PHASE COMPOSITION OF AMORPHOUS FILMS OBTAINED BY VAPOR CONDENSATION DURING HEATING IN VACUUM OF A MIXTURE OF SILICON DIOXIDE AND SILICON

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Abstract

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PHASE COMPOSITION OF AMORPHOUS FILMS OBTAINED BY VAPOR CONDENSATION DURING HEATING IN VACUUM OF A MIXTURE OF SILICON DIOXIDE AND SILICON

(Presented by Academician N. V. Belov, May 13, 1965)

When a finely ground mixture of silica and silicon is heated in vacuum, vapors of silicon monoxide are formed; by condensing them one can obtain yellowish-brown films having characteristic optical and dielectric properties ([1–5]). Electron and X-ray diffraction patterns from these films, often called silicon monoxide, consist of a single diffuse halo corresponding to the Bragg spacing $d = 3.60$ Å, which is usually taken for the identification of solid SiO.

As a result of annealing such silicon monoxide films in an inert-gas atmosphere at temperatures above 600°, the diffraction pattern changes ([1]). After heating for 2 hours at 700°, three blurred halos are observed, corresponding to amorphous silicon and quartz glass; at 900° for 2 hours, a set of sharp rings of polycrystalline silicon and diffuse halos of amorphous quartz glass are observed. The author and other investigators ([6]) conclude that annealing at high temperatures leads to decomposition of silicon monoxide into silicon and quartz glass.

However, thermodynamic studies ([7]) have shown that the solid phase of silicon monoxide is thermodynamically unstable at all temperatures. In ([8]), on the basis of an analysis of the radial-distribution curve obtained from X-ray diffraction patterns of the material called amorphous SiO, it was shown that solid silicon monoxide is a stoichiometric mixture of silica and silicon.

The present work is devoted to an electron-diffraction study of the structure of thin films obtained by condensation in vacuum of silicon monoxide vapors.

Films 300–700 Å thick were obtained by evaporation in a vacuum of $5 \cdot 10^{-5}$ mm Hg of a thoroughly ground mixture of two molar parts of anhydrous silica and one part of metallic silicon, with deposition on copper grids coated with collodion films and positioned at a distance of 165 mm from the evaporator.

The evaporator, in the form of a boat, was made of molybdenum foil; the evaporator temperature was 1250–1300°, and the evaporation time was 60 sec. Before evaporation, the mixture was preliminarily calcined with a gradual increase in temperature for 30–60 min until a stable vacuum was reached. After deposition of the film under investigation, the copper grid was wetted with amyl acetate to dissolve the collodion film.

The dried film on the copper grid was placed in the electron-diffraction camera. The diffraction pattern consisted of a single diffuse halo, $d = 3.6 \pm 0.5$ Å.

To obtain the intensity curve, six electron diffraction patterns with multiple exposures (2; 4; 8; 16; 32;

64 sec), which were microphotometered on an MF-4 microphotometer. The background lines were drawn as on the microphotometric curves for polycrystalline substances.* The normalization of the experimental intensity curve $I(s)$ to the theoretical curve $\sum_i f_i^2(s)$ was carried out by comparing the areas under the curves $\sum_i f_i^2(s)s^2$ and $I_n(s)s^2$ ([10,11]).

To find the effective number of electrons, the formula used was:

$$K_i^2 = \frac{\sum_s f_i^2(s)s^2}{\sum_s f^2(s)s^2}.$$

Taking $K_0 = 1$, we obtain $K_{\mathrm{Si}} = 1.875$. Using data on the density of a silicon monoxide film, equal to $d_{\mathrm{SiO}} = 2.15$ g/cm^3 ([1]), we find the mean atomic density from the formula

$$\rho_0 = \frac{d_{\mathrm{SiO}}}{M m_{\mathrm{H}}} \simeq 0.03 \sum_i K_i \text{ Å}^{-3}.$$

The calculation of the radial distribution function, expressed by the formula

$$4\pi r^2 \sum_i K_i \rho(r) = 4\pi r^2 \rho_0 \sum_i K_i + \frac{2r}{\pi} \int_0^\infty si(s) \sin sr \, ds,$$

was performed on an electronic computer. The intensity curve and the corresponding distribution curve are shown in Figs. 1 and 2.

The radial distribution curve (Fig. 2) has a well-resolved peak at 1.6 Å, a broadened peak between 2 and 3 Å, and a peak at 3.625 Å. The distance of the first peak is equivalent to the distance $r = 1.62$ Å, silicon–oxygen. The area under the first peak is 17.5 el^2. The number of nearest oxygen atoms around a silicon atom is $n_{\mathrm{O-Si}} = 4.68$, which, within the limits of experimental error, agrees with the data for the number of nearest neighbors required in silicates.

Fig. 1 and Fig. 2: diffraction intensity and radial distribution curves

Figure 1: Fig. 1 and Fig. 2: diffraction intensity and radial distribution curves

It is known that the nearest silicon–silicon distance in pure silicon is 2.36 Å, and the edge of the oxygen tetrahedron O–O in quartz is 2.65 Å. On the radial distribution curve, the peaks corresponding to these distances should overlap because of the closeness of the maxima. In our case, in the region from 2 to 3 Å a broadened peak is observed, the area under which is 38.5 el^2. If one assumes, as was done in work ([8]), that the substance investigated in the "silicon monoxide" film is a mixture of Si and SiO_2, then the broadened peak may be regarded as two unresolved peaks at 2.36 Å (Si–Si) and 2.65 Å (O–O). Let us try to resolve these peaks. The area of the peak corresponding to the O–O bond, representing the edge of the tetrahedron, s_{O-O}, is equal to 12 el^2, and thus the area corresponding to the Si–Si bond will be $s_{Si-Si} = 26.5$ el^2, whence the number of nearest silicon neighbors around silicon is $n_{Si-Si} = 3.8 \simeq 4$.

Such a result can be explained by the fact that elemental silicon with the diamond structure is present in the film, along with SiO_2, as an independent phase.

The area corresponding to the peak at 3.625 Å is 107.6 el^2. If this peak is represented as the superposition of two peaks corresponding to the Si–Si bond in the second coordination sphere of the SiO_2 phase ($r = 3.2$ Å) and the Si–Si bond in the second coordination sphere of the silicon phase of diamond

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* Separation of the background by the method of ([9]) gives less preferable results.

type ($r = 3.8$ Å), then in both cases the number of neighbors obtained should be equal to six. Calculation from the area under the peak gives $n = 7.7$, and the difference may be attributed to the approximate nature of the method.

Let us make another assumption about the correspondence of the peaks, namely, that the broadened peak between 2 and 3 Å corresponds to the O–O bond with $r = 2.65$ Å in SiO_2, and the peak at 3.625 Å to the Si–Si bond with $r = 3.2$ Å in SiO_2; then the corresponding coordination numbers will be $n_{O-O} = 19.3$, $n_{Si-Si} = 15.4$, instead of

Fig. 1 **Fig. 2**

the expected $n = 6$. In this case the discrepancy is too large, and the assumption that the second and third peaks correspond to bonds of only one silica phase must be rejected.

Thus, the results of analysis of the radial distribution curve can be interpreted as indicating the presence in the films studied of two independent amorphous or submicroscopic phases, namely, silicon dioxide and silicon, which agrees with the conclusion in work (8).

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