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Development of the surface morphology of germanium upon irradiation with gallium ions

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Abstract. Experimental studies of the germanium surface morphology development under irradiation with a focused gallium ion beam at different angles of incidence and fluences are presented. It is shown that a nanoporous structure formes in the near-surface layer starting with a dose of $5{\cdot}10^{15}$ cm^{-2}.This leads to the formation of a sponge-like morphology with a wall thickness of about 20 nm and a depth up to 150 nm with an increasing dose. Changing the ion beam incidence angle with respect to the surface normal leads to a tilt of the pores walls in the collinear direction.

Keywords: semiconductor, Ge, ion irradiation, surface morphology, pores, sponge-like relief, angle dependence, dose dependence

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Развитие морфологии поверхности германия при облучении ионами галлия

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Аннотация. Представлены экспериментальные результаты исследования развития морфологии поверхности германия при облучении фокусированным пучком ионов галлия при различных углах падения ионов и дозы облучения. Показано, что начиная с дозы $5{\cdot}10^{15}$ см$^{-2}$, в приповерхностном слое образуется пористая структура, которая с ростом дозы приводит к формированию губчатой морфологии с толщиной стенок около 20 нм и глубиной до 150 нм. При изменении угла падения ионного пучка относительно нормали к поверхности наблюдается наклон пор в коллинеарном направлении.

Ключевые слова: полупроводник, германий, ионная бомбардировка, морфология поверхности, поры, губчатый рельеф, угловая зависимость, дозовая зависимость

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Introduction

Germanium is characterized by a rather high mobility of charge carriers and is widely used as a solar cell and optoelectronics elements. In recent years, this material has been considered as an electrode in lithium batteries [1]. In the last case, to increase the electrode-electrolyte system electrical capacity, it is advisable to expand the electrode area without changing its dimensions. The surface area can be enlarged due to the formation of a surface porous structure, applying electrochemical treatment of Ge [2], the method of spark discharge [3], etc. Interest in the method of nanopores formation in thin Ge layers under ion irradiation of the surface with different sorts of ions arose as early since 1977 [4]. A detailed review concerning the application of ion irradiation for the formation of porous Ge is available in the monograph [5]. The results of an experimental study of the morphology development of the Ge surface irradiated with a Ga^+ focused ion beam depending on the fluence and the ion beam incidence angle are presented in this paper.

Materials and Methods

The irradiation experiments of a monocrystalline Ge with a 30 keV Ga^+ ion beam were carried out in a Quanta 3D 200i facility. Four experimental series of rasters were produced for a comprehensive study of possible morphological features of germanium surface.

The first series was devoted to explore the effect of scanning type (serpentine, raster and circle) on the resulting surface topography. For this purpose, four rectangular and two circular rasters were produced. The fluence of 10^{18} cm^{-2} and the incidence angle of the ion beam $\theta = 30°$ remained the same in this series. The rasters for the second series were produced at fixed values of the incidence angle of the ion beam $\theta = 30°$, fluence 10^{18} cm^{-2} and beam current 3 nA. An ion beam diameter was varied: 66 nm (focused), 300 nm, 2 μm, 4 μm and a overlap was varied from 30 to 95%, respectively. Increasing the overlap value simultaneously with decreasing the focus degree is necessary to ensure continuity of scanning. The main irradiation parameters of the third series: fluence was varied from 10^{15} cm^{-2} to $5{\cdot}10^{18}$ cm^{-2}, $\theta = 0°$, beam current 3 nA and 66 nm beam diameter. The fourth series was produced at a fixed fluence of 10^{18} cm^{-2}, $\theta = 0 – 85°$. The other irradiation parameters were the same as in the third series. The surface topography of all samples was explored ex situ by Supra 40 electron microscop in detail.

Results and Discussion

In the following study, it was found that the scan type and the focusing degree of the ion beam (spot size) have no fundamental influence on the surface topography formation, all other conditions remaining equal.

With a step-by-step increasing of the fluence, there is a noticeable modification of the surface relief. The transition from an initially smooth surface to a rough one is observed at a fluence of 10^{15} cm^{-2}. The total modified layer depth can reach 10 nm. Starting with a fluence of $5{\cdot}10^{15}$ cm^{-2} and up to 10^{16} cm^{-2} active formation of a porous surface structure occurs. The thickness of the modified layer increases up to 90 nm, the pore diameter grows from 20 to 50 nm, respectively. Steady-state sponge-like surface morphology has been obtained in the fluence range from $5{\cdot}10^{16}$ cm^{-2} to $5{\cdot}10^{18}$ cm^{-2}. The thickness of the sponge layer in this case rises up to 150 nm. It is notable that the wall thickness between pores in the fluence range from 10^{16} cm^{-2} to $5{\cdot}10^{18}$ cm^{-2} remains constant (20 nm). It can be seen from the profiles of the surface reliefs on the Fig. 1. In other words, the relief develops deeper into the sample bulk.

Fig. 1 demonstrates a significant change of the Ge surface morphology with fluence increasing, in other words, the transition from a porous structure to a spongy one.

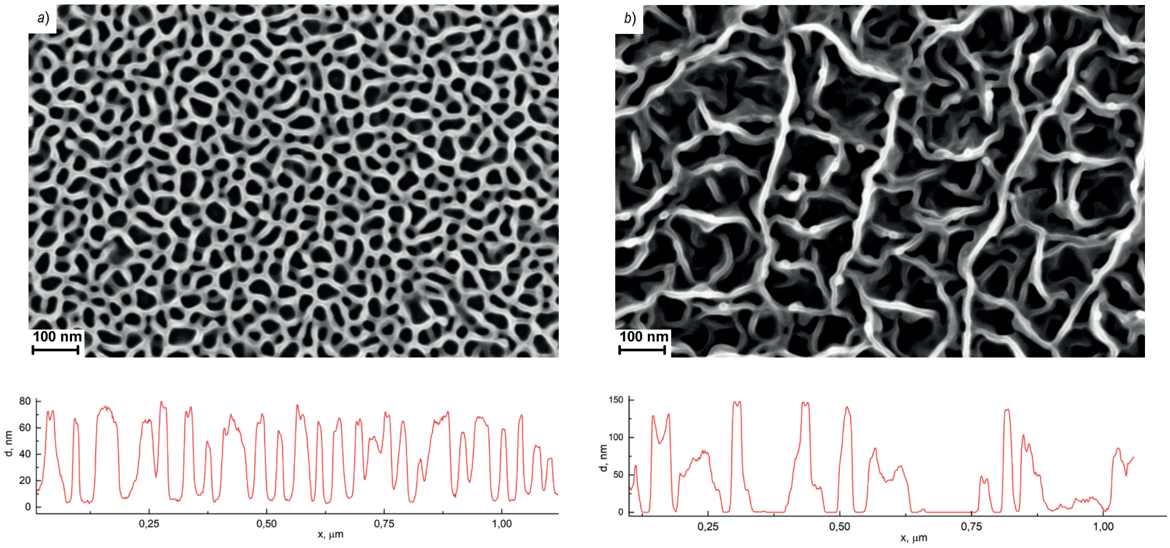

Fig. 1. SEM-images of Ge surface after ion irradiation with fluence of 10^{16} cm^{-2} (*a*), 10^{18} cm^{-2} (*b*). The profiles of the surface reliefs shown below figures (*a*) and (*b*) respectively

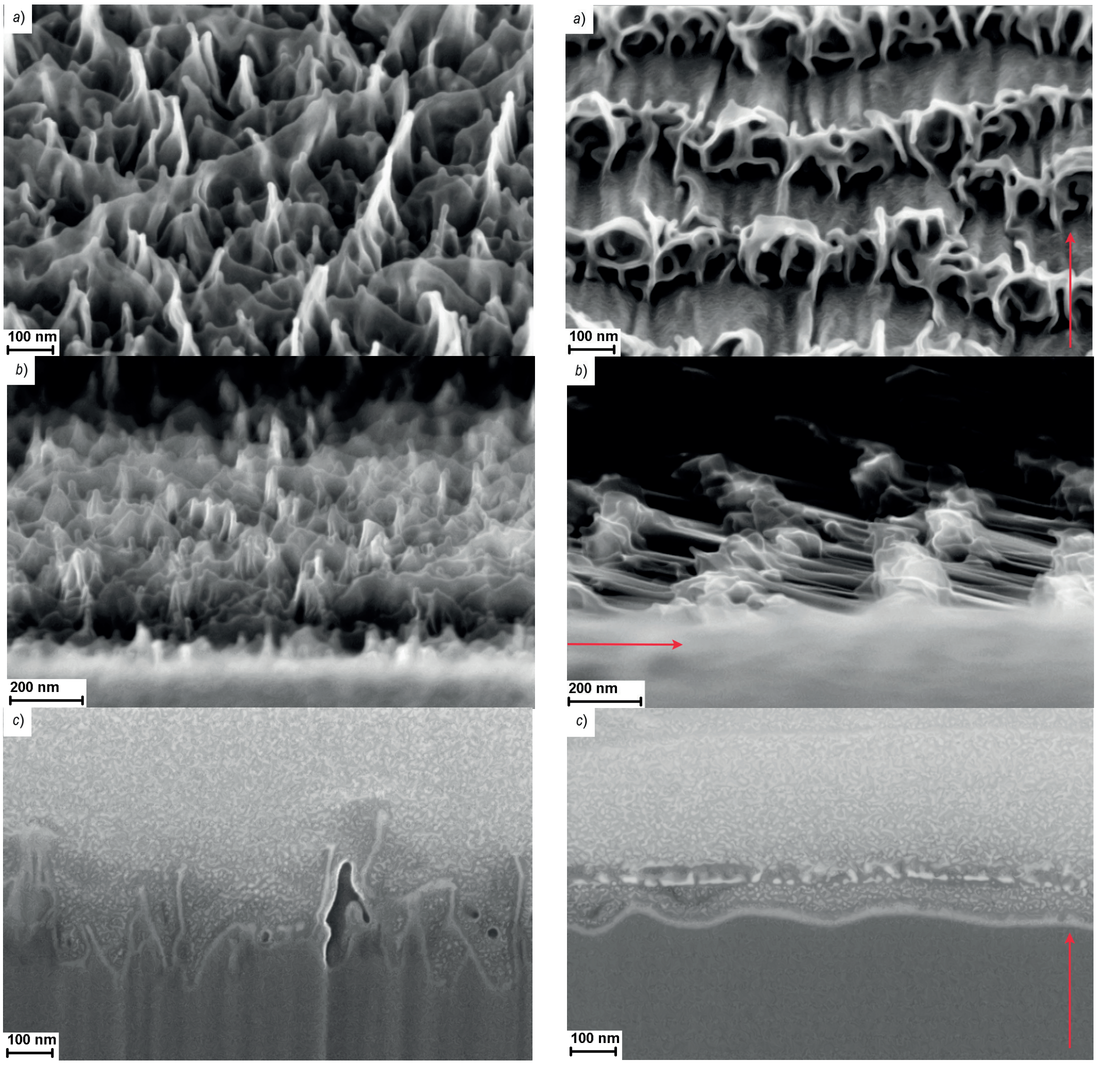

Fig. 2. SEM-images of Ge surfaces under ion irradiation with angle of incidence θ = 0° (left column) and 70° (right column). Figures (*b*) illustrate the tilt of the pores walls. Figures (*c*) represent cross-sectional views of the samples. The arrow indicates the incidence direction of the ion beam

It was established that changing the incidence angle of the ion beam θ causes to a change the tilt of the pores walls α (Fig. 2). Both angles were measured with respect to the surface normal. The tilt direction of this walls is collinear to the direction of incidence ion beam. The dependence α on θ has a direct proportionality character in the whole range of angles under examination. Also, at oblique ion beam incidence, individual clusters of material are observed on the pore tops, which are evidence of germanium melting under the action of irradiation with gallium ions (Fig. 2, *b*) right.

It was established that the amplitude of the surface relief (*d*) has strongly dependent on the incidence angle of the ion beam and the ion fluence. Fig. 3 shows both of these dependences in the entire ranges of angles and fluences.

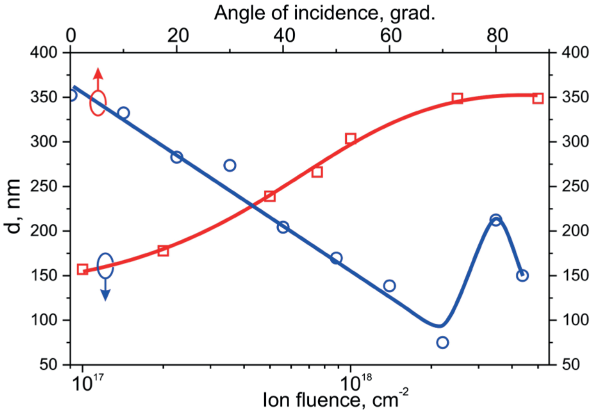

Fig. 3. The relief height estimates as functions of the ion fluence (red) and ion beam incidence angle (blue)

Conclusions

Qualitative and quantitative analyses of the Ge surface morphology irradiated with a 30 keV Ga$^+$ ion beam were carried out. No morphological features of the germanium surface were observed due to changes in scan type and focus degree of the ion beam.

It was found that an increase of the fluence entails structural modifications of the surface topography. At a fluence of 10^{15} cm^{-2}, the surface of the sample becomes rough. In the fluence range from $5 \cdot 10^{15}$ cm^{-2} to 10^{16} cm^{-2} the development of a porous surface structure occurs. When a fluence increase up to $5 \cdot 10^{18}$ cm^{-2}, a steady-state surface morphology (sponge-like) is observed. The mechanism of pore formation at low fluences and the formation of a sponge-like Ge surface structure at higher doses can be explained in terms of the kinetics of ion beam induced defects in the amorphous Ge layer [6].

The deviation of the relief development direction (into the sample bulk) from the normal is due to a corresponding change of θ. We suppose that in the process of inclined porous structure formation, along with the well-known vacancy mechanism of pore formation [7], the "thermal spot model" may be also involved [8]. According to this model, at the initial stage of the collision cascade formation, the ions have an energy (0.1–0.5 eV) sufficient to form a thermal spot and fuse the material. Further development of the collision cascade entails an energy decrease of the participating atoms. In the spot there is a reverse transition of the material from the liquid phase to the solid state. This transition is accompanied by a reduction in the spot volume. As a result, a void and melted material are formed in the spot. Those voids (pores) emerge onto the surface as the sample is sputtered. Traces of melted germanium can be observed on the pore tops, especially in the case of oblique ion beam incidence.

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