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Growth of germanium-rich $Ge_{1-x}Si_x$ solid solutions

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A solid solution $Ge_{1-x}Si_x$ with a calculated Si concentration of 0.6 at.% was obtained by vertical directional crystallization. The distribution of Si along the crystal growth axis and in several cross sections was studied. The results of the studies confirm the formation of a solid solution. The nature of the change in the silicon content is consistent with the concepts of the crystallization process of a solid solution with a silicon distribution coefficient in germanium ($k_{Si} > 1$).

Keywords: solid solution, germanium, silicon, directional crystallization.

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Owing to the convenience of controlling the electrophysical properties by adjusting the lattice period within the range of 0.54308–0.56574 nm [1], $Ge_{1-x}Si_x$ solid solutions have attracted research attention since the middle of 1950s. The high operating frequency of devices based on $Ge_{1-x}Si_x$ with 68−72 at.% of Si and the easy integration of the material production process into silicon technology have made these alloys important for microwave electronics [2]. The combination of increased carrier mobility and reduced thermal conductivity (compared to pure silicon) of the $Si_{80}Ge_{20}$ solid solution provided an opportunity to design efficient thermoelectric generators [3]. The close correspondence of the lattice period of the $Si_{99.98}Ge_{0.02}$ alloy sparked interest in GaAs/SiGe (GaAs on a SiGe substrate) heterostructures in solar power engineering [4]. The growth of Ge−Si crystals by the Czochralski ($Ge_{1-x}Si_x$ with $0.004 < x < 0.03$) [4], zone melting ($Si_{99.98}Ge_{0.02}$) [5], and Bridgman [6] methods was reported. It is known that the dependence of the electrophysical properties of $Ge_{1-x}Si_x$ solid solutions on their composition was modeled in [7], but the results of experimental studies of the electrophysical properties of alloys enriched with Ge have not been published yet.

The lack of published data on the properties of $Ge_{1-x}Si_x$ solid solutions with $0 < x < 0.02$ is worthy of note. This insufficiency of data may be attributed to the difficulty of preparation of solid solutions in which the dissolved substance has a melting point much higher than the solvent ($T_{m\,Si} = 1414\,^\circ C$, $T_{m\,Ge} = 937\,^\circ C$).

The aim of the present study is to develop a laboratory technique for producing $Ge_{1-x}Si_x$ solid solutions with a Si concentration of 0.6 at.% and to reveal the distribution of silicon throughout the ingot volume.

An existing technology, which includes two-stage synthesis of a solid solution [8], was used to obtain solid solution ingots. At the first stage, a mixture of the $Ge_{0.98}Si_{0.02}$ composition containing 19.878 g of germanium and 0.1435 g of silicon was alloyed in a high-temperature furnace in an argon environment at a pressure of $\sim 10^5$ Pa. At the second stage, 40 g of germanium were added to the obtained ingot to reach the design Si concentration of 0.6 at.%, and the resulting mixture was remelted in vacuum using a three-section heater in accordance with the vertical directional crystallization technique [9]. The sample was held for an hour at temperatures of 991, 1023, and 840 °C on the lower, middle, and upper heaters, respectively.

A 2-mm-thick plate was cut from the grown crystal along the growth axis. To remove the damaged layer, one surface of the plate was processed mechanically and by chemical-mechanical polishing. The plate processed this way was etched in a solution of the $HNO_3 : HF : CH_3COOH = 5 : 3 : 3$ composition at room temperature [10].

The prepared surface was examined by energy-dispersive X-ray microanalysis with scanning electron microscopy using a Jeol JCM-6000 PLUS microscope fitted with an energy-dispersive X-ray spectrometer. The silicon content was determined at points positioned with an average pitch of 0.55 mm. The results of measurements of the Si concentration along the crystal length are shown in Fig. 1. It follows from the distribution of Si along the ingot axis (Fig. 1, *b*) that the Si content varies in a jump-like fashion within the range from 0.05 to 1.62 at.%. The presence of a plateau and levelling of the average silicon concentration at 0.17 at.% within 12–33 mm from the bottom of the crystal should be noted. The increased Si concentration in the initial section of the ingot and its subsequent reduction in the process of crystallization are attributable to the fact that the distribution coefficient of silicon in germanium is greater than unity. More significant jumps in silicon content were found in the distribution along the length of the ingot at a distance of 2 mm from the edge of the plate (Fig. 1, *c*).

Similar studies were carried out in cross sections of the plate in order to assess the nature of the distribution of silicon throughout the crystal volume. The obtained results

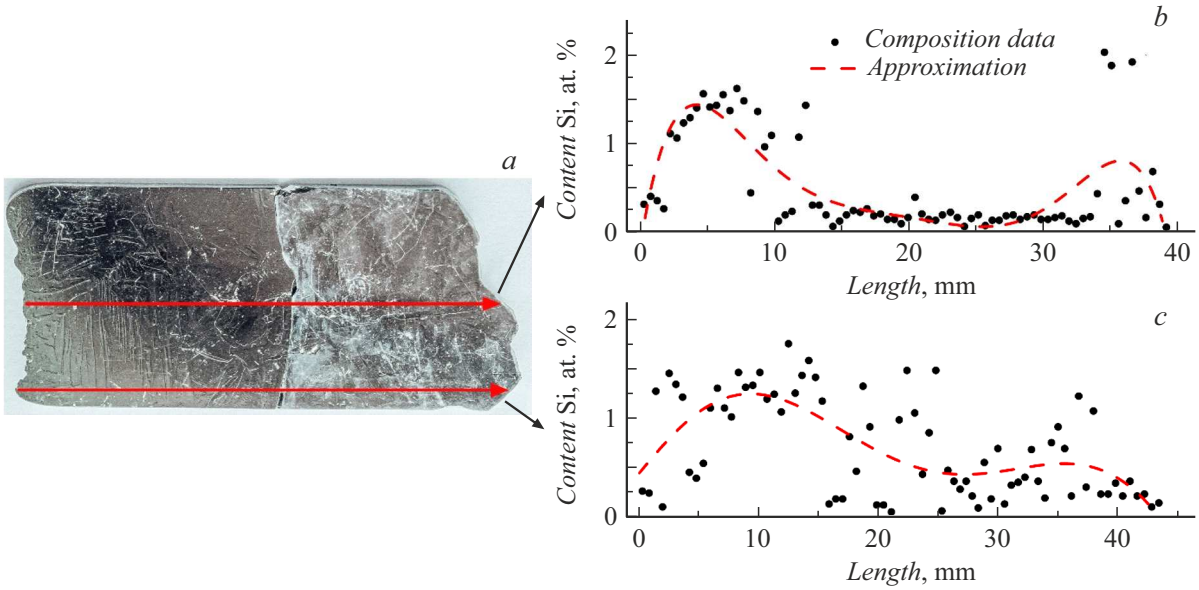

Figure 1. Distribution of Si along the length of the sample. *a* — Sample (arrows indicate the direction of examination of the composition from the onset of crystallization); *b* — Si content along the ingot axis; and *c* — Si content along the ingot edge.

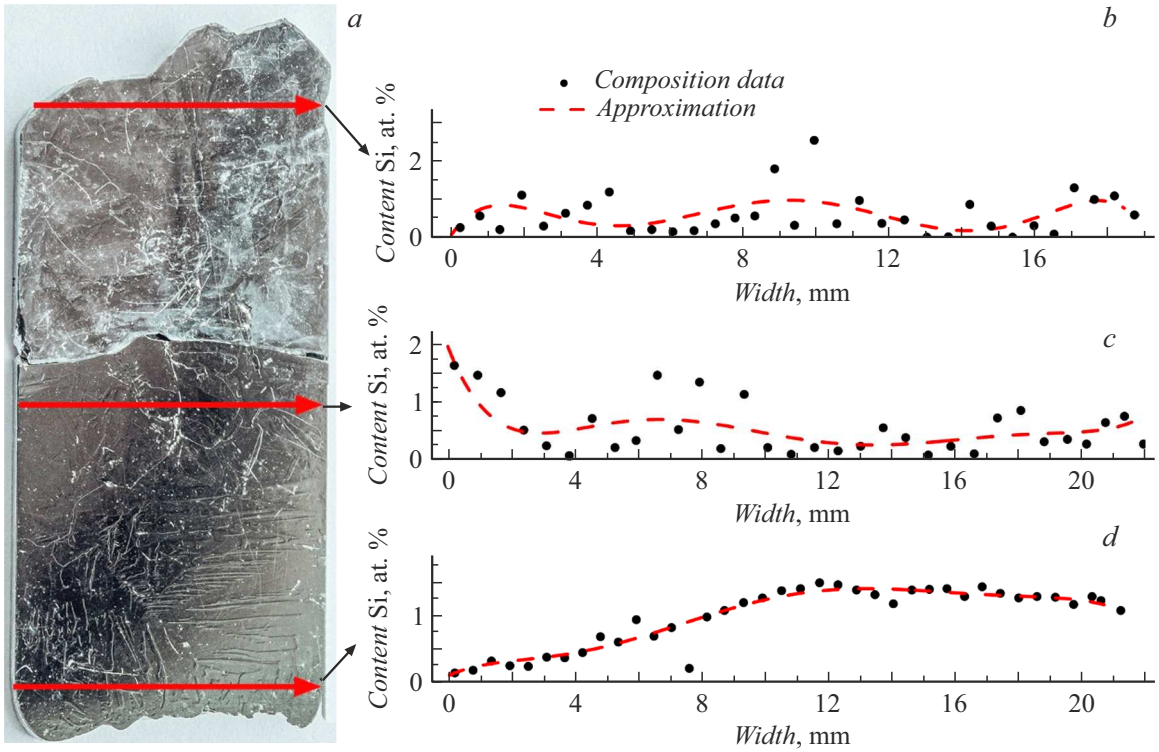

Figure 2. Distribution of Si across the sample diameter. *a* — Sample (arrows indicate the direction of examination of the composition); *b* — Si content in the upper part of the ingot; *c* — Si content in the middle part of the ingot; and *d* — Si content in the lower part of the ingot.

are presented in Fig. 2. The Si content varied significantly within the range from 0 to 2.5 at%. However, one may distinguish a narrow region (3 mm in width), which is symmetrical with respect to the ingot axis, in the middle part of the ingot where the average silicon concentration is maintained at 0.18 at.%. These data are consistent with the average value of silicon concentration along the growth axis at 12–33 mm from the bottom of the ingot (Fig. 1, *b*).

The obtained results suggest that the proposed technique allows one to produce solid solutions of silicon in germanium with a silicon content of several atomic percent. This makes it possible to use a germanium seed to obtain

single crystals of the $Ge_{1-x}Si_x$ solid solution with 0.6 at% of Si. The non-uniformity of distribution of silicon over the length of an ingot and its cross section may be associated with the nature of variation of thermal conditions at the crystallization front in the experiments and the fact that the melt homogenization time before crystallization was insufficient. It is planned to clarify the prevailing causes in further experiments utilizing the proposed laboratory technique.

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Conflict of interest

The authors declare that they have no conflict of interest.

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