Optical properties of GeO_2

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Interpretations for the energies corresponding to the peaks in the reflectivity and the imaginary part (ϵ_2) of the complex dielectric constant ($\epsilon=\epsilon_1+i\epsilon_2$) have been sought successfully using Penn-like model calculations. The valence-band–d-band coupling present in Ge may contribute to the effective number of electrons in GeO_2 at the observed peaks at high energies.

I. INTRODUCTION

Unlike SiO_2, which has a tremendous importance in the semiconductor device industry as well as in glass manufacture, GeO_2 has had limited applications, primarily as an experimental optical-fiber material. Applications have been limited by the hygroscopic character of glassy GeO_2. Because of the fact that the temperature of melting of GeO_2 ($T_m=1150\,^\circ$C) is much less than that of SiO_2 ($T_m=1750\,^\circ$C), preparation of GeO_2 in the glassy form over a range of temperatures and oxygen partial pressures is much less difficult than that of SiO_2. The kinetics of crystallization of GeO_2 and the effect of stoichiometry on the kinetics seem to be well understood.[1] Recently reported studies[2] of the x-ray absorption have shown that the Ge-O and Ge-Ge distances in the GeO_2 glass are close to those of trigonal GeO_2 crystals.

The types and concentrations of intrinsic paramagnetic states in GeO_2 glasses equilibrated at temperatures T_ϕ between T_m, the melting temperature, and T_b, the boiling temperature, and cooled at various rates have been reported.[3–5] The intensity of an optical-absorption band at 245 nm (first observed by Garino-Cannina[6]) has been shown to have an Arrhenius dependence on the glass equilibration temperature (T_ϕ) with an activation energy of 2.3 eV. This band has been attributed to an oxygen deficiency of GeO_2.[4] However, some very basic problems of GeO_2 remain unresolved. One such problem concerns an analysis of the optical spectra of GeO_2. Here, we report an analysis of the reflectivity spectra of GeO_2.

Pajasova[7] has reported detailed experimental measurements of the reflectivity spectra of crystalline (c) and glassy (g) GeO_2 in the photon-energy (E) range of 0.5–25 eV. Utilizing the Kramers-Kronig relation, the optical constants including the ϵ_2-E spectra have been derived. However, no interpretation for the observed peaks and the corresponding energy has been offered. In Figs. 1 and 2, the reflectivity spectra and the ϵ_2-E spectra, reported earlier by Pajasova, respectively, for c- and g-GeO_2 are presented. As is expected because of the crystalline nature, c-GeO_2 exhibits peaks which are sharper than those of g-GeO_2. However, the second peak in the ϵ_2-E spectra of c-GeO_2 is spread out in energy. The maxima in intensities and the corresponding energy in Figs. 1 and 2 are listed in Table I. The reflectivity spectra of c-GeO_2 exhibit several kinks, at 5.94 eV ($R=11.5\%$), 7.25 eV ($R=10.4\%$), and 12.2 eV ($R=13.5\%$). It is interesting to note that the first two kinks are absent in the reflectivity spectra of g-GeO_2 while the third kink is shifted in energy; 11.59 eV ($R=11.05\%$). This may be attributed to the absence of translational symmetry in glasses.

While the maximum reflectance R_{max} is higher for c-GeO_2 than that of g-GeO_2, the energies corresponding to the peaks are the same (Table I). In Fig. 2, ϵ_2 remains practically zero until 4.85 eV, and increases abruptly to a value of 0.9 in the energy range of 4.85–6.6 eV for c-GeO_2. In a narrow energy range of 6.6–7.0 eV, ϵ_2 increases from 0.9 to 2.34. The kinks observed in the reflectivity spectra of c-GeO_2 are all evidenced in the ϵ_2-E spectra, 6.6 eV ($\epsilon_2=0.9$), 7.95 eV ($\epsilon_2=1.6$), and 14 eV ($\epsilon_2=2.34$), except that the kinks are shifted in energy. None of the kinks are resolved in the ϵ_2-E spectra of g-GeO_2. While the $\epsilon_{2,max}$ in c-GeO_2 has a higher value than in g-GeO_2, the energy corresponding to the first

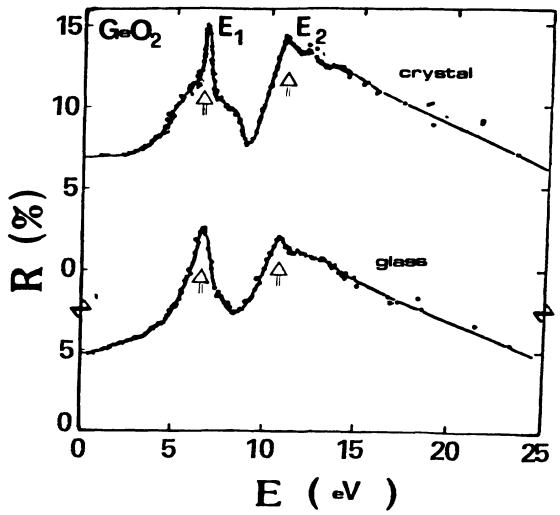

FIG. 1. Reflectivity spectra of crystalline and glassy GeO_2 (from Pajasova, Ref. 7).

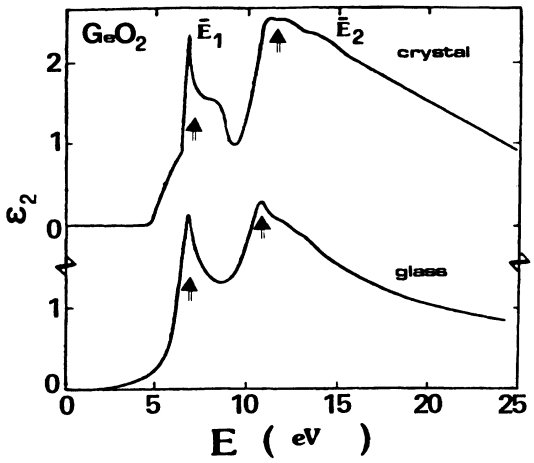

FIG. 2. ϵ_2 as a function of photon energy for crystalline and glassy GeO_2 [see Pajasova (Ref. 7) for further details].

peak ($\bar{E}_1$) is the same for both phases. The second peak in the ϵ_2-E spectra of c-GeO_2 is spread out in energy and occurs at an energy higher than that of g-GeO_2 (Table I).

II. APPLICATION OF PENN MODEL

It is well known that the reflectivity spectra or the ϵ_2-E spectra of a given material are determined by its band structure. By definition, an intensity maximum in ϵ_2 (or R) in the ϵ_2-E spectra (or R-E spectra) represents a maximum number in the optically induced electronic transitions in the material. The energy corresponding to the peak should therefore correspond to a band-to-band energy difference or a band gap. Since this is a macroscopic gap,[8] it should be related to the high-frequency dielectric constant ϵ_∞ ($\simeq n^2$), where n is the refractive index.

Several models have been proposed[8-10] to interpret the frequency and wave-vector dependence of the dielectric function. All these models have, however, been proposed for elemental semiconductors. Extrapolation of the applicability of these models to amorphous semiconductors,[11] and narrow- and wide-gap materials including alkali halides[12-14] has been carried out with reasonable success. Here, we demonstrate the applicability of one such model to c- and g-GeO_2.

For a model semiconductor, the high-frequency dielectric constant is given by[8]

TABLE I. Reflectivity and ϵ_2 data of crystalline and glassy GeO_2. See Figs. 1 and 2 for definitions of E_1, E_2, $\bar{E}_1$, and $\bar{E}_2$. $E_R=(E_1+E_2)/2$; $\bar{E}=(\bar{E}_1+\bar{E}_2)/2$.

Property	c-GeO_2	g-GeO_2
R_{max} (%)	15.44	12.50
E_1 (eV)	6.52	6.52
R_{max} (%)	14.70	11.62
E_2 (eV)	10.72	10.72
$\epsilon_{2,max}$	2.34	2.22
$\bar{E}_1$ (eV)	7.03	7.03
$\epsilon_{2,max}$	2.53	2.38
$\bar{E}_2$ (eV)	11.72–12.81	11.09

$$\epsilon_\infty = 1+(\hbar\omega_P/E_P)^2[1-(E_P/4E_F)+\tfrac{1}{3}(E_P/4E_F)^2] \quad (1)$$

or

$$1/E_P = 1/8E_F+[(\epsilon_\infty-1)/(\hbar\omega_p)^2-\tfrac{1}{3}(1/8E_F)^2]^{1/2}\ , \quad (2)$$

where the valence-electron plasmon energy $\hbar\omega_p$ is given by[15]

$$\hbar\omega_p = 28.8(N_{\rm eff}\rho/M)^{1/2}\ ,$$

E_P is the Penn gap[8] or the macroscopic gap accounting for all the possible optically induced electronic transitions in the material, E_F is the Fermi energy evaluated using the relation[13]

$$E_F = 0.2947(\hbar\omega_p)^{4/3}\ ,$$

$N_{\rm eff}$ is the number of valence electrons per atom determined by

$$N_{\rm eff} = Ma+N(8-b)$$

for a compound of the A_MB_N type, where a is the number of valence electrons per atom of type A, and b is the corresponding number for type B, and M and N are the respective atomic fractions of the elements A and B, and ρ is the density.

For GeO_2, $N_{\rm eff}=1\times4+2(8-6)=8$ electrons per atom. In Table II, the results of the calculations are presented. GeO_2 is known to have two crystalline structures apart from its glassy form with significant differences in densities (Table II). The most studied crystalline form of GeO_2 is its hexagonal structure, which is easily soluble in water. The quoted value of the density and the reflective index (or ϵ_∞) for g-GeO_2 concerns a glass for which $T_\phi=1650$ °C. As can be seen in Table II, the calculated value of E_P is very close to E_R, the average of all the energies corresponding to the peaks in the reflectivity spectra, for c-GeO_2. E_P of c-GeO_2 is also in good accord with $\bar{E}$, the average of the energies corresponding to the peaks in the ϵ_2-E spectra. However, for g-GeO_2, E_P differs considerably from $\bar{E}$ (or E_R). This may be due to the fact that ρ and ϵ_∞ quoted in Table II for g-GeO_2 do not pertain to the same g-GeO_2 on which the optical measurements were made. In fact, these values in Table II concern nonstoichiometric g-GeO_2. It is worthwhile to note here that such a procedure comparing the calculated E_P with the average of the energies corresponding to the peak in ϵ_2 (or R) was proposed by Phillips.[16]

Although, in principle, germanium has four electrons per atom in its outermost shell, it has a d band very close to the top of its valence band.[12] The effect of this d band is to increase $N_{\rm eff}$. Van Vechten[12] has considered, in detail, the effect of d electrons on the dielectric properties of semiconductors. In Table II, we also evaluate the Penn gap incorporating the d-electron contribution to $N_{\rm eff}$ (in parentheses in Table II). A comparison between Tables I and II indicates that $\epsilon_{2,max}$ has a maximum corresponding to $\bar{E}_2$ for both forms of GeO_2. It is notable that the evaluated E_P incorporating the d-electron contribution is in very good agreement only

TABLE II. Properties of crystalline and glassy GeO_2. N_{eff} is the effective number of valence electrons per atom. $\hbar\omega_p$ is the valence-electron plasmon energy. E_F is the Fermi energy. ϵ_∞ is the high-frequency dielectric constant. E_P is the Penn gap. $\bar{E}$ is the average of all the energies corresponding to the peaks in ϵ_2. E_R is the average of all the energies corresponding to the peaks in reflectivity. E_G is the energy gap. The numbers in parentheses correspond to the derived optical properties considering the contribution due to the d electron.

Structure	Crystalline–tetr.	Crystalline–hex.	Glassy
Solubility (in H_2O)	insoluble	soluble	soluble
Density ρ (g/cm^3)	6.239[a]	4.228[a]	3.677[b]
Mol wt. M	104.59	104.59	104.59
N_{eff}	8 (9)	8 (9)	8 (9)
$\hbar\omega_p$ (eV)	19.90 (21.10)	16.38 (17.37)	15.27 (16.20)
E_F (eV)	15.89 (17.18)	12.26 (13.26)	11.17 (12.08)
ϵ_∞		2.72	2.59[c]
E_P (eV)		8.68 (11.80)	10.69 (11.37)
$\bar{E}$ (eV)		9.64	9.06
E_R (eV)		8.62	8.62
E_G (eV)		5.56	5.63

[a]Reference 18.
[b]Reference 19.
[c]Reference 20.

with $\bar{E}_2$, for both g and c forms of GeO_2. This rather interesting result seems to suggest the tendency of the valence-band–d-band coupling present in germanium to contribute to the effective number of electrons in GeO_2 only at the observed peaks at high energy in the optical spectra, and, to the maximum of $\epsilon_{2,max}$.

The successful extrapolation of the application of Penn-like models[8–10] to crystalline and glassy GeO_2 leads to interesting conclusions. Although Fritzsche[17] finds it useful to distinguish between glasses and amorphous materials in terms of their structure and the average covalent coordination, disorder or lack of order in these systems does not seem to have any influence on the variation of the optical properties such as reflectance (or ϵ_2) on photon energy. An isotropic, nearly-free-electron model, such as the Penn model, seems to be valid for almost all materials, irrespective of their structure and the energy gap, in explaining the energies corresponding to the peaks in reflectivity spectra (or the ϵ_2-E spectra) and correlating these energies to the band structure of the material.

III. CONCLUSION

Penn-like model calculations have been utilized with reasonable success to explain the optical spectra of the crystalline and glassy GeO_2. The increased effective number of electrons in GeO_2 due to the valence d-band coupling in elemental Ge is seen to favor the increased ϵ_2 at high photon energies.

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