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FEATURES OF NANOCLUSTERS FORMATION IN THE DEPOSITION MODE OF SUPERTHIN FILMS SI(GE)

A.S. Strogova
Head of the PhD Department BSUIR, PhD, Associate Professor

A.A.Kovalevskiy
Leading researcher of the Center 4.13, PhD, Associate Professor

Belarussian State University of Informatics and Radioelectronics, Republic of Belarus
E-mail: strogova@bsuir.by

Аннотация. With the use of the scanning, transmission and atomic-force microscopy and Raman scattering of ranges the features of nanoclusters formation of Si, Ge, and solid SiGe solution the deposition mode of superthin films Si(Ge) are studied. The leading mechanism in the process of films crystallization with silicon, germanium and silicon-germanium nanostructures alloyed by Ge on all types of initial surfaces of substrates is the migration of silicon and germanium atoms on a surface of films are established. For the self-organization of SiGe nanoclusters a small shift of surface atoms of complex structures on a clean surface with the formation of bonds like Ge–Ge or Si–Si is favorable. It is caused by the fact that under the thermal treatment the atoms rejected from an ideal position in a crystal grid create additional force fields and it leads to the change of elastic properties of the whole nanocrystal.

Ключевые слова: nanocluster, silicon films, germanium, nanostructure.

Introduction. Currently two-dimensional nanostructures are relevant; historically they include thin films with a thickness of up to hundreds of nanometers, as well as two-dimensional arrays of objects which dimensions lie in the nanometer range. Unlike most nanomaterials, two-dimensional nanostructures of such kind have long been found to be actually used in a variety of ways. They are widely used as optical and anti-adhesive coatings, in the technology of producing cables based on superconductors, in creating chemical or optical sensors, as well as in micro- and nanoelectronics. Due to the wide distribution in completely different areas of technology, the creation of a unified approach to obtain two-dimensional nanostructures is simply impossible. In each case, it is necessary to choose the optimal technology. Therefore, the studies of the self-organization of quantum dots (nanoclusters) of silicon and germanium are relevant because of the prospects for using these structures to create electronic products that work on optical transitions between hole quantization levels. However, to obtain such structures with desired properties, it is important to be able to control the size and density of germanium quantum dots or a silicon-germanium solid solution, which is the goal of this research.

Method Experimental techniques. Film deposition with silicon, germanium and silicon-germanium nanostructures were deposited in the isothermal zone of a horizontal reduced pressure reactor with hot walls “Isotron 4–150” at the temperature of 560–630 ° C. The temperature of 620 ± 5 °C was chosen as the main temperature. The temperature profile was maintained with an accuracy of ±1°C. In the experiments, 100% SiH_4 and a mixture were used: 3% GeH_4 - 97% Ar, 3% GeH_4 - 97% H_2, HP classification (highly pure). Silicon plates with a diameter of 100 mm, 150 mm, coated with thermal silicon oxide (10 nm ÷ 40 nm, 100 nm) were installed perpendicular to the gas flow. The length of the isothermal zone of the reactor was 750 mm. The plates were evenly placed in the isothermal zone of the reactor at a distance of 5 mm from each other.

Studies of the surface topography of the structures obtained were carried out using an Ntegra Prima atomic force microscope. Silicon cantilevers with a radius of rounded vertices of probing pyramids 15–20 nm (SCNC12, NT-MDT) were used as probes, as well as whiskers, a distinctive feature of which is the completion of the probing pyramid with an elongated narrow and sharper cone made of carbon-based material (NCC05, NT -MDT). The use of whiskers significantly improved the contrast of images of Si, Ge and SiGe islands. In addition, the density, size, and shape of nanoclusters were determined using an atomic force microscope.

Changes in the structure of Si, Ge, and SiGe - nanoclusters were analyzed on the basis of Raman spectroscopy data. Raman spectra on optical phonons were obtained by irradiating of Ar structures with a laser with a wavelength λ = 514.5 nm and were recorded using a DFS-52 spectrometer. Spectra were recorded at room temperature.

The componentwise composition of the obtained nanostructured structural objects was determined using microprobe X-ray spectral analysis on a Cameca-MBX facility.

The 2D to 3D transitions and hut in the dome were determined using the profile of the RHEED pattern (diffraction of fast electrons) from the heat treatment time.

The geometric dimensions of the particles and their quantitative size distribution were determined from photographs from an S-4800 scanning electron microscope (Hitachi, Japan) with the resolution of 1.0 nm. The average size of the nanoparticles was determined by X-ray diffraction on the crystalline core of the particle.

Results of Research. Conducting the research, it was established that the intensity of peaks of the Raman scattering of light (CDL) from Ge-Ge links is very significant and disproportionately increases with the concentration of Ge in films. In its turn, peaks from Ge-Si links, on the contrary, are expressed poorly. In this case it is possible to say that a heteroborder is rather distinct, without transitional layer from solid SiGe solution (Fig. 1).

The leading mechanism in the process of films crystallization with silicon, germanium and silicon-germanium nanostructures alloyed by Ge on all types of initial surfaces of substrates is the migration of silicon and germanium atoms on a surface of films. Superficial mass transfer defines the process of recrystallization of films with silicon, germanium and silicon-germanium nanostructures.

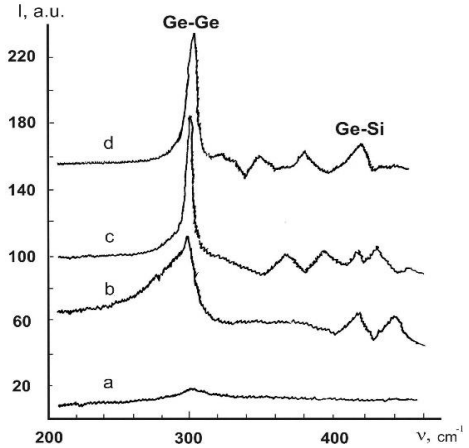


Figure *1*. – Ranges of combinational dispersion in samples with Ge nanoclusters in films with silicon, germanium and silicon-germanium nanostructures 25 nm thick with various contents germanium is contents germanium N, at·cm^{-3}: and – a) clean substrate of silicon (100), b –10^{17}, c – 10^{18}, d –5 10^{19}.

If the border of crystallite (block) is sated with dislocations, then the interaction of germanium atoms with them can lead to the change of defective structure type. It was observed also in our experiments which showed that after alloying Ge films with silicon, germanium and silicon-

germanium the concentration of 5×10^{19} at·cm^{-3} the diffraction picture (Fig. 2) for films with silicon, germanium and silicon-germanium nanostructures changed corresponding to the change of subnanostructure of a silicon film alloyed by a germanium.

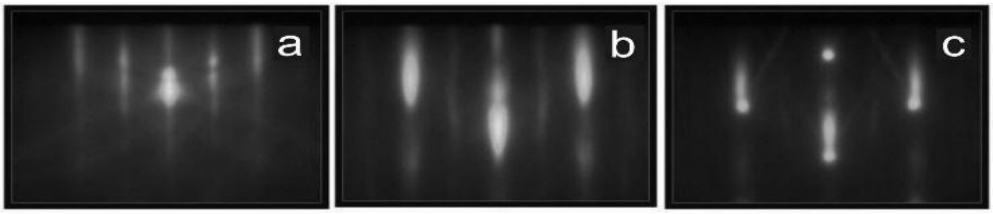
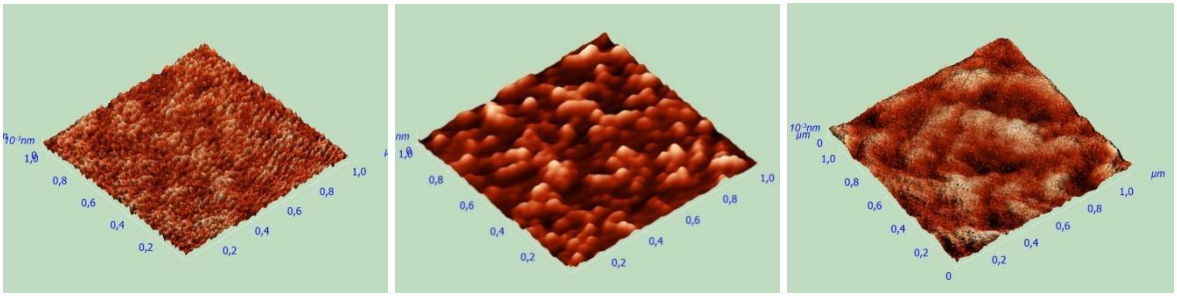
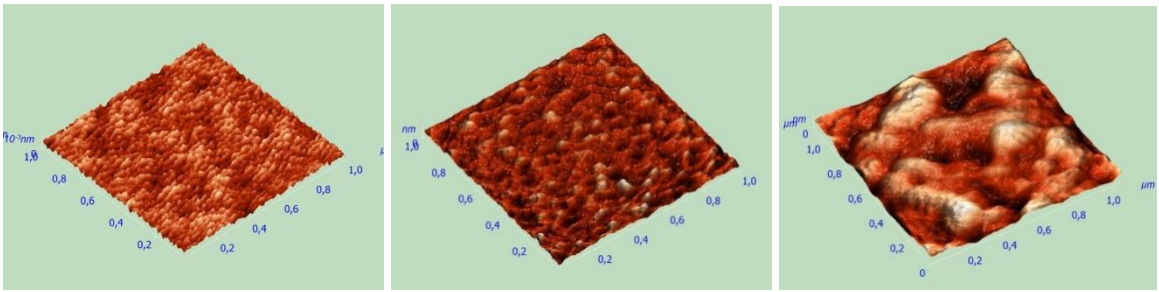


Figure *2*. – Diffraction pictures from a surface of Si (100) (a); from films (2D) (b) and from a surface of nanostructures (3D) (c) with silicon, germanium and silicon-germanium nanostructures.



a b c

Figure *3*. – Evolution of germanium nanoclusters and silicon-germanium solid solution depending on heat treatment temperature during 30 minutes exposure in argon: a - after deposition, b - after heat treatment at 700 ° C, in - at 900 ° C



a b c

Figure *4*. – Evolution of germanium nanoclusters and solid solution silicon-germanium depending on heat treatment duration at a temperature of 700 °C in the environment of argon: and – after sedimentation, – after the 30th minute heat treatment, in – after the 60th minute heat treatment.

In Figure 3 and Figure 4 the evolution of relief change of nanoclusters on the surface of initial substrates with the increase in temperature and time of thermal influence is presented. It is visible that the initial surface of a substrate is covered with arrays of nanodimensional clusters, mainly, of cone-shaped ones. The increase in temperature and time of thermal influence, leads to the merge of small nanoclusters in larger ones both on height, and lateral sizes. Because of this fact the quantity of them per acre decreases and, respectively, the probability of their merge in a continuous nanofilm increases.

For the self-organization of SiGe nanoclusters a small shift of surface atoms of complex structures on a clean surface with the formation of bonds like Ge–Ge or Si–Si is favourable. It is caused by the fact that under the thermal treatment the atoms rejected from an ideal position in a

crystal grid create additional force fields and it leads to the change of elastic properties of the whole nanocrystal.

The nanocrystal surface itself is a defect. The relaxation of near-surface atoms changes the rigidity of crystallite in this area therefore the compressibility of nanocrystals depends on the condition of their surface and the sizes of a nanocrystal in general.

Degree of nanoclusters growth dependence on temperature of heat treatment is evaluated according to activation energy. At the same time the speed of their growth in time was considered with the use of the Arrhenius equation. In fact, activation energy is the excess amount of energy (in comparison with average value) which the nanocluster at the time of collision with other nanocluster should possess at the moment of collision with another nanocluster to be capable to full merge with the formation of agglomerate. For the most part the increase in TP promotes the gain of such interaction. At increase in TP the growth rate of clusters and agglomerates increases considerably (Fig. 5). Growth activation energy of the linear sizes of nanoclusters is equal 211.2 kJ/nanocluster that demonstrates a strong temperature dependence of the growth rate of nanoclusters in sizes with the increase in temperature.

In its turn the process activation energy of filling the area with nanoclusters is equal 630.8 kJ/nanocluster. It is three times more than growth activation energy of the nanoclusters linear sizes. Such difference in the size of activation energy demonstrates stronger temperature dependence of the area filling process with nanoclusters, than their direct growth.

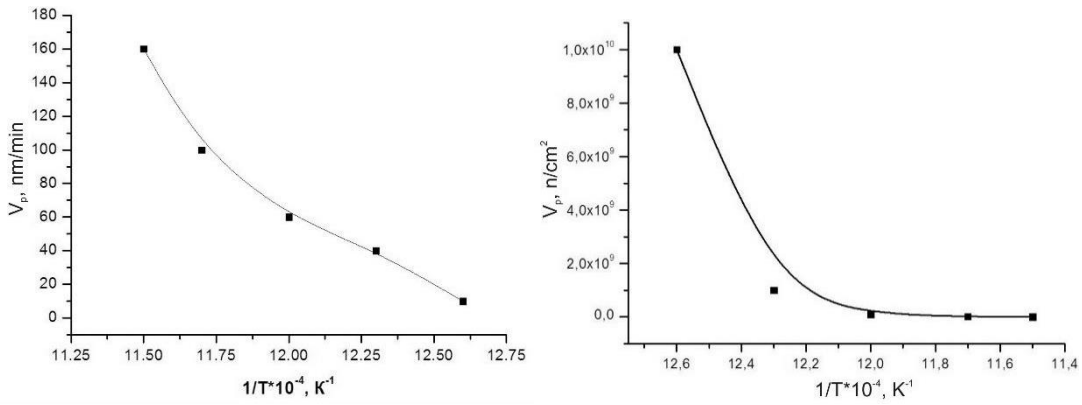


Figure *5*. – Regularity of change of growth rate of the linear sizes (a) and speed of increase in density (b) of nanoclusters with a temperature in the course of sedimentation of films with silicon, germanium and silicon-germanium nanostructures, alloyed by a germanium.

Conclusion. The growth rate, linear dimensions, and rate of increase in the density of nanoclusters are determined by the deposition temperature and the temperature itself and time of the subsequent heat treatment.

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