SiO_x as a model medium with large-scale potential fluctuations

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(Submitted 3 April 1981)

Pis'ma Zh. Eksp. Teor. Fiz. **34**, No. 1, 6–9 (5 July 1981)

A model of large-scale potential fluctuations resulting from a local composition inhomogeneity is constructed from data on SiO_x found by photoelectron spectroscopy. Electron-transport experiments confirm the predictions of the three-dimensional theory of percolation in a large-scale potential relief.

PACS numbers: 72.20.Dp, 79.60.Eq

Shklovskiĭ and Éfros[1,2] have proposed a model for large-scale potential fluctuations in a compensated semiconductor in which the fluctuations result from an inhomogeneous distribution of donors and acceptors. Gadzhiev *et al.*[3] have shown that this picture is valid in neutron-bombarded *n*-type germanium. The local gap width remains constant in this model. A fundamentally new possibility is raised by the syn-

 0021-3640/81/10003-04$00.60

thesis of heterogeneous materials in which fluctuations of the local gap width $E_g(Z)$ result from a composition inhomogeneity.

In this letter we will use experimental data to construct a potential-fluctuation model for SiO_x, and we will report an experimental test of the predictions of the three-dimensional theory of percolation in strong electric fields.[4]

The amorphous SiO_x films ($x = 1.8, 1.6, 1.4, 1.2, 0.6$) were synthesized from the gas phase in a reaction of SiH_4 and N_2O at $T = 640°C$. The film composition was varied by varying the ratio SiH_4/N_2O. Figure 1 shows photoelectron spectra of the $2S$ levels of silicon in SiO_x samples of various compositions (the excitation energy was $E = 1586$ eV). The experimental spectra may by described as superpositions of peaks corresponding to the binding energies of the $2S$ electrons in SiO_2 and Si and a broad peak whose position is apparently determined by the degree of oxidation of the silicon in the matrix film, which we denote as SiO_y. These SiO_x films are thus heterogeneous, consisting of a mixture of Si, SiO_2, and SiO_y. The accuracy of the present experiments was such that we could not obtain more-detailed information on the composition.

The photoelectron spectra of the SiO_x valence band indicate that in the films containing a relatively large amount of silicon ($x = 0.6, 1.4$) the top of the valence band lies 5 ± 1 eV below the electron level in a vacuum. This result correlates well with the threshold ($E = 5.2 \pm 0.1$ eV) for photoemission of electrons from amorphous silicon into vacuum.[5] As x is reduced, the top of the valence band descends monotonically from the vacuum level, to 9 ± 1 eV in SiO_2. The latter result agrees with the threshold for electron photoemission from SiO_2 into vacuum.[6] The shift of the top of the valence band from the vacuum level is accompanied by an increase in the optical width of the SiO_x energy gap, from 2 to 4 eV.

We can use these results to reconstruct the energy-band scheme of SiO_x. According to Fig. 2, SiO_x consists of clusters of Si and SiO_2 which are "floating" in a

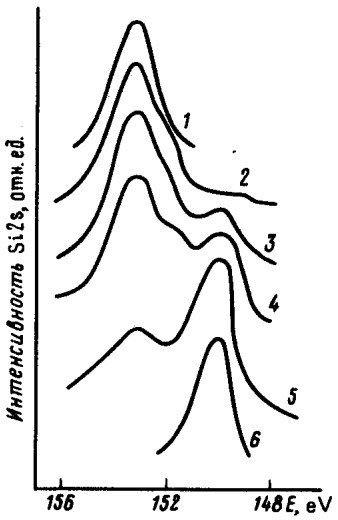

FIG. 1. Photoelectron spectra of the $2S$ levels of Si in SiO_x for various values of x. 1–SiO_2; 2–$SiO_{1.8}$; 3–$SiO_{1.6}$; 4–$SiO_{1.4}$; 5–$SiO_{1.2}$; 6–Si. The energy is reckoned from the Fermi level of the spectrometer.

medium SiO_y of intermediate composition. The characteristic dimensions of the inhomogeneities in the SiO_x are 10^{-6} cm, according to electron microscopy. A fundamental distinction between the scheme in Fig. 2 and the band-bending model[2] is that the internal fields tend to promote the recombination of nonequilibrium electron-hole pairs. The percolation energies for the electrons and the holes (E_n and E_p, respectively) are generally not equal in absolute value, in contrast with the band-bending model, because the potentials corresponding to the band edges E_c and E_v are not mirror images of each other.

The theory of percolation in a potential relief with large-scale potential fluctuations in strong fields predicts[4]

$$j = j_0 \exp\left[-\frac{E_n - (Cea\,FV_0^{\gamma})^{\frac{1}{1+\gamma}}}{kT}\right]. \quad (1)$$

Here $C = 0.25$ is a constant (Shklovskii[4] makes no claim that his theory yields an accurate value for this constant), $\gamma = 0.9$ is the critical index, a is the spatial dimension of the fluctuation, and V_0 is the amplitude of the fluctuation. If γ is replaced by unity, expression (1) becomes the Poole–Frenkel' law. Study of the conductivity of SiO_x as a function of the field and the temperature indicates that expression (1) approximates the experimental data satisfactorily for $x = 1.4$, 1.6, and 1.8. At higher silicon contents (lower x) the dielectric constant of SiO_x increases, and the slope of

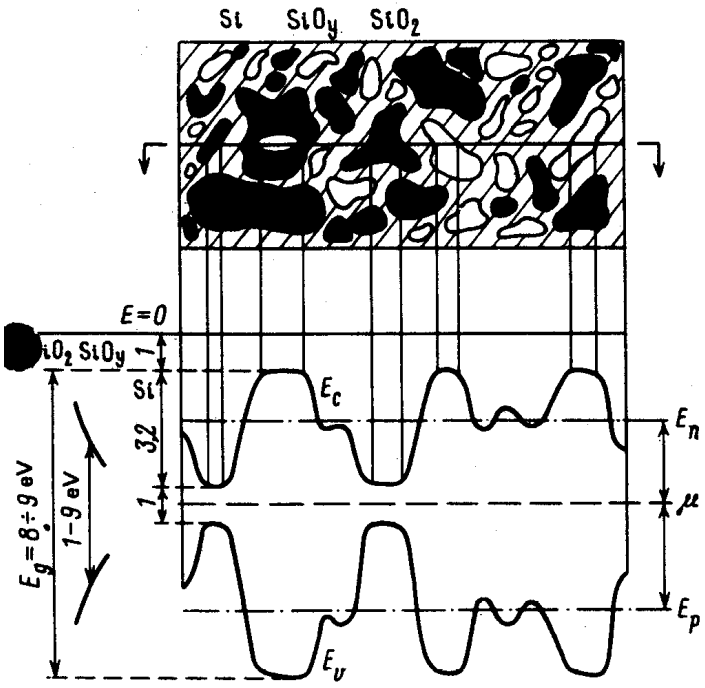

FIG. 2. (Top) Structure of SiO_x, (bottom) energy diagram of SiO_x. E_n, E_p–Percolation levels for electrons and holes; dashed line in the energy gap–Fermi level.

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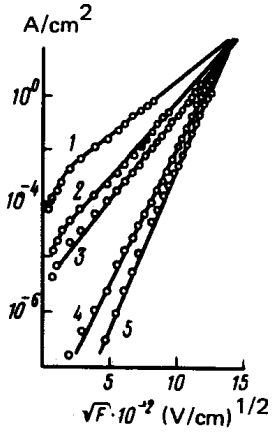

FIG. 3. I-V characteristics of $SiO_{1.4}$ at various temperatures. 1–T = 470 K; 2–390 K; 3–290 K; 4–190 K; 5–80 K.

the I-V characteristics, plotted as $\log j - \sqrt{F}$, increases. The usual interpretations of the the SiO_x conductivity in terms of the Frenkel' effect[7] or a contact-limited Schottky effect contradict the experimental data, since both interpretations predict a decrease in the slope of the I-V characteristic with increasing dielectric constant: $d\log j/d\sqrt{F} \sim \epsilon^{-1/2}$. The SiO_x percolation energy found from the experimental data ranges from 0.4 to 1 eV, depending on the composition. Figure 3 shows the experimental I-V characteristics. The percolation energy for this sample is $E_{perc} = 0.4 \pm 0.1$ eV, and we find the product $aV_0 = 6 \times 10^{-7}$ eV · cm. With $V_0 = 1$ eV, a is 6×10^{-7} cm. We should therefore assume that the SiO_x conductivity results from a percolation of electrons through the potential relief formed by the Si and SiO_y. The fraction of the volume occupied by these phases (which can be estimated from Fig. 1) is 0.25 ± 0.1, higher than the critical fraction of 0.15 required for the formation of an infinite cluster in the overlapping-sphere model.[8] Percolation theory in strong fields has been derived for a homogeneous medium with $E(Z) = \text{const}$. For a correct description of percolation in inhomogeneous media, we need a theory which incorporates the redistribution of the electric field caused by fluctuations of the dielectric constant, $E(Z)$.

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Translated by Dave Parsons
Edited by S. J. Amoretty