CRYSTALLIZATION OF AMORPHOUS SILICON DIOXIDE FILMS UNDER ION BOMBARDMENT AND SUBSEQUENT ANNEALING

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Abstract

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CRYSTALLIZATION OF AMORPHOUS SILICON DIOXIDE FILMS UNDER ION BOMBARDMENT AND SUBSEQUENT ANNEALING

(Presented by Academician N. V. Belov, 21 X 1969)

When glass is irradiated with high-energy inert-gas ions, a transition from the amorphous to the crystalline state is observed ([1]). To clarify the influence of ion species and irradiation dose on the crystallization processes of amorphous SiO_2 films during annealing, we carried out electron-diffraction studies. Films 800–1000 Å thick were deposited in a high-frequency low-energy argon–oxygen plasma of a gas discharge onto a fresh NaCl cleavage. The starting material was tetraethoxysilane.

In Fig. 1, 1 an electron diffraction pattern obtained from a film before irradiation is shown. The presence of two diffuse rings corresponding to Bragg spacings $d_1 = 4.14$ Å ($\sin\theta/\lambda = 0.12$) and $d_2 = 1.24$ Å ($\sin\theta/\lambda = 0.4$) indicates their amorphous structure. Subsequent annealing at a temperature of 1200° for 1 hour did not lead to any change in the diffraction pattern.

After irradiation of films situated directly on NaCl with Ar^+, P^+, and B^+ ions with an energy of 50 keV, in doses from 1 to 10^4 $\mu C/cm^2$, and subsequent annealing in the range 500–1000°, their structure changes substantially. Fig. 1 and Table 1 clearly illustrate the changes taking place. It is seen that at certain temperatures, depending on the dose and species of ions, a pattern characteristic of a polycrystalline phase appears in the electron diffraction patterns. Measurement of the Debye rings gave interplanar spacings consistent with the spacings in the structure of α-cristobalite (Table 2).

Table 1

Annealing temperature (in °C)

Dose, $\mu C/cm^2$	Argon: crystallization onset temp.	Argon: texture appearance temp.	Phosphorus: crystallization onset temp.	Phosphorus: texture appearance temp.	Boron: crystallization onset temp.	Boron: texture appearance temp.
$1 \cdot 10^3$	650	900	675	950	750	800
$5 \cdot 10^3$	600	800	600	800	700	850
$1 \cdot 10^4$	500	700	550	750	675	800

At certain temperatures, depending on the ion species and irradiation dose, arcs characteristic of a texture with the L_2 axis arise against the background of the Debye rings.

As the temperature increases, the intensity of the Debye rings decreases and that of the arcs increases; however, the rings themselves do not disappear completely even at an annealing temperature of 1000°, i.e., in the film, together with the texture, there is a small number of randomly oriented crystallites.

Thus, there is a direct relationship between the type of ions and the irradiation dose, on the one hand, and the temperatures corresponding to the onset of crystallization and the onset of texture formation, on the other. (The heavier the ion and the greater the irradiation dose, the lower the temperatures at which the indicated processes begin.) This relationship is confirmed by the critical irradiation doses below which crystallization processes do not begin during annealing. Thus, when films are irradiated with argon ions ($Z = 18$), crystallization does not begin at doses less than or equal to

Table 2

Interplanar spacings (in Å)

X-ray data ([2]) α-cristobalite	Our data after irradiation with B^+ ions	Our data after irradiation with P^+ ions	Our data after irradiation with Ar^+ ions	X-ray data ([2]) α-cristobalite	Our data after irradiation with B^+ ions	Our data after irradiation with P^+ ions	Our data after irradiation with Ar^+ ions
4.04	4.06	4.03	4.04	1.494	–	–	–
3.13	3.21	3.13	3.15	1.43	1.43	1.43	1.44
2.85	2.85	2.87	2.83	1.40	1.42	–	–
2.48	2.43	2.47	2.49	1.399	–	–	–
2.11	2.13	2.12	2.11	1.37	1.34	1.36	1.37
2.02	2.04	2.02	2.04	1.30	–	–	–

X-ray data ([2]) α-cristobalite	Our data after irradiation with B^+ ions	Our data after irradiation with P^+ ions	Our data after irradiation with Ar^+ ions	X-ray data ([2]) α-cristobalite	Our data after irradiation with B^+ ions	Our data after irradiation with P^+ ions	Our data after irradiation with Ar^+ ions
1.93	1.95	1.93	1.96	2.79	–	–	–
1.87	1.86	1.87	1.88	1.235	1.21	–	1.23
1.69	1.65	1.70	1.69	1.203	–	–	1.20
1.61	1.59	1.60	1.61	1.81	1.19	1.18	1.14
1.57	1.58	–	1.55	1.095	–	–	1.08
1.53	1.53	1.53	1.53				

1 $\mu C/cm^2$; when irradiated with phosphorus ions ($Z = 15$), at doses less than or equal to 10 $\mu C/cm^2$; and when irradiated with boron ions ($Z = 5$), at doses less than or equal to 30 $\mu C/cm^2$.

To understand the crystallization processes, it is convenient to describe the structure of amorphous films as consisting of zigzag chains of silicon–oxygen tetrahedra (with the motif $[Si_2O_7]$ ([3,4])) of various lengths, which are deformed to one degree or another and close into four-, five-, and, mainly, six-membered rings of SiO_4 tetrahedra, arranged at various angles and connected into an irregular spatial continuous network. Such a description is consistent with the ideas about the structure of glassy substances set forth in work ([5]), and the results obtained by us, in which the structure of α-cristobalite is as if "revealed" after irradiation and subsequent annealing, confirm this.

The presence of chains accounts for the films' ability to form glass. Their correct orientation is hindered more strongly the longer the chains are. With this interpretation of the structure, it is quite permissible for small ordered regions to exist in the film, their sizes and number being such that on the curve of the radial distribution of atomic density they may not manifest themselves in any way.

The behavior of the films after irradiation and annealing is apparently connected, as in the case of Ge and Si ([6]), with the formation and accumulation of radiation defects. During ion bombardment a considerable number of bonds are broken (the concentration of defects increases with increasing ion mass and dose ([7])); therefore, some of the chains, in addition to becoming shorter, are no longer connected with one another. It follows from this that they must have somewhat greater mobility than before irradiation. The increase in the mobility of atoms (due to the increase in defects) and chains condi-

is accompanied by intensive crystallization during annealing. The nuclei of the crystalline phase may be the ordered regions mentioned above, which grow at the expense of defective disordered regions.

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