved experimentally. The frequencies calculated for SL^{isl} are in better agreement with experimental values than those obtained for SL^{WL}. This result is in agreement with the experimental observations (see the inset to Fig. 4) indicating that WLs do not contribute to the spectrum or at least the contribution is so weak that it cannot be observed experimentally. Eventually, we come to a conclusion that the series of the low-frequency Raman peaks are related to the SL regions containing QDs but not to those containing wetting layers only.

In order to generalize our conclusion, we studied a tenfold SL with much smaller nanoislands (height of 1.5...2 nm and lateral size of ~ 20 nm), but with significantly higher area density, obtained at the growth temperature of 300 °C. Since the intensity of the FAP peaks in the Raman spectrum is strongly dependent of the ratio d_1^{isl}/d of the SL, the spacer thickness was reduced to 11 nm, in proportion to the island height. As stated above, the Si content in the islands grown at 600 °C, is ~ 40 %. It results in the increase of the total island volume by about twice as compared to that of nominally deposited Ge (8 ML). Therefore, in order to provide equal total volumes of the islands for the samples grown at 600 and 300 °C, the number of periods in the latter structure was increased to 10. The Raman spectrum of this structure is featured by more peaks as compared to the discussed above sample grown at 600 °C (Fig. 4) what indicates a better interface quality in the samples grown at lower temperatures. We calculated the periodicity of the structure using the experimental FAP frequencies for two cases: (i) assuming they originate from the SL^{isl}, or (ii) from the SL^{WL}. Much better agreement with the value of $d = 12.4$ nm, obtained by HRXRD, is achieved with $d = 12.3$ nm for the SL^{isl}, than with $d = 13.4$ nm obtained for the SL^{WL}. Such a small difference in the d value for the SL^{isl} and the SL^{WL} of ~1 nm is completely reliable due to high sensitivity of the FAP frequencies to the SL periodicity. It was determined from the Raman spectra in the optical phonon frequency range that the nanoislands grown at 300 ºC contain < 10 % of Si and are almost fully strained. The strain-induced change of the LA phonon frequency [20] was taken into account at the calculations.

As to some higher folded LA peak intensities for the fivefold structure grown at 600 °C (Fig. 4, curve 1), they can result from more favorable resonance conditions. The presence of resonance enhancement was evidenced by measuring the Raman spectra for the SLs grown at 300 °C under excitation with 647.1 and 514.5 nm wavelengths (Fig. 6). It was found that the increase of the excitation energy from 1.9 eV (647.1 nm) to 2.4 eV (514.5 nm) shifts the maximum of the spectrum envelope to the higher frequency side from ~ 20 up to ~ 50 cm^{-1}. Thus, at higher excitation energies, enhancement occurs for phonons with higher energies. The observed shift of the resonance maximum was observed ealier in Ref. [11] and explained with regard to interaction between bulk-like acoustic phonons and confined electronic states.

Experimental and calculated (for SL^{isl} and SL^{WL}) Raman frequencies for the structure under study.

Folding index m		+1	–2	+2	–3	+3	–4	+4	–5
		Raman shift, cm^{-1}							
Theory	SL^{isl}	14.4	15.1	24.1	24.8	34	34.6	43,8	44.6
	SL^{WL}	15	15.8	24,9	25.7	35	35.8	45.1	45.8
Experiment		15		24.5		34.4		44.5	

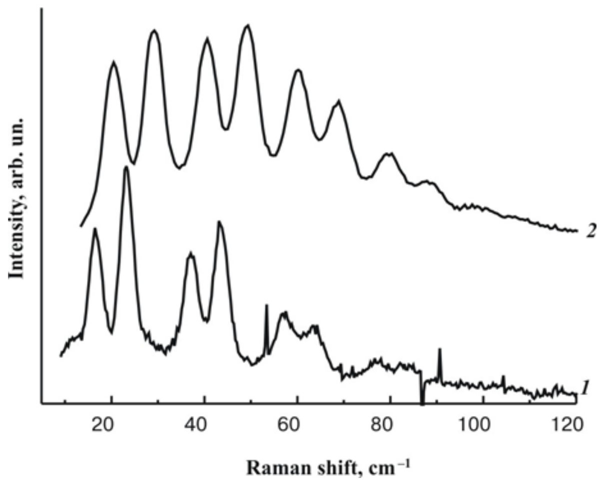

Fig. 6. Raman spectra due to the scattering by folded LA phonons in the multilayer with $Si_{1-x}Ge_x$ nanoislands grown at 300 °C excited with 647.1 nm (1) and 488.0 nm (2) laser lines.

4. Conclusions

Multilayers with SiGe nanoislands grown in the temperature range from 300 to 600 ºC are studied using Raman spectroscopy, HRXRD, AFM and compared with similar multilayers without islands. It is shown from Raman spectra that the islands grown at 300 ºC are fully strained. As the growth temperature increases, Si content in the islands also increases, partially relieving the strains. These structural transformations manifest themselves in both the intensity and frequency of the optical Raman peaks. Due to composition- and strain-induced changes in the island band structure, measurements conditions with Ar^+-laser line excitation comes out of resonance, reducing peak intensity. We have shown that at the interpretation of the Raman scattering by folded acoustic phonons for structures with nanoislands the real structure of the island layer should be considered. The observed series of the low-frequency Raman peaks, for the SL with $N \leq 10$, is due to the acoustic phonon modes within the islands but not in WLs. The enhancement of the scattering intensity due to resonance of the excitation light with the electronic transitions within the islands plays a significant role.

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