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Abstract

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STRUCTURE OF AMORPHOUS GERMANIUM OBTAINED FROM CRYSTALLINE GERMANIUM BY BOMBARDMENT WITH ARGON IONS

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As was established in works [1–3], when germanium is bombarded with ions of medium energies, the latter passes from the crystalline state into the amorphous state. The nature of this transformation is not yet clear. To shed light on this question, it is of interest to determine the structure of the short-range order of atoms in the amorphous substance obtained upon irradiation. Indeed, if it turned out, for example, that the short-range order in the present case is similar to the short-range order of liquid germanium, this would be confirmation of the determining role of thermal spikes in the process of amorphization [1,3] (melting in the spike region and rapid quenching). If, however, the amorphous state is formed directly from the crystalline one, it should be considered probable that the short-range order existing in the latter is preserved.

We carried out experiments with germanium films obtained by vacuum deposition onto NaCl substrates heated to 400°. The film thickness was 500 Å. Electron-diffraction photographs taken immediately before ion bombardment showed that the films were polycrystalline.

Bombardment with argon ions was carried out in an electrostatic accelerator with a magnetic analyzer. The ion energy was 50 keV, the dose 1000 $\mu C/cm^2$ at an ion-current density of ~ 4 $\mu A/cm^2$. The vacuum in the target region was no worse than $2 \cdot 10^{-5}$ mm Hg. In order to reduce adsorption of organic vapors during irradiation, a liquid-nitrogen trap was used, and the target was heated to 100°. The Ge films were irradiated directly on the NaCl substrates.

After bombardment the films were transferred to copper grids, and a series of electron-diffraction patterns was taken with multiple exposures of 4, 8, 16, 32, and 64 sec. On the electron-diffraction patterns two diffuse rings were observed ($\sin\theta_1/\lambda = 0.15$; $\sin\theta_2/\lambda = 0.27$). The constant $2L\lambda$ was 67 mm · Å. The corresponding photometric curves are presented in Fig. 1.

The interpretation of the structure was carried out by means of Fourier analysis using blackening curves according to the procedure proposed in [4]. The radial distribution function of the atomic density was determined according to the known equation

$$4\pi r^2\rho(r) = 4\pi r^2\rho_0 + \frac{2r}{\pi}\int_0^\infty si(s)\sin sr\,dr, \tag{1}$$

where $\rho(r)$ is the atomic density at a distance r from the center of a given atom; ρ_0 is the mean atomic density (we took it equal to the density of crystalline germanium); $i(s) = (I - f^2)/f^2$; I is the normalized scattering intensity; f is the atomic electron scattering factor; $s = 4\pi\sin\theta/\lambda$ (the maximum value of s used in the calculation was $s_{\max} = 8.4$).

The radial distribution curve is shown in Fig. 2.
Table 1 gives the positions of the maxima of the curve and the interatomic distances of crystalline germanium. Also presented are summary data from work (5) for various specimens of amorphous germanium obtained by evaporation in vacuum.

Fig. 1 Fig. 2

Fig. 1. Microphotometric curves of electron diffraction patterns recorded with multiple exposures

Fig. 2. Radial distribution curve of amorphous germanium obtained from crystalline germanium by ion bombardment

As can be seen from Fig. 1, the first maximum is located at a distance $r_1 = 2.45$ Å, and the corresponding coordination number N_1, calculated from the area under the maximum, is equal to 3.5. Evidently, the position of this maximum corresponds to the radius of the first coordination sphere of crystalline germanium ($r = 2.43$ Å, $N = 4$).

Table 1

Positions of the maxima of the radial distribution curve (in Å) for amorphous germanium obtained by ion bombardment (1), by sublimation (5) (2), and the interatomic distances in crystalline germanium (3)

1	2	3
2.45	2.41–2.54	2.43
(3.65)	3.95–4.14	3.97
4.12	5.60	4.65
5.07	5.95–6.16	5.62
5.82	6.80	6.12
(6.70)*	7.30	6.87
7.15		7.31

* The peak is indistinct.

The same result is also obtained for ordinary amorphous germanium produced by sublimation in vacuum (5).

The second maximum is not symmetric and, geometrically, can be divided into two (r_2 = 3.65 Å and r_3 = 4.12 Å). It may be assumed that, as a result of bombardment, such a rearrangement occurs among the atoms of the second coordination sphere of crystalline germanium (at r = 3.97 Å) that it leads to asymmetry of the peak. Another possibility is that the peak at 4.12 Å corresponds to germanium, while the peak at 3.65 Å belongs to germanium dioxide, which could have formed in a small amount on the surface of the film as a result of its exposure to air (in the "insoluble" modification of GeO_2, the shortest Ge–Ge distance is 3.4 Å (6)). An analogous peak (r = 3.6 Å) was found in the study of amorphous germanium obtained by evaporation in work (7), where the presence of an admixture of GeO_2 is likewise assumed.

Thus, in our case, as in crystalline germanium, the first coordination sphere has a radius of 2.45 Å and is characterized by a tetrahedral configuration, in contrast to the octahedral configuration (at r = 2.7 Å) in liquid germanium (8). If it is assumed that

amorphization occurs by means of local melting in the regions of thermal spikes, then one must assume that during the lifetime of the thermal spike (10^{-11}—10^{-12} sec) the rearrangement of atoms required to reduce the coordination number from 8 to 4 has time to take place. For the transition from the crystalline state directly into the amorphous state such rearrangement is not required; only a disorientation of the elementary tetrahedra with respect to one another is needed. Of course, the final choice of a model of amorphization under ion bombardment requires further accumulation of experimental material.

Let us note that the second principal maximum on the radial distribution curve (r_3 = 4.12 Å) is expressed more strongly in our case than in work ([5]), which indicates a greater degree of ordering. However, the more distant maxima agree with the interatomic distances in crystalline germanium worse than is the case in ([5]). This is apparently connected with the fact that under ion bombardment the chains of tetrahedra or packets of atomic planes are not preserved, as they are in sublimation. Thus, there is no peak at r = 6.12 Å, corresponding to one of the distances between the internal atoms of a chain, clearly expressed in work ([5]).

In conclusion, we express our gratitude to R. V. Kudryavtseva and T. N. Strizheva for their assistance in carrying out the electron-diffraction exposures and preparing the germanium films.

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Note: Figure translations are in progress. See original paper for figures.