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Features of the Stress State of Germanium Nanocrystals in SiO_x Matrix

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Features of mechanical stresses in germanium nanocrystals synthesized in amorphous SiO_x matrix with Si_xN_y buffer layer were studied by means of the Fourier transform infrared absorption spectroscopy, Raman scattering, and computer modeling. It was found that the germanium nanocrystals are under significant compressive stress with a magnitude of up to 2.9 GPa. Such a high strain value can be explained by a partial penetration of the nanocrystals into the silicon substrate. In this case, the lattice mismatch between silicon and germanium is the principal source of mechanical stresses.

Keywords: Nanocrystal, Quantum dot, Mechanical stress, Heterostructure.

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1. INTRODUCTION

Over the last decade, heterostructures with germanium nanocrystals (quantum dots) in amorphous dielectric matrixes have received recognition as promising materials for the production of highly-efficient light-emitting devices [1], IR radiation detectors [2], solar cells [3], thermoelectric converters [4], memory cells [5]. Large absorption coefficient, larger Bohr radius of Ge (25 nm) than of Si (4 nm) and, as a consequence, stronger manifestation of the quantum restriction effects, low synthesis temperatures of Ge compared with Si are the main advantages of such nanostructures. Moreover, methods for producing Ge quantum dots are fully compatible with modern technology of silicon integrated circuits.

Properties of Ge nanocrystals significantly depend not only on their sizes and shape, but also on the mechanical stresses (strains) appearing in the synthesis of heterostructures. It is established that strains in nanocrystals cause the changes in the optoelectronic properties by influencing the energy bands, charge carrier dynamics, and processes of their recombination [7]. But questions about the origin of mechanical stresses are still open. In the majority of the known works it is reported that germanium quantum dots grown in amorphous SiO_2 matrix undergo compressive stresses, whose value depends on the synthesis method and is approximately equal to 1 GPa [8, 9]. Nature of these strains is usually associated with cubical expansion of germanium ($\Delta V \sim 6$ %) at the formation of nanocrystals from a liquid phase. It is also shown that sizes, density and perfection of Ge quantum dots influence the value of the compressive stresses in SiO_2 matrix [10]. Individual investigations demonstrate the possibility of appearance in nanocrystals of the tensile strains in SiO_2 matrix with increased density [11]. The authors of [12] have revealed the effect of sign change of mechanical stresses in quantum dots depending on the stoichiometry of dielectric SiO_x matrix.

At the same time, a question concerning the ways of controlled changes of mechanical stresses in quantum dots remains virtually unstudied. Among the options of influence on the stress state of nanocrystals it was proposed, in particular, to use silicon nitride as a covering layer, choice of the material of a dielectric matrix and annealing technique [13], although the subsequent studies have not been conducted.

In the present work, investigations of the stress state of germanium nanocrystals in amorphous SiO_x matrix with Si_xN_y buffer layer are carried out by using experimental techniques and theoretical calculations. Explanation of the generation mechanism of high compressive stresses in nanocrystals is proposed.

2. INVESTIGATION TECHNIQUE

For the study, we used heterostructures containing a silicon substrate with subsequently grown on it Si_xN_y buffer layer of the thickness of 37 nm and $Si_{0.83}Ge_{0.17}$ film of the thickness of about 300÷500 nm. Germanium nanocrystals with the average diameter of about 4 nm and density of ~ 10^{12} cm^{-2} (by the electron microscopy data), immersed in SiO_x layer and, partly, in thin Si_xN_y layer and Si substrate, were formed in the film by the oxidation method at the temperature of 900 °C. Two structures containing, in the first case, a silicon substrate with a silicon oxide layer of the thickness of ≈ 350 nm and, in the second case, Si_xN_y layer of the thickness of about 80 nm on the silicon substrate, were also studied for the comparison.

Composite analysis of the investigated structures was carried out using the IR Fourier-spectrometer Spectrum BX-II by Perkin Elmer. Recording of IR transmission spectra (FTIR) was performed in the frequency range from 400 cm^{-1} to 1600 cm^{-1} with resolution not less than 0.8 cm^{-1}. A silicon plate of the n-type with resistivity of 4.5 Ohm·cm (similar to that which served as the substrate in the investigated samples) was used as the key sample. FTIR spectra of the studied samples were normalized on the spectrum of this plate.

The stress state of nanocrystals was experimentally investigated by the Raman scattering spectra. The spectra are obtained in the backscattering geometry on the spectrometer Horiba Jobin-Yvon T64000 using Ar^+ laser ($\lambda = 514.5$ nm). Diameter of a spot, in which light is

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focused on the sample surface, was approximately equal to 0.7 μm, and spectral resolution – 0.15 cm^{-1}. All measurements were conducted at room temperature.

3. RESULTS AND DISCUSSION

In Fig. 1 we present the IR transmission spectra of the studied heterostructures. Presence of the absorption band near 615 cm^{-1} that corresponds to the stretching vibration frequency (the stretching mode) of the Si-Si bands is noticeable in the spectra of all the samples. In the FTIR-spectrum of the structure with SiO_x film on a silicon substrate (curve 2, Fig. 1) there appear 3 clearly defined absorption bands in the vicinity of 460 cm^{-1}, 820 cm^{-1} and 1090 cm^{-1}, which are associated with three oscillation modes of the Si-O bands in the compound of the stoichiometric composition of SiO_2: the rocking-mode, the bending-mode and the stretching-mode, respectively [14]. For the sample with Si_xN_y film (curve 1, Fig. 1), spectral band near 460 cm^{-1} does not appear completely, and band 1090 cm^{-1} is appreciably reduced in intensity compared with the spectrum of the sample 2. This can imply an insignificant content of oxygen incorporated into the heterostructure.

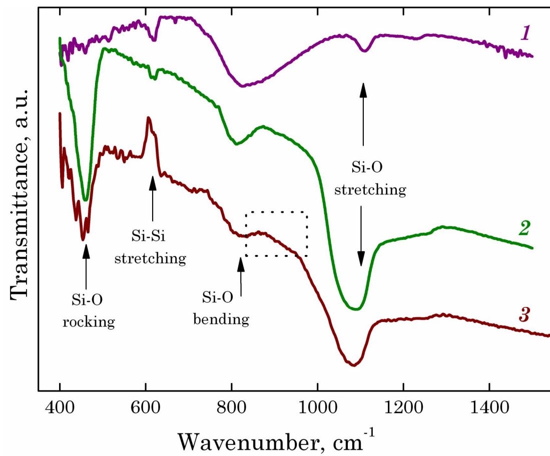

Fig. 1 – FTIR-spectra of the following studied heterostructures: 1 – Si / Si_xN_y layer substrate, 2 – Si / SiO_x layer substrate, and 3 – Si / Si_xN_y layer/ SiO_x layer substrate with Ge nanocrystals of the diameter of 4 nm

Sample with Ge nanocrystals exhibits a slight decrease in absorption of the Si-Si bands on 615 cm^{-1} (see curve 3, Fig. 1). A substantial decrease in the light transmission in the range of 835-975 cm^{-1} (rectangular region in Fig. 1) and the corresponding tailing of the absorption band on 820 cm^{-1} are the characteristic features of this sample. Broadening of the FTIR-spectrum near 820 cm^{-1} is also observed in the spectrum 1 of Fig. 1 that indicates the presence of additional absorption bands in the vicinity of the specified frequency. Decomposition of the absorption spectrum in the range of 700÷1000 cm^{-1} allowed to reveal here two components (Fig. 2): the first band 815 cm^{-1} corresponds to the Si-O stretching-mode, while the second one – 899 cm^{-1} – is most probably connected with the stretching-mode of the Si-N bond vibrations in Si_xN_y film [15].

Spectral position of the latter band depends on the stoichiometry of Si_xN_y compound (x/y ratio) as [16]

$$\nu_{\text{Si-N}}(x/y) = 21.4(x/y - 4/3) + 840 \ \ (\text{cm}^{-1}) . \quad (1)$$

The value of $\nu_{\text{Si-N}} = 899$ cm^{-1} obtained in the experiments allows to conclude that the studied Si_xN_y film is supersaturated with silicon with the component ratio of $x : y \approx 4 : 1$.

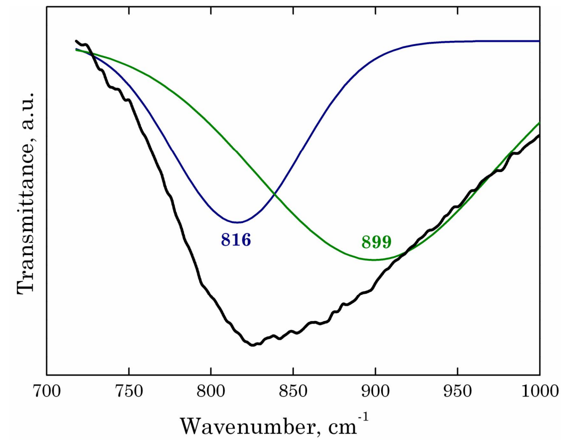

Fig. 2 – Decomposition of the FTIR-spectrum of Si substrate / Si_xN_y layer sample (curve 1, Fig. 1) near the Si-O bending-mode

The feature of asymmetric broadening of the absorption band in the vicinity of 820 cm^{-1} of heterostructures with germanium nanocrystals (curve 3, Fig. 1) also indicates its multicomponent structure. Five bands, namely, 815 cm^{-1}, 882 cm^{-1}, 920 cm^{-1}, 1024 cm^{-1} and 1090 cm^{-1}, are separated by decomposition of the spectral region between Si-O bending and Si-O stretching modes (Fig. 3) in the specified range. The first and the latter of them correspond to the bending and stretching modes of Si-O bond vibrations in SiO_2 film. Appearance of the band 920 cm^{-1} is most probably caused by Si-N-O bond vibrations in Si_xN_y buffer layer and indicates the presence of SiN_xO_y clusters there [17]. Two other absorption bands in the spectrum (882 cm^{-1} and 1024 cm^{-1}) are caused by Ge nanocrystals and we associate them, correspondingly, with Ge-O-Ge and Si-O-Ge bond vibrations [18, 19].

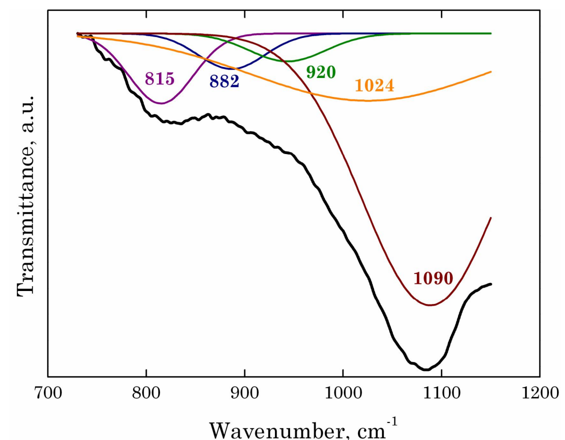

Fig. 3 – Decomposition of the FTIR-spectrum of Si substrate / Si_xN_y layer / SiO_x layer sample (curve 3, Fig. 1) in the region between Si-O bending and Si-O stretching modes

It is known that spectral position of the $\nu_{\text{Ge-O-Ge}}$ band associated with the Ge-O-Ge bond vibrations is linearly changed depending on the content of oxygen x by the correlation [18]

$$\nu_{\text{Ge-O-Ge}}(x) = 72.4x + 743 \ \ (\text{cm}^{-1}) . \quad (2)$$

Substituting experimental value $\nu_{Ge\text{-}O\text{-}Ge} = 882\ cm^{-1}$ into (2), we will find the oxygen fraction $x \approx 2$. The obtained value of x which corresponds to the stoichiometric GeO_2 compound gives reason to assume the presence of the transition oxide region between germanium quantum dots and SiO_2 matrix.

To characterize the stress state of germanium nanocrystals, the Raman spectroscopy was used. Only weak phonon band (curve 1, Fig. 4) with the maximum near 305 cm^{-1} associated with the second-order scattering by acoustic phonons of a silicon substrate is registered in the Raman scattering spectrum of a silicon substrate with SiO_2 film in the studied range. The sample with Si_xN_y film has the same view of the spectrum (it is not shown in Fig. 4). An intense vibration band (curves 2, 3, Fig. 4) with the maximum at ~ 303 cm^{-1} identified as the Ge-Ge phonon mode is registered in the Raman spectra of the samples with Ge nanocrystal inclusions into SiO_2 matrix. A line with the maximum near 407 cm^{-1} (spectrum 3, Fig. 4), which we associate with the Si-Ge phonon mode conditioned by the remains of $Si_{1-x}Ge_x$ solid solution has also appeared in some samples depending on the registration point.

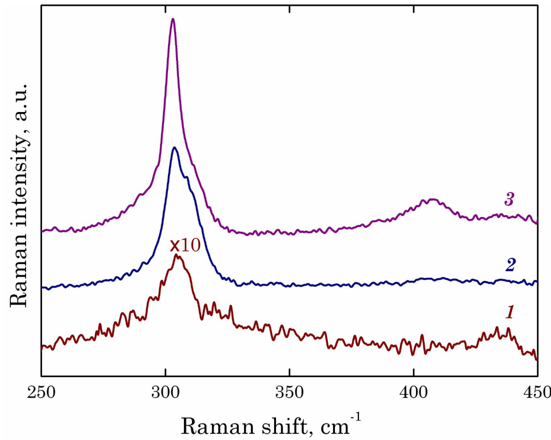

Fig. 4 – Raman scattering spectra of the studied structures: 1 – Si substrate/ Si_xN_y layer; 2, 3 – Si substrate / Si_xN_y layer / SiO_x layer with germanium nanocrystals of the diameter of 4 and 13 nm, respectively. Intensity of the spectrum 1 increased in 10 times

The detailed analysis of the Raman spectra in the region of Ge-Ge vibrations for a large amount of spectra implies a high-frequency shift and clearly defined two-component character of the given phonon band. Based on the features of the strain in the considered structure, a high-frequency shift of the spectral maximum can be associated with the initiation of the compressive stresses in germanium nanocrystals, and presence of two components – with the existence of space regions which are located in substantially different stress states. In the present work, analysis was performed within two-component structure of the Raman peak.

The first component which has higher intensity exhibits the maximum in the range of 302÷304 cm^{-1} depending on the registration point on the samples surface and, most probably, is caused by Ge nanocrystals embedded in SiO_2. Maximum of the second component of lower intensity is shifted towards the region of larger wavenumbers (309÷311 cm^{-1}). Variation of the spectral position and intensity ratio of the optical phonon band imply a non-equilibrium distribution of the mechanical stresses in the sample.

The value of the mechanical stresses σ and their sign in the structure can be determined from the relation [9]

$$\Delta\omega = 3.85 \cdot \sigma - 0{,}039 \cdot \sigma^2 , \qquad (3)$$

where $\Delta\omega = \omega - \omega_0$, ω_0, ω is the frequency position of the Ge-Ge Raman peak in unstrained and strained crystal, respectively. Substituting $\omega_0 = 300.6\ cm^{-1}$ and the experimental values $\omega = 309÷311\ cm^{-1}$ into (3), we obtain $\sigma = -(2.4÷2.9)$ GPa. This corresponds to the mean strain $\varepsilon = -(1.1÷1.4)$ %. Sign "–" denotes that Ge quantum dots undergo compressive stresses.

It is known that stress in germanium nanocrystals in amorphous matrix can be caused by several factors: (a) change in the volume of germanium during high-temperature treatment and formation of nanocrystals from a liquid phase; (b) structural mismatch between germanium lattice and SiO_2 matrix; (c) composition non-uniformities of the matrix around nanocrystals; (d) incomplete surface reconstruction during growing of quantum dots [9, 20, 21]. But all the listed factors cause strains in nanocrystals, the value of which, as a rule, is equal to tenths of a percent.

Conservative values of ε obtained in the present work can be associated with the fact that at small thickness of Si_3N_4 buffer layer nanocrystals can partly penetrate into a silicon substrate with the formation of the heterojunction Ge nanocrystal / Si substrate. Appearance of the Si-Ge lines in some Raman spectra (spectrum 3, Fig. 4) can testify in favor of the given assumption. Under these conditions, quantum dots undergo substantial compressive strains (to 4 %) because of the mismatch between silicon and germanium lattices. The value of stresses will be determined by the immersion depth of nanocrystals into the substrate and by their sizes. These quantum dots with increased strain will contribute into the Raman scattering spectra which are registered over the sample surface conditioning a high-frequency shift of the germanium optical phonon line.

Modeling of the stress state of germanium nanocrystals was performed in the work in order to confirm the proposed mechanism. We have considered the structure containing a silicon substrate, nitride and silicon oxide layers and spherical germanium nanocrystal of diameter D immersed to a depth of h into the substrate (the inset, Fig. 5). The following system of equations of the theory of elasticity was solved for this structure using the finite element method [22]:

$$\frac{d\sigma_{ij}}{dx_i} = 0 , \qquad (4a)$$

$$\sigma_{ij} = C_{ijkl}(\varepsilon_{kl} - \varepsilon_{0kl}) , \qquad (4b)$$

$$\varepsilon_{0kl} = \frac{1}{2}\left(\frac{\partial u_k}{\partial x_l} + \frac{\partial u_l}{\partial x_k}\right) , \qquad (4c)$$

where u_i is the elastic displacement vector; ε_{kl}, σ_{ij}, C_{ijkl} are the tensors of strain, mechanical stresses and elastic constants, respectively. Initial strains are denoted as ε_{0kl} in the equation (4b). For a part of Ge nanocrystal, which is located in the silicon substrate, ε_0 is determined by the mismatch between Si and Ge lattices and is equal

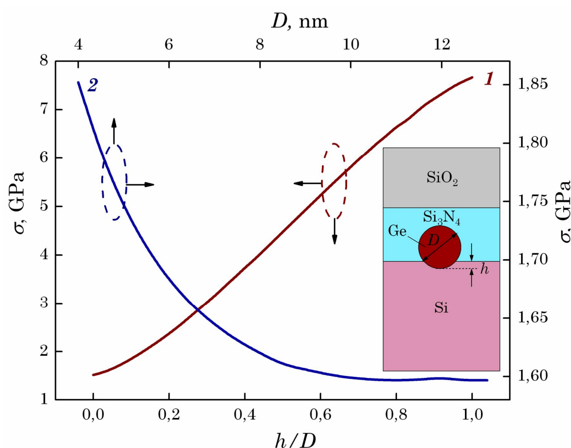

Fig. 5 – Dependence of the value of mechanical stresses in Ge nanocrystal on the dimensionless penetration depth h / D into the substrate (curve 1) and on its diameter D at the fixed value $h = 1$ nm (curve 2). On the inset: geometry of the structure for which mechanical stresses were calculated

to $\varepsilon_0 = -0.04$ [22]. In another part of the quantum dot localized in silicon nitride, two sources of strains are possible: 1) cubical expansion of Ge during the formation of a nanocrystal from a liquid phase, to which strain $\varepsilon_0 = -0.02$ corresponds [9]; 2) difference $\Delta\alpha$ of the coefficients of thermal expansion of Ge and silicon nitride with the corresponding value of the strain $\varepsilon_{02} = \Delta\alpha\ \Delta T$ (ΔT is the temperature variation). Since the difference $\Delta\alpha = 1.8 \times 10^{-6}$ °C [22], then at typical values $\Delta T = 500$-900 °C, ε_{02} does not exceed 0.002, that is one order of magnitude less than ε_{01}, therefore it is possible to neglect this source of strains.

In Fig. 5 we show the calculated dependences of the mechanical stresses σ in Ge nanocrystals on the depth of their penetration h into the substrate and diameter D. The calculation results imply that with increasing h the value of stresses in quantum dots increases in several times relative to the similar values for nanocrystals in amorphous SiO_x or Si_xN_y matrixes (curve 1, Fig. 5). For the same penetration depth h into the silicon substrate, the smaller diameter of nanocrystals, the larger stresses in nanocrystals (curve 2, Fig. 5). Taken together, these results confirm the proposed explanation of high values of mechanical stresses in quantum dots obtained from the Raman scattering spectra.

In summary, the experimental and theoretical investigations of the stress state of germanium nanocrystals in amorphous matrix of silicon oxide with silicon nitride buffer layer have been performed in the present work. It is revealed that quantum dots undergo significant compressive stresses from the matrix that is explained by partial penetration of nanocrystals into the substrate of single-crystal silicon.

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