JETP Letters, Vol. 79, No. 7, 2004, pp. 333–336. Translated from Pis'ma v Zhurnal Éksperimental'noĭ i Teoreticheskoĭ Fiziki, Vol. 79, No. 7, 2004, pp. 411–415.
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Elemental Composition of Nanoclusters Formed by Pulsed Irradiation with Low-Energy Ions during Ge/Si Epitaxy

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Received February 24, 2004

Multilayer silicon structures with built-in layers of Ge nanoclusters were studied experimentally by Raman light scattering. The built-in layers were formed by the pulsed action of a low-energy beam of intrinsic ions during molecular-beam epitaxy. It is found that the ion-stimulated nucleation and the subsequent growth make it possible to obtain Ge nanoclusters almost free of Si. *© 2004 MAIK "Nauka/Interperiodica".*

PACS numbers: 81.15.Hi; 68.55.-a; 61.80.Jh; 81.07.-b

At present, the most promising method of quantum-dot (QD) array formation is based on the effects of self-organization of semiconductor nanostructures in heteroepitaxial systems [1–4]. The deposition of a material with a lattice constant differing substantially from the substrate lattice parameter induces elastic strains in the epitaxial film and in the islands on its surface. These strains are the key factor in both the morphological transition from a flat to the islanding film (Stranski–Krastanov mechanism) and the subsequent changes in sizes, shape, and spatial distribution of islands, providing, under certain conditions, the formation of an array of coherently strained nanometer-sized islands.

The problem of the controlled formation of QD arrays is associated with the necessity of creating new promising devices such as quantum transistors, high-speed memory elements, narrow-band light-emitting diodes, heterolasers with radiation of a required color, and infrared photodetectors. In order to realize the unique characteristics of new devices in practice, it is necessary to maintain a high density of QDs. In combination with the requirement for small QD sizes (<10 nm), the layer density must be on the order of 10^{12} cm^{-2} (at higher densities, QDs of the indicated size are joined together into a continuous layer).

The authors of [4] developed a method for the low-temperature molecular-beam epitaxy (MBE) of Ge on Si(100) that provides the formation of nanosized islands with a surface density of $(3–5) \times 10^{11}$ cm^{-2}. The average size of pyramidal Ge clusters was 15 nm (pyramid base), the pyramid height was 1.5 nm, and the size inhomogeneity was no worse than 17%. The typical conditions for the formation of Ge/Si structures included the processes of homoepitaxy on Si(100) at 700°C with a rate of 1–2 monolayers (MLs) per second, Ge heteroepitaxy at 300°C (0.2 ML/s), and Si epitaxy over the Ge islands at 500°C. A sufficiently low temperature in the deposition of Ge and in the subsequent overgrowth of the Si layer ensured the suppression of the process of mixing between two materials; as a result, the Ge nanoclusters practically did not contain Si [5].

The method proposed by us for the controlled formation of a QD array consists in the pulsed irradiation by low-energy (~100 eV) intrinsic ions during the heteroepitaxy at certain instants of time according to the degree of monolayer filling [6–8]. We found that the irradiation with low-energy Ge ions during Ge heteroepitaxy on silicon led to the stimulated nucleation of Ge islands and to a decrease in the critical thickness of the pseudomorphic Ge film, at which a transition from two-dimensional layer-by-layer growth to three-dimensional growth takes place. In this case, the average size of three-dimensional (3D) Ge islands decreases, their density increases, and the mean-square deviation from the average value decreases as compared with the corresponding values for molecular-beam epitaxy (the effect of self-organization of an ensemble of Ge nanoclusters upon pulsed irradiation with low-energy ions during heteroepitaxy).

Because the ion irradiation can stimulate the mixing process for dissimilar materials [9], the final elemental composition of QDs in the formed Ge/Si nanostructures remained unclear.

This work is devoted to determining the elemental composition of QDs using Raman scattering in the structures formed as a result of the effect of self-organization of an ensemble of nanoclusters upon pulsed irradiation by low-energy ions during Ge heteroepitaxy on Si(100).

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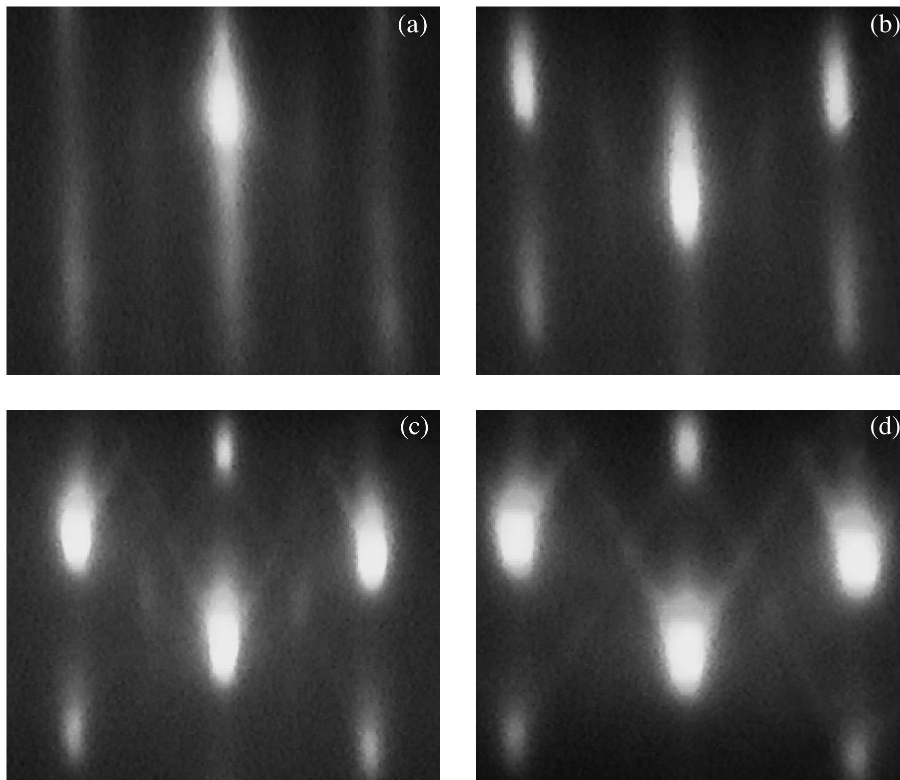

Fig. 1. Diffraction patterns obtained during (a) and (c) conventional Ge/Si(100) heteroepitaxy without ion irradiation and (b) and (d) heteroepitaxy with pulsed (0.5 s) irradiation by low-energy (≈100 eV) Ge^+ ions; the substrate temperature was 350°C; two effective thicknesses of the deposited Ge were used: (a) and (b) 5 ML and (c) and (d) 7 ML.

The samples to be studied were grown in an MBE system with a built-in ion-molecular source of germanium (for more detail, see [6, 7]). The Ge/Si structures were formed by two methods: (1) Ge MBE on Si and (2) pulsed (with a duration of 0.5 s) irradiation with Ge^+ ions with an energy of about 100 eV during Ge MBE on Si. The pulses were supplied at instants of time corresponding to the deposition of each Ge monolayer. The Ge deposition rate was 0.1 ML/s (1 ML = 6.8×10^{14} atom/cm^2), the Si deposition rate was 1.2 ML/s, and the substrate temperature was 350°C.

Each method was used to grow structures of two types differing in the amount of the deposited germanium (5 and 7 ML). A Si layer 50-nm thick was grown over the deposited Ge film, and this procedure of sequential Ge/Si growth was repeated ten times. The final capping Si layer was grown to a thickness of 100 nm at a temperature of 500°C.

The thickness and morphology of the deposited films was controlled by reflection high-energy electron diffraction (RHEED). The selection of the two values of the deposited Ge amount (5 and 7 ML) was based on the RHEED data. When 5 ML of Ge were deposited by MBE, three-dimensional Ge islands were not yet formed (Fig. 1a). Under the same growth conditions, pulsed ion irradiation leads to the formation of 3D islands on the Ge/Si surface (Fig. 1b). For thicker layers of deposited Ge (7 ML), the islands form even in the conventional MBE. Therefore, the diffraction patterns from Ge films formed by both methods show virtually no difference, and, according to the RHEED data, a transition from the growth of 3D islands in the form of hut clusters to the growth of islands in the form of dome clusters is observed (Figs. 1c, 1d).

The samples were studied using Raman spectroscopy. The multilayer character of the Ge/Si structure provided a sufficient intensity of the Raman signal. The spectra were recorded at room temperature using an automated setup based on a DFS-52 spectrometer. An Ar^+ laser ($\lambda = 514.5$ nm) was used as the source of excitation. The Raman experiments were carried out in the quasi-backscattering geometry. The following polarization geometry was used in the scattering experiments: the polarization vector of the incident radiation was directed along the crystallographic $\langle 100 \rangle$ direction of the structures, and the scattered light was detected in the $\langle 010 \rangle$ polarization. This allowed us to avoid the complications in the interpretation of Raman spectra considered in [10].

The experimental Raman spectra are presented in Fig. 2. Each spectrum shows a peak positioned in the range from 307 to 315 cm^{-1}, which corresponds to the Raman scattering by the optical vibrations of the Ge–Ge bonds. A decrease in the thickness of the Ge layer

shifts this peak toward lower frequencies, whereas the mechanical compressions lead to a shift of the peak toward higher frequencies. All peaks exhibit a low-frequency wing due to the contributions from both the higher-order localized modes and the wetting Ge layer. The peaks observed in the range from 370 to 430 cm^{-1} correspond to the Raman scattering by the optical vibrations of the Ge–Si bonds [10, 11].

The characteristics of the Ge–Si nanostructures were determined on the basis of the Raman data using numerical calculations of the fundamental frequencies and modes in the Born–von Karman approximation. The Ge–Ge elastic constants were determined by comparing the experimental data with the calculated phonon dispersions in bulk germanium [12]. The Raman spectra were calculated from these data using the Wolkenstein model of additive bond polarizabilities [13]. The calculation was performed within the framework of a one-dimensional approximation, because the lateral sizes of three-dimensional islands formed during Ge/Si(100) heteroepitaxy are usually much larger than their height. It follows from the calculations that the Raman-active Ge–Ge frequencies decrease with decreasing thickness of the germanium layer. In the case of a flat (unstrained) Ge layer, the frequency of the main Ge–Ge peak is 290 cm^{-1} for a thickness of 5 ML, 294 cm^{-1} for a thickness of 7 ML, and 298 cm^{-1} for a thickness of 10 ML.

Mechanical strains were not considered in the calculation, but their effect can be taken into account by shifting all frequencies by a value proportional to the strains, as was done in [14, 15]. According to our estimates, the shift of the Ge–Ge Raman peak as a result of the mechanical strains in Ge islands elastically strained in Si (because of a difference of 4.2% in lattice constants) reaches 17 cm^{-1} with respect to the frequency of the optical phonon in the unstrained bulk Ge (302 cm^{-1}). In the structures with an effective Ge thickness of 5 ML grown by the conventional MBE, the peak is located at 307.5 cm^{-1} (Fig. 2). The vibrational frequency calculated for an unstrained Ge film uniform in depth equals 290 cm^{-1} for a thickness of 5 ML. The high-frequency shift of 17.5 cm^{-1} is in good agreement with the estimates given for a strained structure and with the RHEED data, which point to the absence of 3D Ge islands.

In the spectra of the samples with the same average thickness of the deposited germanium grown by MBE with pulsed ion irradiation, the peak of the Raman signal of the Ge–Ge bonds is located at 315 cm^{-1}. In this case, the difference between the experimental and calculated peak positions is 25 cm^{-1}. This is considerably larger than the highest possible shift caused by the effects of compression strains (17 cm^{-1}). Such a shift cannot be interpreted as the effect of mechanical strains. Evidently, the germanium layer in this case is not two-dimensional but contains 3D islands in which

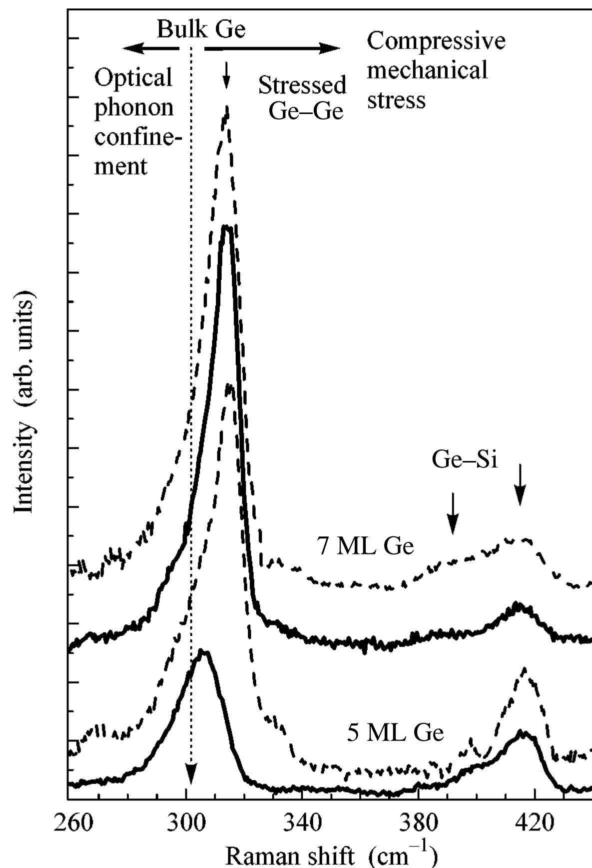

Fig. 2. Raman spectra of multilayer Ge/Si heterostructures for two thicknesses of the deposited Ge: 5 and 7 ML. The solid line corresponds to the structures obtained by the conventional MBE, and the dashed line corresponds to the structures obtained by the MBE with pulsed ion irradiation.

the thickness of germanium is much larger than the average thickness, in agreement with the RHEED data. The variation of the position and shape of diffraction reflections under conditions of growth with pulsed ion irradiation corresponds to the appearance of three-dimensional islands shaped as hut clusters (Fig. 1b).

In this case, according to the STM and RHEED data [8], the overall height of the 3D islands and the wetting Ge underlayer makes up about 10 ML. For the island structure of such sizes, the calculated peak position equals 298 cm^{-1}. The difference between the calculated and experimental peak positions is 17 cm^{-1}, which is close to the maximum possible shift due to mechanical strains. This result indicates that the plastic relaxation of mechanical strains is absent in the 3D islands obtained under the ion-irradiation conditions.

As the average thickness of the deposited germanium increases to 7 ML, the Raman spectral differences between the samples grown under conditions of pulsed irradiation by Ge^{+} ions and by the conventional MBE virtually disappear (Fig. 2), which agrees with the RHEED data (Figs. 1c, 1d). The small displacement of

the Raman peak from the Ge–Ge bonds toward the value corresponding to the bulk material, as compared to the Raman peak in the structures with a thickness of 5 ML grown under pulsed action, is, evidently, associated with a partial relaxation of strains by approximately 10–20% (Fig. 2).

The amounts of germanium in the structures under study were estimated from the ratio of peak intensities for the Si–Ge and Ge–Ge bonds. In the samples with an effective thickness of 5 ML grown by the conventional molecular-beam epitaxy, the ratio of integral peak intensities (I_{SiGe}/I_{GeGe}) equals 0.43. For the structures with the same average thickness of the deposited germanium obtained under pulsed ion-irradiation conditions, the I_{SiGe}/I_{GeGe} ratio decreases to 0.2. As the effective film thickness increases to 7 ML, the Raman intensities for the optical Si–Ge vibrations further decrease, compared to the peak intensities for the Ge–Ge bonds (Fig. 2). Based on the ratio of the Si–Ge and Ge–Ge peak intensities, the ratio of the amounts of the silicon and germanium bonds (N_{SiGe}/N_{GeGe}) in the layers is estimated as

$$\frac{I_{SiGe}}{I_{GeGe}} \simeq B\frac{N_{SiGe}}{N_{GeGe}}, \quad (1)$$

where $B \approx 3.2$ (see [11, 16]).

In the structures with an effective thickness of 5 ML grown under pulsed ion-irradiation conditions, the N_{SiGe}/N_{GeGe} ratio equals 0.64. In the structures with an effective thickness of 7 ML, this ratio decreases to 0.5. The fractional Ge content χ was estimated from the ratio of the number of bonds. For the structures grown from an ion-molecular beam, $\chi > 0.75$. The Ge islands reside in the Si environment, and the Si–Ge bonds at the phase boundary can contribute to N_{SiGe}; therefore, the above estimate is the lower limit of the Ge content. The obtained value of N_{SiGe}/N_{GeGe} can be compared with the ratio of the number of bonds in a model structure containing Ge islands ($\chi = 1$) shaped as hut clusters built-in in a silicon matrix. The lateral size of the islands was chosen equal to 10 nm, the height was 1 nm, the effective thickness of the Ge layer was 5 ML, the thickness of the wetting layer was 3 ML, and the island density was 10^{12} cm^{-2}. In this case, the N_{SiGe}/N_{GeGe} ratio equals 0.52. The obtained value for the chosen model structure proved to be rather close to the experimental values. Thus, the comparison of the experimental and calculated results allows the suggestion that the Ge nanoclusters in the heterostructures obtained by ion-molecular beam epitaxy contain almost no Si.

An important conclusion from the results obtained in this work is that the pulsed ion irradiation during the growth of Ge/Si structures does not lead to a significant mixing of the Ge and Si layers. The germanium content in the three-dimensional islands obtained by the conventional epitaxy and epitaxy with ion irradiation practically proved to be similar.

This work was supported by the Russian Foundation for Basic Research (project no. 02-02-16020), INTAS (project no. 2001-0615), and the Federal Research and Technical Program (contract no. 40.012.1.1.1153).

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Translated by A. Bagatur'yants