STRUCTURE OF OXIDE FILMS OBTAINED BY BOMBARDMENT OF A SILICON SURFACE WITH OXYGEN IONS

CRYSTALLOGRAPHY

1967

SovietRxiv

Fig. 1

Figure 1: Fig. 1

Abstract

Full Text

UDC 539.235

CRYSTALLOGRAPHY

P. V. PAVLOV, E. V. SHITOVA

STRUCTURE OF OXIDE FILMS OBTAINED BY BOMBARDMENT OF A SILICON SURFACE WITH OXYGEN IONS

(Presented by Academician N. V. Belov, March 28, 1966)

In semiconductor electronics, silicon dioxide films are widely used as insulating layers, and also as masks in selective doping of semiconductors by diffusion or ion bombardment using a defocused ion beam; these films can be obtained by various methods ([1–4]).

In the present work we investigate the structure and composition of films obtained in the ion accelerator of the I. V. Kurchatov Institute of Atomic Energy by bombardment with oxygen ions of the (111) surface of n-type silicon with a resistivity of 1 $\Omega \cdot$ cm. The thickness of the films studied was $\sim 0.15\ \mu$. Their etching rate in hydrofluoric acid before and after annealing at 1250° in a stream of dry argon was considerably lower than the rate for thermally grown films. During chlorine etching the initial thickness of the film decreased almost by a factor of two, which can be explained by nonuniformity of composition. The film may contain, as independent phases, silicon, silicon monoxide, and silicon dioxide. The change in etching rate, as well as in film thickness during etching, is probably associated with the presence of these phases. In a stream of chlorine, silicon and silicon monoxide are readily etched, whereas silicon dioxide is not etched at all ([5]).

Fig. 1. Infrared absorption spectrum of a film obtained by bombardment of the silicon surface with oxygen (1) and by thermal oxidation of silicon (2).

The distribution of implanted atoms during ion bombardment has the form of curves with a maximum inside the layer ([6]). It may be assumed that the near-surface part, as well as the region adjacent to the substrate, are depleted in oxygen; therefore, in composition they differ from the SiO_2 phase. To verify this, before etching in a stream of chlorine we carried out studies of infrared absorption spectra and electron-diffraction studies. The presence of an absorption

Fig. 2. Curves of the radial distribution of electron density for reflection (1), for transmission (2)

Figure 2: Fig. 2. Curves of the radial distribution of electron density for reflection (1), for transmission (2)

peak (Fig. 1) at $\lambda = 10\ \mu$ indicates the presence of SiO in the film, and the peak at $\lambda = 9.2\ \mu$ indicates SiO_2 ([7]).

On the basis of electron-diffraction patterns taken in reflection from the film surface with short exposures of 4, 8, 16, 32, and 64 sec, curves of the radial distribution of electron density were constructed by the Fourier analysis method (Fig. 2, 1). The presence on the curve of maxima at $r = 2.5$ Å and $r = 3.5$ Å is significant; these maxima can be explained by the presence of silicon and silicon monoxide in the film.

Specimens for taking transmission electron diffraction patterns were prepared in the following way. Silicon plates of size $5 \times 5 \times 0.2$ mm^3, on one of whose surfaces an oxide film had been deposited, were placed in a platinum boat and etched in a stream of chlorine at a temperature of 800° for 3–4 min. In this process the silicon was etched away, while the film was preserved. The film was transferred to a Petri dish with alcohol and caught on a platinum mesh. To construct the experimental intensity curve, 5 electron diffraction patterns with multiple exposures of 4, 8, 16, 32, and 64 sec were taken on one photographic plate. On all electron diffraction patterns one diffuse ring of diameter 23 mm was observed, which corresponds to an interplanar spacing of 4.13 Å, in good agreement with the interplanar spacing 4.14 Å in the structure of β-cristobalite ([8]).

According to microphotometric data obtained from the electron diffraction patterns on an MF-4 microphotometer, the curves of the radial distribution of electron density were calculated by the formula

$$4\pi r^2 \sum_i k_i \rho_i(r) = 4\pi r^2 \rho_0 \sum_i k_i + \frac{2r}{\pi} \int_0^\infty s\, i(s) \sin sr\, ds.$$

The effective number of electrons was calculated from the expression

$$\sum_i k_i^2 = \sum_s f_i^2(s) s^2 \Big/ \sum_s f_{\mathrm{II}}^2(s) s^2.$$

Fig. 2. Curves of the radial distribution of electron density for reflection *(1)*, for transmission *(2)*

Using the value of the density of the silicon dioxide film, 2.2 g/cm^3 ([1]), the mean atomic density was found from the relation

$$\rho_0 = \frac{d_{\mathrm{SiO_2}}}{Mm_{\mathrm{H}}} = 0.022 \sum_i k_i \ \text{Å}^{-3}.$$

The normalization of the experimental intensity curve $I(s)$ to the theoretical curve $\sum f^2(s)$ was carried out by the method of equating the areas under the curves $\sum f_i^2(s)s^2$ and $I(s)s^2$.

For calculating the radial distribution curve, values were taken in the interval from 1 to 6 Å at every 0.2 Å. The calculations were performed on an electronic computer.

The radial distribution curve is presented in Fig. 2, 2. The first peak of the curve corresponds to the distance between silicon and oxygen atoms (Si—O = 1.60 Å) in the SiO_4 tetrahedron. The area under the peak is 15.6 el^2; then the number of nearest oxygen neighbors around a silicon atom is $n_{\mathrm{Si-O}} = 4.15$, which agrees well with the number of silicon neighbors in silicate structures. The peak at 2.8 Å is asymmetric and probably consists of two peaks, corresponding to the O—O = 2.65 Å bond in the SiO_4 tetrahedron and the Si—Si = 3.1 Å bond in two nearest tetrahedra joined at their vertices. The area under the peak is 51 el^2. The area corresponding to the O–O bond at $n = 6$ is 24 el^2. Thus, the area corresponding to the Si–Si bond will be 27 el^2, whence the nearest number of neigh-

around silicon, $n_{\mathrm{Si-Si}} = 3.9$, which agrees well with the number of neighbors in β-cristobalite.

It may also be assumed that the material of the film under study is a mixture of Si and SiO_2; then the peak at $r = 2.8$ Å can be represented as the sum of peaks for the bonds $\mathrm{Si-Si} = 2.36$ Å (area under the peak 27 el^2) in pure silicon with the diamond structure, and $\mathrm{O-O} = 2.65$ Å (area under the peak 24 el^2) in SiO_2. Since, first, the calculated number of nearest neighbors around silicon in this case turns out to be $n = 13.5$ instead of $n = 4$ in silicon, and, second, the mean distance between the peaks is found to be 2.5 Å instead of 2.8 Å, this assumption is not valid.

The third asymmetric peak at $r = 4.2$ Å, as in the preceding case, can be divided into two: at $r = 3.88$ Å, which corresponds to the $\mathrm{Si-O}$ bond, and at $r = 4.36$ Å, corresponding to the $\mathrm{O-O}$ bond.

The last, fourth peak, observed at a distance of 5.2 Å, is evidently the superposition of two peaks: the first–at $r = 5.03$ Å (corresponds to the $\mathrm{Si-Si}$ distance in the second coordination sphere of the β-cristobalite structure), and the second –at $r = 5.27$ Å, corresponds to the $\mathrm{Si-O}$ distance.

Thus, the investigations carried out make it possible to judge with complete certainty the presence, in films obtained by ion bombardment, of an independent amorphous phase of silicon dioxide with the structure of β-cristobalite, and to allow for the existence of phases of silicon and silicon monoxide.

In conclusion, the authors express their sincere gratitude to Acad. N. V. Belov for his interest in the work, and also to T. N. Strizheva for carrying out the electron-diffraction photographs and to M. I. Guseva for kindly providing samples of oxidized silicon.

Gorky Research
Physico-Technical Institute
of Gorky State University
named after N. I. Lobachevsky

Received
1 III 1966

CITED LITERATURE

1. Bruel F. Deal, J. Electrochem. Soc., **110**, No. 6, 527 (1963).

2. I. R. Ligenza, J. Appl. Phys., **36**, No. 9, 2703 (1965).

3. E. L. Jordan, J. Electrochem. Soc., **108**, No. 5, 478 (1961).

4. Leslie L. Alt, S. W. Ing, K. W. Landle, J. Electrochem. Soc., **110**, No. 5, 465 (1963).

5. R. E. Morrison, I. E. Sandor, J. Electrochem. Soc., **109**, No. 3, 221 (1962).

6. R. R. Ferber, I. E. E. E. Trans., **10**, No. 5, 15 (1963).

7. Hiroshi Edagawa, Yoshinori Morita, Schun-ichi Moikawa, Japan, J. Appl. Phys., **2**, 12, 765 (1963).

8. L. I. Mirkin, *Handbook of X-Ray Structural Analysis of Polycrystals*, Moscow, 1961.

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