Solid-phase disordering of bulk Ge and Si samples under pressure

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Transitions of the metallic GeII and SiII modifications upon reduction of pressure at low temperatures have been studied. Experiments have shown that, depending on the temperature, amorphous tetrahedral phases, in addition to the usual metastable SiIII, GeIII, and GeIV modifications, can form in massive Ge and Si samples. Calorimetric studies of the crystalline and amorphous phases have been carried out at atmospheric pressure. Crystallization of bulk samples (characteristic size ≈ 2 mm) of amorphous Ge and Si was observed at temperatures close to the standard crystallization temperatures of amorphous films: 700–730 K and 940–980 K, respectively.

Amorphous silicon and germanium have until now been obtained exclusively as thin films (of thickness ≈ 1 μm) by the irradiation, deposition, or evaporation methods.[1,2] Interest in these entities is linked with the basic features of the physics of disordered media and with the prospects of their commercial application. It is unclear, on the other hand, which characteristics of the amorphous Si and Ge are linked with the quasi-two-dimensional nature and which are characteristic of a strictly disordered tetrahedral grid of atoms of the given substances. In view of this circumstance, synthesis of bulk samples of amorphous silicon and germanium and study of these materials are of considerable interest.

In our experimental study we used a method of solid-state disordering, which is based on the search for such experimental values of the *P–T* parameters at which the crystal structure of the high-pressure phase becomes unstable, while the transition to a stable modification is kinetically hindered. The material becomes disordered in this case and the amorphous state has a short-range-order structure corresponding to a more stable phase.[3] This method was previously used to obtain bulk samples of amorphous Ga–Sb (Ref. 4), Cd–Sb, Zn–Sb (Ref. 5), SiO_2 (Ref. 3), etc. In the present letter we report the results of an experimental study of the feasibility of obtaining amorphous phases of Si and Ge in bulk samples. We also present the results of a study of their thermal stability.

To obtain a high pressure in the range 1–13 GPa, we used a toroidal-type high-pressure chamber, in which BK-6 hard alloy spacers were installed and which was calibrated on the basis of the phase transitions of Bi (2.55, 2.7, 7.7 GPa), of Sn (9.6 GPa), of Fe (11.7 GPa), and of Pb (13.2 GPa).[6] A cylindrical sample of single-crystalline Ge or Si 1.5 mm high and 2 mm in diameter was inserted into a pyrophillite container. The sample was heated by passing an alternating current through it. The

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chamber was immersed into a vessel filled with liquid nitrogen. The temperature was measured in the range 80–1500 K, with a Chromel–Alumel thermocouple which was placed near the sample. The resistance of the sample was determined from the *I-V* characteristic of the current which was passed through it. The phase analysis of the synthesized material was carried out in a RKU-114 λ CuKα chamber and with a DRON-3 diffractometer, using the x-ray diffraction data. A derivatograph-C (MOM, Hungary) was used for the calorimetric measurements. The amount of test material was in the range 1–20 mg and the heating and cooling rates were in the range 0.05–20 K/min. The calibration of the calorimetric measurements apparatus is described in Ref. 3.

To obtain high-pressure phases, we raised the temperature of the GeII and SiII samples, which were held at pressures of 11 and 13 GPa, respectively, to 100–330 °C for 1 min. The chamber was then cooled with liquid nitrogen to a temperature T_r, at

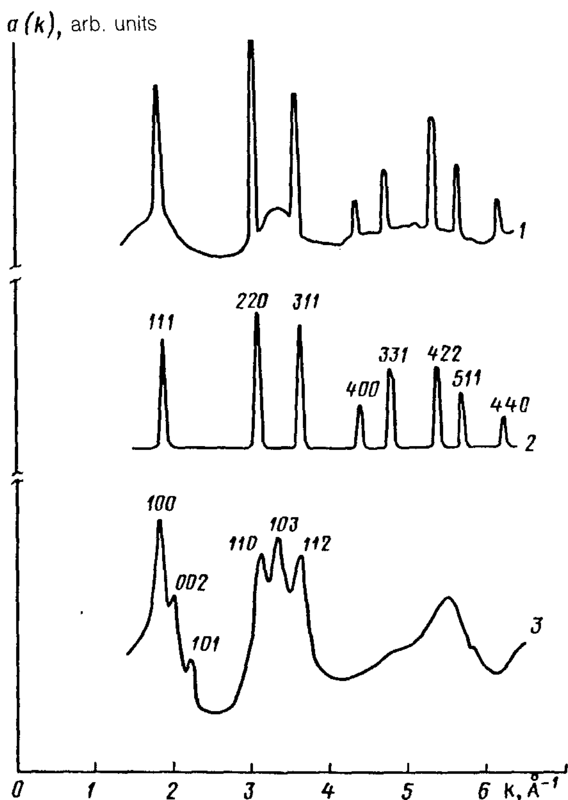
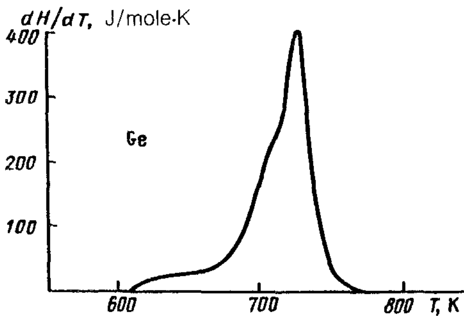


FIG. 1. Structure factors of germanium samples obtained from the x-ray scattering data ($k = 4\pi \sin \theta / \lambda$, where θ is the scattering angle). 1—A mixture of the crystalline GeI phase and amorphous modification; the presence of the GeI phase is attributable to an incomplete GeI–GeII transition under pressure. The calorimetric data put the content of the amorphous phase at $\sim 40\%$; 2—the same sample as above, but after annealing at a temperature of 900 K; 3—a mixture of the crystalline GeV phase and amorphous modification ($\sim 50\%$).

which the pressure was gradually decreased (at a rate of ≈ 1 GPa/min). The transition to the semiconductor phase was determined from the electrical resistance. The pressure of the transition to the semiconductor phase, P_{tr}, and the modification of the material changed as a function of the temperature T_r. At $T_r \sim 200$–300 K and $P_{tr} \sim 4.5$–8.5 PGa, for example, the metallic phase of GeII undergoes a transition to the GeIII modification which has a tetragonal structure ($a = 0.580$ nm, $c = 0.663$ nm). At $T_r \sim 170$–200 K, a mixture of the GeIII phase and the GeIV phase (a phase with a bcc structure, $a = 0.697$ nm) is formed after the loss of pressure. It was previously reported[7] that GeIV was obtained in dry ice after the loss of pressure (at $T = 190$ K). A nearly pure GeIV phase ($P_{tr} \sim 3$–4 GPa) was formed at $T_r \sim 160$–170 K. At T_r 130–160 K, we obtained a mixture of GeIV and a glassy phase. At lower temperatures $T_r \sim 90$–130 K and pressures $P_{tr} \sim 1$–2 GPa, we obtained samples with a large amount of the glassy phase (Fig. 1).

The metallic phase of SiII at $T_r \sim 120$–300 K changes to the SiIII modification with a bcc structure ($a = 0.664$ nm) at pressures of ~ 2–9 GPa. At lower temperatures we obtained an amorphous phase. The maximum amount of disordered silicon was obtained in samples cooled to $T_r \sim 90$–110 K.

The calorimetric studies of the synthesized phases have made it possible to determine the temperatures of the transitions, T_c, to a more stable phase, the activation energies ΔG, and the heat evolution ΔH. In the transition to diamond-like GeI modifi-



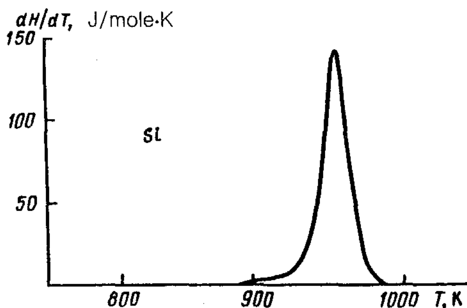


FIG. 2. Heat-evolution peaks associated with the crystallization of the amorphous Ge and Si phases as a result of isochronous annealing at a heating rate of 20 K/min.

cation, these values for an amorphous germanium are $T_c \sim 700$–730 K, $\Delta G \sim 200$ kJ/mole, and ΔH (for a sample which has the largest amount of the amorphous phase) ~ 10 kJ/mole. For Si, these values are respectively $T_c \sim 940$–980 K, $\Delta G \sim 300$ kJ/mole, and $\Delta H \sim 5$ kJ/mole (Fig. 2). Typical initial relaxation peaks have been observed before the crystallization.[2] Using the standard published data on the crystallization heat of amorphous films,[2] we can estimate the content of the disordered phase in the samples; it was found to be up to 80% for Ge and up to 50% for Si.

The other metastable Ge and Si phases were annealed in the same manner. The SiIII phase changes to the SiIV phase with a wurtzite-type hexagonal structure ($a = 0.380$ nm, $c = 0.628$ nm). In this case, $T_c \sim 480$–520 K, $\Delta G \sim 150$ kJ/mole, and $\Delta H \sim 6.5$ kJ/mole. The formation of a SiIV phase as a result of annealing SiIII was previously reported in Ref. 8. Modification of GeIV as a result of annealing causes it to change to a wurtzite-like hexagonal GeV phase ($a = 0.394$ nm, $c = 0.655$ nm) at $T_c \sim 320$–350 K, $\Delta G \sim 90$ kJ/mole, and $\Delta H \sim 4.2$ kJ/mole. At room temperature the transition is completed in about 24 h. Such a modification of Ge so far has been obtained only in the form of thin layers.[9] Upon heating, the GeIII phase undergoes a transition to the normal GeI modification. In this case we have $T_c \sim 520$–560 K, $\Delta G \sim 160$ kJ/mole, and $\Delta H \sim 8.5$ kJ/mole.

We have analyzed the thermal stability of the hexagonal GeV and SiIV modifications. The temperatures at which these compounds undergo a transition to the GeI and SiI modifications are 770–820 K and 1000–1050 K, respectively. Diffuse thermal absorption peaks (0.2 kJ/mole), however, occur in this case. Subsequent slow cooling (at $T < 1$ K/min) in this case causes a partial inverse transition SiI–SiIV in the Si samples which are heated to temperatures of 1050–1150 K. These surprising results can be explained by the fact that the SiIV–SiI and GeV–GeI transitions are equilibrium transitions, and that the wurtzite-like SiIV and GeV phases are stable at low temperatures. The same situation was discussed in the case of lonsdelite, diamond,[10] wurtzite, and sphalerite GaN phases.[11] To verify the assumption that SiIV and GeV are stable low-temperature phases, we subjected SiI and GeI polycrystals to isothermal and isochronous annealings (at a cooling rate of 0.05–0.1 K/min) in the temperature ranges 800–1100 K and 600–900 K, respectively. After annealing, an x-ray diffraction analysis revealed the presence of hexagonal wurtzite-like phases in some samples. After annealing an Si polycrystal for 25 h at 900–950 K, the powder diagrams revealed 2–3 faint lines which correspond to the lines of the wurtzite-like modification [the intensity ratio I(1,1,1) SiI/I(0.0.2) SiIV is 60]. The impurity content in the samples determined by the mass-spectroscopic analysis was within 0.1%. Since the energies of these modifications are approximately equal, and since the kinetics of the inverse transition from the high-temperature phase is extremely slow, the stability ratio of these phases probably depends strongly on the presence of impurities and defects. The relative stability of diamond-like and wurtzite-like modifications of the compounds with tetrahedral bonds will be clarified in further studies.

It can be concluded on the basis of experimental data that by controlling the kinetics involved in bringing the metallic He and Si phases to more stable states it is possible to select the P–T parameters at which the transition occurs through the intermediate disordered phase. The size of the amorphous sample in this case is limited

strictly by the capabilities of the high-pressure apparatus.

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