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Metastable phase of GeO_x

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Optical and electron diffraction data for sufaces of SiO_2, GeO_2, and partially oxidized Si are reviewed. It is concluded that an intermediate phase GeO_x can be formed at the surface of GeO_2, and that this phase may be a metastable crystalline film. Patches of an amorphous film of nearly the same composition may be found on partially oxidized Ge surfaces, in analogy with patches of similar material on partially oxidized Si surfaces, as observed in electron-diffraction energy-loss experiments.

Ibach and Rowe[1] have studied second-derivative electron-energy-loss spectra (ELS) of partially oxidized Si (111) and (100) surfaces. The ELS spectrum they obtained is qualitatively similar to the optical-reflectance spectra studied earlier by Philipp,[2] but it exhibits relatively more structure, presumably because ELS is more sensitive to details of the surface conditions than reflectance.

A curious feature of the ELS data for SiO_2 is the presence of three peaks at 3.5, 5, and 7 eV, interpreted by Ibach and Rowe as an indication of the presence of a less than completely oxidized surface film of SiO. This is probably qualitatively correct, but other evidence suggests that this film may be a metastable phase of MO_x (M = Si or Ge, depending on the substrate). As we shall see below, the metastable phase is very thin, perhaps only one-unit-cell thick at most parts of the surface. However, in GeO_x only it may exhibit crystalline properties associated with long-range order, which indicates that whatever the value of x, there is a definite composition intermediate between $x=0$ and $x=2$ at which the metastable phase exists.

A metastable phase of MO_x with M = Ge is more likely than with M = Si, because GeO_2 has two morphotropic forms, the hexagonal or quartz form and the tetragonal (SnO_2) form. In the former, each (SnO_2) M atom is approximately tetrahedrally coordinated, whereas in the tetragonal form the M coordination is sixfold. Some of the physical properties of SiO_2 and GeO_2 in the quartz or hexagonal form are contrasted with those of GeO_2 in the tetragonal form in Table I. From the properties it can be seen that hexagonal GeO_2 is a metastable phase intermediate in structural properties between hexagonal SiO_2 and tetragonal GeO_2. This makes it more likely that hexagonal GeO_2 will support a metastable surface phase of composition MO_x than either hexagonal SiO_2 or tetragonal GeO_2.

Reflectivity data have been reported for GeO_2 in hexagonal crystalline and glassy bulk states by Pajasova.[3] A tracing of her data for $\epsilon_2(\omega)$, obtained from a Kramers-Kronig transform of $R(\omega)$, is shown for the reader's convenience in Fig. 1. Both the crystalline and glassy spectra are interesting, and the difference between them is indicative of the formation of a very thin metastable crystalline phase on the surface of the hexagonal crystalline substrate. When the substrate is amorphous or glassy, the metastable phase GeO_x is also amorphous.

The spectrum of SiO_2 studied by Philipp[2] exhibits a series of oscillatorlike peaks beginning near 10 eV. The peaks are almost symmetrical, and probably arise because of final-state Coulomb interactions between excited electrons and holes, which give rise to exciton resonances superimposed on the interband continuum. Similar nearly symmetrical resonances are found in other large-gap ionic insulators such as the alkali halides.[4]

The chemical and structural differences between hexagonal SiO_2 and hexagonal GeO_2 are small, and one would expect strong similarities in their optical spectra. According to Fig. 1, above 10 eV this is found to be the case; the chief difference in this energy range is that the exciton resonances seen in SiO_2 are greatly broadened in GeO_2, the natural widths for the former being of order 1 eV or less, but being 2 or 3 eV or more in the latter.

In the low-energy region below 10 eV, a band spectrum is found for GeO_2 that is completely absent in the reflectivity spectrum of bulk SiO_2. This spectrum, which lies between 4 and 9 eV, is called a band spectrum because it exhibits asymmetrical peaks and shoulders. Structure of this kind arises because interband critical points give rise to analytic singularities in the interband density of states.[4] Note in Fig. 1 the interband threshold near $\hbar\omega_0 = 4$ eV, with $\epsilon_2(\omega) \propto (\omega - \omega_0)^{1/2}$, a second threshold and strongly asymmetrical peak near 6 eV, and a saddle-point shoulder[4] near 8 eV. All of these features are qualitatively different from the nearly symmetrical resonances, superimposed on the interband background, which are found about 10eV.

Qualitatively speaking, the interband spectrum in the region 4–9 eV resembles the interband spectrum[4] of pure Ge, except that its center has been

TABLE I. Physical properties of SiO_2 and GeO_2.

Material	$<M$-O-M(deg)	ϵ	$d(M$-O)Å	ω(cm^{-1})	$-\Delta H_f^0$ (kcal/mole)
Hex. SiO_2	114[a]	2.34[b]	1.607[a]	1097[c]	217.7[d]
Hex. GeO_2	130[a]	2.82[b]	1.739[a]	885[c]	133.0[e]
Tetrag. GeO_2	90[f]	3.96[b]	1.857[g]	720[c]	139.4[e]

[a] G. S. Smith and P. B. Issacs, Acta. Crystallogr. 17, 842 (1964).

[b] Landölt-Börnstein, *Zahlenwerte und Funktionen* (Springer-Verlag, Berlin, 1962), Vol. II, Pt. 8.

[c] E. R. Lippincott *et al.*, J. Res. Natl. Bur. Stand. 61, 61 (1958).

[d] D. D. Wagman *et al.*, Natl. Bur. Std. Tech. Note No. 270-3, 1968 (unpublished).

[e] M. M. Faktor and J. I. Carasso, J. Electrochem. Soc. 112, 817 (1965).

[f] W. H. Baur, Acta Crystallogr. 9, 519 (1956). The value quoted is the average of three inequivalent angles, which are actually 80°, 90°, and 100°.

[g] R. W. G. Wyckoff, *Crystal Structures* (Interscience, New York, 1963), Vol. I.

shifted from near 4.5 eV to near 6 eV. This shift can be used to estimate x in the formula GeO_x for the stoichiometry of the metastable film. In the one-band approximation,[5] the average energy gap E_g of the interband spectrum of a crystal with a valence-electron plasma frequency ω_p determines the dielectric constant ϵ_0 through the relation

$$\epsilon_0 = 1 + (\hbar\omega_p/E_g)^2. \qquad (1)$$

In GeO_2, $\epsilon_0 = 2.82$ according to Table I, compared to $\epsilon_0 = 16$ in Ge. The valence electron densities make $\omega_p^2(GeO_2)$ about 30% greater than $\omega_p^2(Ge)$, so that $E_g(GeO_2)$ should be about three times as large as $E_g(Ge)$, i.e., about 13.5 eV. If we assume that E_g is a linear function of x, an assumption which holds fairly well for semiconductor alloys,[5] we obtain

$$x \cong 2(6-4.5)/(13.5-4.5) \cong 0.33. \qquad (2)$$

The small value of x found in Eq. (2) is consistent with the observation that the low-energy interband spectrum of the metastable film qualitatively resembles that of Ge.[4]

Another striking similarity between the GeO_x and Ge spectra is the way these spectra change on going from the crystalline to the amorphous state. Penn predicted[6] that the interband spectrum of an amorphous semiconductor with only one kind of bonding (e.g., sp^3 bonding in semiconductors of the diamond, sphalerite, or wurtzite families) would exhibit an interband spectrum with a single asymmetric peak of the form $\epsilon_2(\omega) \propto (\omega - \omega_g)^{1/2}$, suitably broadened by small departures from his isotropic model. This behavior has since been confirmed in a number of cases,[7] and it is clearly exhibited in Fig. 1. Note that this behavior is characteristic of an interband spectrum, and not of exciton resonances, so that even in the amorphous state there is still a qualitative difference, not only in the position but also in the character of $\epsilon_2(\omega)$ between GeO_x and GeO_2.

The similarity between the spectra of Ge and GeO_x can be exploited to estimate the thickness of the metastable film. We anticipate the answer, which is that the film thickness d is very much less than the wavelength λ of the light in this energy range. Then the parameter $\gamma = 4\pi d/\lambda \ll 1$, and we can expand the reflectivity $R(\gamma)$ at normal incidence in powers of γ and in terms of the complex optical constants $n + ik$ of the film and $n_2 + ik_2$ of the GeO_2 substrate.[8] With $\epsilon_2 = 2nk$ the result to lowest order in γ is

$$R(d)/R(0) = 1 + (2\epsilon_2/n_2^2 - 1)\gamma; \qquad (3)$$

and with $n_2^2 = 2.82$ this reduces to

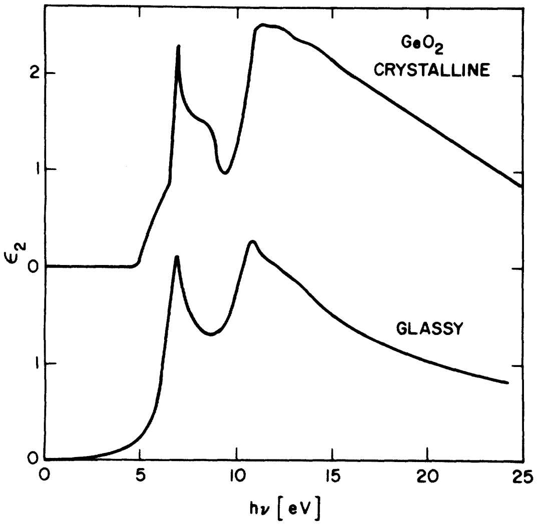

FIG. 1. Comparison of optical spectra of hexagonal and glassy GeO_2. Note the dramatic change in the shape of the interband spectrum between 4 and 9 eV. Experimental data from Ref. 3.

$$\Delta R/R(\mathrm{O}) = 1.1\,\epsilon_2\gamma . \qquad (4)$$

Assuming that the optical spectrum of GeO_x is similar to that of Ge, but displaced upwards in energy by about 1.5 eV, the peak in ϵ_2 at 4.5 eV with a value of $\epsilon_2 = 40$ should be found at 6 eV ($\lambda = 2000$ Å) in GeO_2. At this energy $R = 15\%$ compared to $R(\mathrm{O}) = 7\%$. Thus $\Delta R/R(\mathrm{O}) = 1.1$, $\epsilon_2\gamma = 1$, and

$$d = \frac{\lambda}{4\pi}\,\frac{1}{10} = 4\ \text{Å} . \qquad (5)$$

The approximations which have led to this result are admittedly rough ones, but if the film is uniform the estimate should be correct to within about 30%. The lattice constants of Ge in a wurtzite structure should be close to those of ZnSe, $a \approx 4$ Å, $c \approx 6.5$ Å. The wurtzite unit cell contains four atoms, hence Eq. (5) corresponds to a film three or four atom layers thick.

For diamond-type crystals, (111) surfaces have the lowest free energy.[9] The (111) planes occur in pairs, with one outside dangling bond normal to each atom in each plane. The atoms are trigonally coordinated with atoms in the adjacent plane. One expects that initially deposition of oxygen on Si (111) or Ge (111) would result in utilization of the outside dangling bonds. At this stage, corresponding to coverages $\theta \lesssim 2$ in the notation of Ref. 1, a peroxide model of adsorbed oxygen molecules seems appropriate.[1] For higher coverages the characteristic structure at 3.5, 5, and 7 eV (SiO_x) or 4–9 eV (GeO_x) is much broadened, corresponding to the formation of MO_x. This suggests the following picture for the structure of metastable MO_x.

This phase may consist of a pair of (111) M planes, with a certain fraction of the interior M-M bonds occupied by O atoms. If we consider a unit cell of six M atoms and two O atoms, three M atoms in each plane, then there are nine M-M bonds, two of which are converted to M-O-M bonds. It would be unreasonable to pursue geometrical questions of this kind further until the presence of the postulated crystalline phase MO_x is resolved by a careful low-energy-electron-diffraction study of a hydrothermally grown GeO_2 sample such as that used by Pajasova.[3]

To conclude this discussion, one may note that hexagonal GeO_2 is soluble in water,[10] whereas hexagonal SiO_2 and tetragonal GeO_2 are not. The solubility, then, is not determined solely by the openness of the quartz structure (because hexagonal SiO_2 is not soluble in water), nor by the chemical makeup (because tetragonal GeO_2 is not soluble in water). Perhaps this unusual behavior is a consequence of a two-stage chemical reaction:

$$GeO_x + H_2O \rightarrow Ge(OH) + H_2 , \qquad (6)$$

$$GeO_2 \rightarrow GeO_x + O_2 . \qquad (7)$$

No effort has been made to "balance" Eqs. (6) and (7), as the state or nature of association of Ge in water, as well as the value of x, is not known. The equations merely illustrate the point that the metastable phase may serve to catalyze the solution of hexagonal GeO_2 in water.

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[1] H. Ibach and J. E. Rowe, Phys. Rev. B (to be published).

[2] H. R. Philipp, Solid State Commun. 4, 73 (1966).

[3] L. Pajasova, Czech. J. Phys. B 19, 1265 (1969).

[4] J. C. Phillips, Solid State Phys. 18, (1966).

[5] J. C. Phillips, Rev. Mod. Phys. 42, 317 (1970).

[6] D. Penn, Phys. Rev. 128, 2093 (1962).

[7] J. Stuke, in *Proceedings of the Tenth International Conference on the Physics of Semiconductors*, edited by S. P. Keller, J. F. Hensel, and F. Stern (U.S. AEC, Division of Technical Information, Washington, D.C., 1970), p. 15; J. Stuke and G. Zimmerer, Phys. Status Solidi B 49, 513 (1972).

Zimmerer, Phys. Status Solidi B 49, 513 (1972).

[8] F. Abeles, Rev. Opt. 32, 260 (1953).

[9] J. I. Pankove, RCA Rev. 15, 75 (1954).

[10] M. M. Faktor and J. I. Carasso, J. Electrochem. Soc. 112, 817 (1965).