Structural and optical properties of two-dimensional Si and Ge layers formed by molecular beam epitaxy on CaF_2/Si(111) substrates

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Approaches to the formation of epitaxial structures containing two-dimensional Si and Ge layers embedded in a CaF_2 dielectric matrix have been developed. Raman study demonstrates the presence of narrow peaks related to Si−Si- and Ge−Ge-bond vibrations in the growth plane of structure. In the photoluminescence spectra of the created structures, emission bands, which can be associated with the radiative recombination of charge carriers in two-dimensional Si and Ge layers embedded in CaF_2 have been found.

Keywords: silicon, germanium, two dimensional, calcium fluoride, molecular beam epitaxy, electron irradiation, atomic structure, photoluminescence.

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1. Introduction

Presently, there is the increased interest worldwide in graphene-like materials based on silicon and germanium [1–4]. It is expected that these materials will have an electron structure with the direct band gap, which must lead to effective photoluminescence [3,4]. It is possible to identify the two main groups of methods of producing the two-dimensional materials based on germanium and silicon. The first group may include chemical methods of impact on various lamellar materials, whose crystal lattice includes the graphene-like monolayers Si (silicene) or Ge (germanene) in order to single out these two-dimensional layers [4,5]. The second group may include epitaxial methods based on deposition of monolayer or submonolayer Si and Ge coatings onto special substrates contributing to the formation of the graphene-like surface structure [6–8]. Usually, the silicene and the germanene are synthesized by using the inert atomically clean surface of the substrates of the noble metals [6,7] or the pyrolytic graphite [8]. The said substrates are highly-conductive, thereby making it difficult using the produced two-dimensional materials as active areas of the electron instruments [9]. Practically, it is relevant to create the two-dimensional layers of silicon and germanium on non-conductive crystal substrates. The present study is focused on developing physical approaches for formation of the two-dimensional Si and Ge layers on the surface of the CaF_2/Si(111) dielectric substrate, as well as on investigating their structural and luminescent properties.

2. Experimental procedure

The structures were synthesized by the molecular beam epitaxy. The first stage included the epitaxial growth of the CaF_2 film of the thickness of 40 nm on the Si(111) substrate doped with boron (KDB-10). The second stage included depositing the ultra-thin Si or Ge layers with the effective thickness of about 1 atomic bilayer to the surface of the CaF_2 film. The structures with one Si bilayer have been synthesized for the two substrate temperatures: 300 and 550°C, whereas the structures with one Ge bilayer have been formed at the temperature of 550°C. The third stage included covering the created structures with the CaF_2 protective layer of the thickness of 5 nm at the same temperatures at which the Si or Ge layers were deposited. The surface morphology of the grown structures were studied by the atomic-force microscopy (AFM) or the scanning electron microscopy (SEM). In order to control the change of the surface state in the growth process, the reflection high-speed electron diffraction (RHEED) was used to controllably affect singled-out surface sections of the formed structure by an electron beam of the diffractometer. The electron beam was applied along the crystallographic direction [110] with the accelerating voltage of 20 kV and the current density of 50 μA/cm^2. The

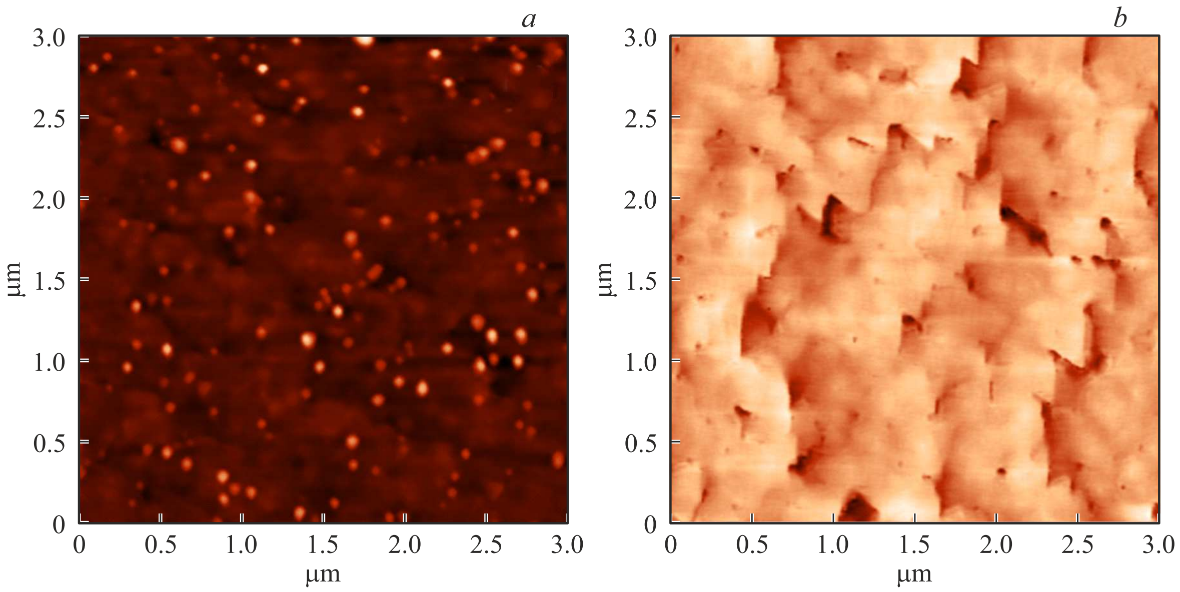

Figure 1. AFM-images of the surface of the structures produced by deposition of one Si bilayer to the surface of the CaF_2/Si(111) film of the thickness of 40 nm at the two substrate temperatures: 300 (*a*) and 550°C (*b*).

electron beam incidence angle in relation to the surface did not exceed 2°. The deposition rates of CaF_2, Si and Ge were 0.3, 0.1 and 0.05 Å/s, respectively. The elementary composition and the luminescent properties of the created structures were investigated using the Raman scattering (RS), the energy dispersion X-ray spectroscopy (EDX) and the photoluminescence (PL). The PL was measured at the room temperature (300 K) and the helium temperatures ($\sim$ 5 K). The charge carriers were photo-excited by a laser with the radiation wavelength of 405 nm. The focused and non-focused laser beams were used. The focused beam was sized to be of $\sim 0.1\,\mathrm{mm}^2$, so was the non-focused one — $1\,\mathrm{mm}^2$.

3. Results and discussion

The surface morphology of the grown structures produced by deposition of one Si bilayer to the surface of the CaF_2/Si(111) film (areas unaffected by the diffractometer electron beam) was studied to show that for the structure grown at the temperature of 300°C the surface has compact elevations (Fig. 1, *a*), which apparently can be correlated to formation of three-dimensional silicon islands. In accordance with the AFM data, the height of these islands ranges from 4 to 10 nm, so does the base size from 50 to 100 nm. Whereas, the surface of the structure, which is grown at the higher temperature (550°C), is characterized by the presence of quite wide and flat terraces without any signs of agglomeration of Si to the three-dimensional islands (Fig. 1, *b*). In the latter case, the surface roughness does not exceed 0.5 nm. The obtained result allow us to conclude that the temperature of 550°C is more preferable for the formation of solid and uniform-thickness Si layers on the surface of the CaF_2 film than the temperature of 300°C.

Fig. 2 shows the RS spectra of the created structures measured in the areas unaffected by the electron beam. For the structure with one Si bilayer formed at the temperature of 550°C, there is evidently a prominent narrow peak at $418\,\mathrm{cm}^{-1}$ (Fig. 2, the curve *1*). This peak is caused by light scattering at the vibrations of the Si–Si bonds within the plane of the two-dimensional Si layer intercalated by calcium [12]. Whereas, for the structure grown at the temperature of 300°C, this peak is not detected (Fig. 2, the curve *2*). The RS spectra of the said structures exhibit the peak at $445\,\mathrm{cm}^{-1}$. Most likely, this peak is correlated to the CaF_2/Si(111) heterointerface. It is confirmed by the fact that for the test structure grown in the same conditions, but without the Si bilayer, this peak is kept, while there is no peak at $418\,\mathrm{cm}^{-1}$ (Fig. 2, the curve *4*). It should be noted that at all the RS spectra of the above-analyzed structures, there is a peak at $300\,\mathrm{cm}^{-1}$, which is correlated to the Si(111) substrate (Fig. 2, the curve *5*). This signal corresponds to the two-phonon light scattering at the vibrations of the Si–Si bonds in the bulk crystal silicon [10].

Within an area affected by the electron beam falling at the small incidence to the surface of the growing structure, a light area is forming to have a typical metal blaze. This area is shaped as an ellipse strongly oblong along the direction of incidence of the electron beam. The typical width of the area is $\sim$ 2 mm, while the length can be of several centimeters (see, for example, the picture of „a trace“ resulting from affecting the surface of the CaF_2 growing film by the diffractometer electron beam, as shown in the study [11]). The RS spectra from surface structure area affected by the electrons have evidently three

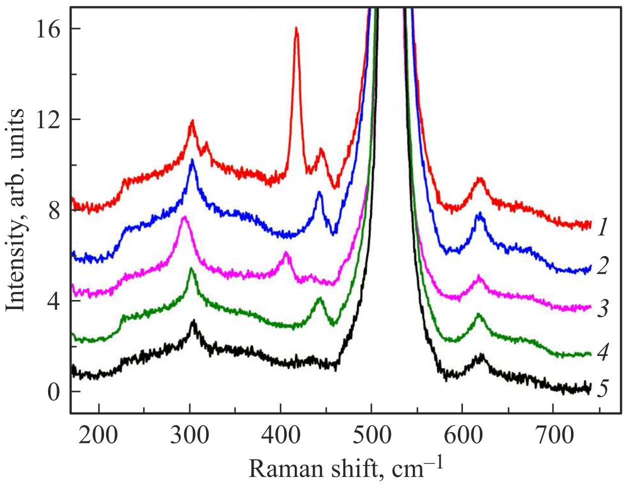

Figure 2. RS spectra of the epitaxial structures produced by deposition of one Si bilayer at the two temperatures: 550 and 300°C (the curves *1, 2*) or of the one Ge bilayer (the curve *3*) at the temperature of 550°C to the surface of the CaF_2/Si(111) film. For comparison, the RS spectra of a test structure and the Si(111) initial substrate (the curve *5*) are given. This test structure is the CaF_2 film of the thickness of 40 nm grown at the temperature of 550°C (the curve *4*). The spectrum *3* was measured for an area of the surface of the structure formed in the electron irradiation conditions. The spectra *1* and *2* are obtained from areas of the surface of the structure formed without electron irradiation. (A color version of the figure is provided in the online version of the article).

peaks 416, 388 and 346 cm^{-1}, which are typical for the $CaSi_2$ crystal layers [11]. As it has been shown in the studies [11,13], the $CaSi_2$ is formed by decomposition of CaF_2 to Ca and F as stimulated by the electron irradiation. The fluorine is desorbed from the surface, while the remaining calcium starts reacting with silicon, which at the quite high temperatures (> 350°C) comes to the surface by thermally activated diffusion out of the Si(111) and (or) by direct deposition of silicon from the molecular beam.

The luminescent properties were investigated outside the RHEED-affected area to show that there is a radiation band with the maximum at 680 nm ($\sim$ 1.85 eV) [13]. It can be correlated to radiative recombination of the charge carrier in the Si two-dimensional layer embedded to the CaF_2 dielectric matrix. This PL band was not observed in the test structure grown in the same conditions, but without the Si bilayer.

For the structure produced by deposition of one Ge bilayer to the surface of the CaF_2 film in the condition of irradiation by the electron beam, the RS spectra exhibit a strong dependence on a location on the surface within the irradiation area. This is caused by heterogeneous distribution of the intensity across the section of the electron beam. In accordance with the AFM data, a central part of the area affected by the electron beam (where the electron irradiation intensity is the highest) forms a developed surface relief with faceting typical for the $CaSi_2$ epitaxial layers grown on the Si(111) substrates [5,13], whereas at the periphery (near the edges of this area) of the lesser irradiation intensity, the surface has a less developed relief. The SEM and EDX studies have shown that these areas form the two-dimensional Ge islands (Fig. 3, *a* and *b*). According to the data obtained, the average size of the islands is $\sim$ 300 nm, thereby the formation of these islands can be regarded as an initial stage of the formation of the two-dimensional Ge layer. The RS spectra obtained at the surface areas with the lesser electron impact show the presence of the two peaks at 295 and 407 cm^{-1} (Fig. 1, the curve *2*). The spectral position of the first peak is close to the scattering peak at the vibrations of the Ge–Ge bonds in the single-crystal Ge (301.5 cm^{-1}) [14]. The second peak corresponds to the scattering on the vibrations of the Ge–Si bonds in the Ge/Si heterostructures [14]. We correlate the peak at 295 cm^{-1} to the stressed two-dimensional Ge islands, which are formed on the CaF_2 surface affected by the electron beam. The RS spectra obtained at the surface areas with more intense electron impact show the presence

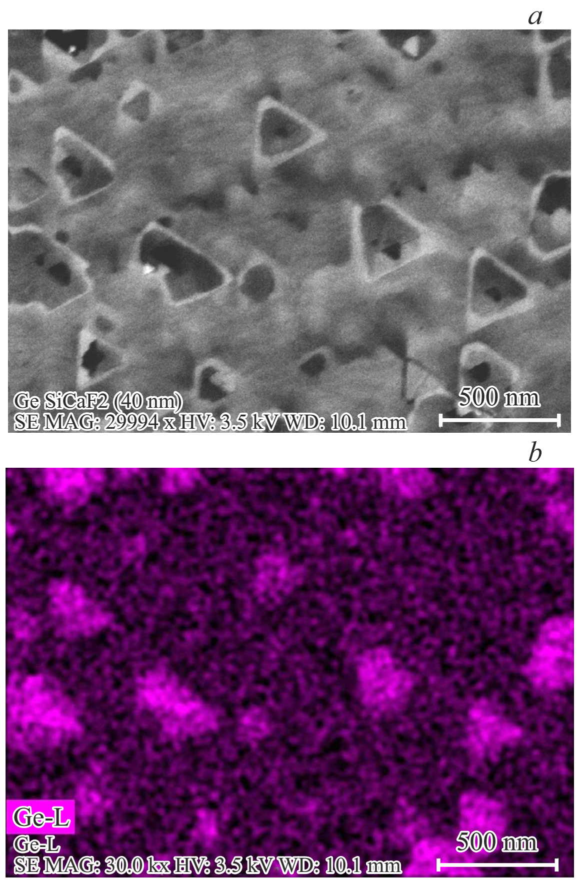

Figure 3. *a* — SEM-image of the surface of the structure produced by deposition of one Ge bilayer to the surface of the CaF_2/Si(111) film of the thickness of $\sim$ 40 nm near the periphery of the electron beam-irradiated area; *b* — the map of distribution of Ge along the structure surface.

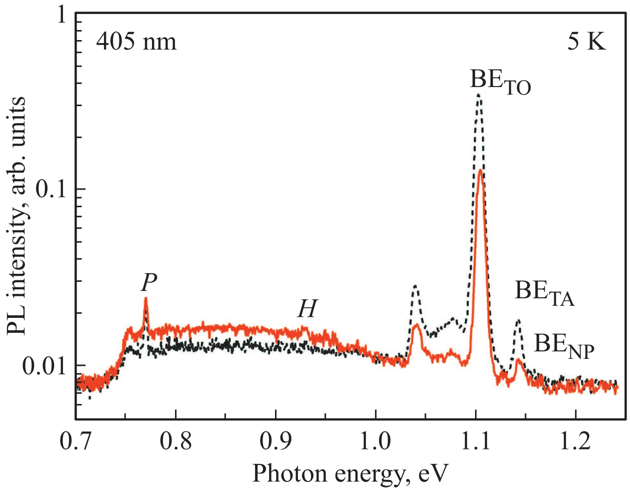

Figure 4. PL-spectrum for the CaF_2/Ge/CaF_2/Si(111) structure, produced by deposition of one Ge bilayer to the surface of the CaF_2 film of the thickness of 40 nm in the electron irradiation conditions (the solid line) and without it (the dashed line). The measurement temperature was ~ 5 K. The photoexcitation was made by the laser of the radiation wavelength of 405 nm by the laser beam focused to $\sim 0.1\,\mathrm{mm}^2$. The BE_{NP} band is caused by zero-phonon radiative recombination of the excitons bounded on the boron atoms in silicon; so are the BE_{TA} and BE_{TO} bands — by the recombination of the bounded excitons with participation of the transverse optical phonons in the crystal lattice of the Si substrate [16]. The *H* and *P* bands are related to thermal defects of the structure in silicon, which in their composition include the atoms of residual technological impurities — oxygen and carbon [17,18].

of the three peaks 408, 383, 341 cm^{-1}, which can be also correlated to the formation of the calcium silicide [12,13]. The slight shift in the peak position in comparison with the structure with a single silicon bilayer can be caused by the presence of the Ge atoms in the composition of the silicide film.

It should be noted that for the structure produced by deposition of one Ge bilayer, for the surface areas unaffected by the irradiation the RS spectra have no peak correlated to the vibrations of Ge–Ge and Ge–Si. This can be explained by the fact that without the electron irradiation almost the entire deposited Ge is desorbed from the structure surface at our synthesis temperature of 550°C. It follows from the results obtained that the irradiation by the electron beam results in the increase in the energy of the Ge bond with the CaF_2 surface and contributes to the growth of the two-dimensional Ge islands. The increase in the energy of the Ge bond with the CaF_2 surface when being affected by the electron beam agrees with the data of the study [15].

The luminescent properties of the created structures with the two-dimensional Ge islands embedded in CaF_2 have been studied. Fig. 4 shows the PL spectra measured outside the electron beam irradiated area (Fig. 4, the dashed line) and inside this area (Fig. 4, the solid line) at the temperature of ~ 5 K and the photoexcitation by the laser of the radiation wavelength of 405 nm with the laser beam focused to $\sim 0.1\,\mathrm{mm}^2$. It is clear from the comparison of the FL spectra that the electron irradiation results in the increase in the intensity of the FL signals by ~ 20–25% within the spectrum range 0.75–0.95 eV. Whereas, in the photoexcitation by the non-focused laser beam of $\sim 1\,\mathrm{mm}^2$, no increase in the PL intensity has been observed and the PL spectra taken inside and outside the irradiation area have turned out to be identical.

4. Conclusion

The results obtained indicate a promising trend of the developed approaches to creating the two-dimensional structures based on Ge and Si, which are embedded in CaF_2. For the silicon-based structures, conditions for formation of the Si two-dimensional layers have been found, which is confirmed by the RS data, which demonstrate the narrow peak correlated to the vibrations of the Si–Si bonds within the plane of the growth of the two-dimensional layer. In contrast to the silicon-based structures, the formation of the two-dimensional germanium-based structures requires the electron impact. For these structures, the RS spectra taken in the areas affected by the electron beam demonstrate the presence of the two peaks correlated to the vibrations of the Ge–Ge and Ge–Si bonds. Whereas, these peaks are not observed without the electron impact. The SEM and EDX studies have shown the formation of the two-dimensional Ge islands in the electron irradiation conditions, which can be regarded as the initial stage of the formation of the two-dimensional Ge layer.

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Conflict of interest

The authors declare that they have no conflict of interest.

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