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A study of the optical properties of amorphous thin films of germanium and silicon monoxide

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Amorphous films of Ge–SiO have been co-evaporated and some of their optical properties are reported. The optical constants have been measured and estimated. At the high absorption end of the absorption edge, an equation due to non-direct transitions in k-space is found to match the optical absorption data. The variation of the optical band gap E_{opt} with film composition is reported. The infrared spectrum of a mixed layer is presented and a simple conclusion is drawn.

1. Introduction

The optical behaviour of an optically isotropic solid and in particular a semiconductor is usually described by two optical constants, the refractive index, n_f, and the absorption index, k. The former gives the phase shift of an electromagnetic plane wave inside the material, whereas the latter describes the attenuation of that wave. The absorption coefficient $\alpha(\omega)$ which describes directly the attenuation of radiation intensity rather than that of the field [1] is related to the absorption index as $\alpha(\omega) = (4\pi/\lambda)k(\omega)$.

Furthermore, analysis of the optical absorption with photon energy ($\hbar\omega$) can yield information about the band gap and the electronic structure in semiconductors. Amorphous non-metallic solids, however, exhibit absorption edges which are less abrupt and well defined than those typical of the corresponding crystalline form. In the high absorption region where $\alpha(\omega) \geqslant 10^4\,\text{cm}^{-1}$, the absorption of light in amorphous solids depends on the energy of the incident photons and on the optical energy gap (E_{opt}) of the material given by an equation of the form

$$\alpha(\omega) = B(\hbar\omega - E_{\text{opt}})^n/\hbar\omega \qquad (1)$$

where the component n is equal to 1, 2 or 3, ω is the angular frequency of the radiation and B is a constant. Tauc *et al.* [2] first derived Equation 1 to explain the optical absorption in amorphous Ge and took $n = 2$. Davis and Mott [3] later derived the general form of Equation 1 due to different possible optical transitions in k-space. Under the assumption that k is not a good quantum number and that consequently the k-conservation selection rule is relaxed in amorphous semiconductors, they estimated the absorption coefficient for non-direct transitions to be given by a quadratic equation similar to that given by Tauc. Equation 1 with $n = 2$ seems to offer the best fit for the optical absorption data in many amorphous or glassy materials and indeed it has been applied to estimate the optical band gap in many oxide and chalcogenide glasses [4, 5]. It has also recently been successfully applied to thin amorphous oxide films [6, 7].

The absorption edge may also be represented in many amorphous semiconductors, particularly at the lower values of absorption, by an equation of the form

$$\alpha(\omega) = \text{const} \times \exp\left(\frac{\hbar\omega}{E_1}\right) \qquad (2)$$

where E_1 is broadly interpreted as a measure of the width of the tails of localized states in the band gap. Equation 2 was first proposed by Urbach [8] to describe the edge in alkali halides. The necessity for new materials for example in anti-reflection coatings and other technological applications has been appreciated in recent years.

TABLE I: Values of E_{opt}, E_1 of Ge–SiO samples of three thicknesses

Thickness (l) (nm)	Number	Ge–SiO samples (% SiO)	E_{opt} (eV)	E_1 (eV)
170	1.	37	0.600	0.850
	2.	41	0.675	0.750
	3.	100 (rapid evaporation)	2.250	0.530
420	4.	60	0.150	1.600
	5.	88	2.150	0.495
	6.	100 (slow evaporation)	2.720	0.285
600	7.	80	1.350	0.533
	8.	96	2.250	0.400
	9.	100 (slow evaporation)	2.700	0.218

Note: The values of constants obtained, particularly when the content of Ge is substantial are seen to be very sensitive to the preparation conditions. The values of E_{opt} for the slowly evaporated SiO_x films are more nearly typical of a sample containing SiO_2 whereas the rapidly evaporated sample gives a standard value for SiO.

One way of obtaining these materials is to use different mixing ratios [9, 10] of two low- and high- index materials in composite thin films. In this note we have studied the optical constants and have estimated values of the optical energy gap from the optical absorption spectra for thin amorphous Ge–SiO films as functions of composition. The analysis of the so-called Urbach rule for these edges is also presented along with the infrared absorption spectra.

One purpose of the present investigation is to seek for differences of electrical and optical properties in particular between thin dielectric films made by the co-evaporation of SiO and GeO_2 [11] and by the co-evaporation of SiO and Ge. It may be expected that provided similar overall compositions are finally attained that the measured properties should be similar but the different starting materials may suggest that the local amorphous bonding could be different in the two cases and consequently lead to different observed properties.

2. Experimental work

The co-evaporation technique described by Hogarth and Wright [12] was used to produce thin evaporated layers of Ge, SiO and Ge–SiO. Clean Corning 7059 glass was used as a substrate and held at pressure of the order of 10^{-6} torr in a Balzers BA510 coating unit. Molybdenum and tantalum boats were used for the evaporation of Ge and SiO respectively. The substrate temperature during evaporation was 373 K. The film thickness was initially adjusted by the use of quartz crystal monitors and finally measured by multiple-beam interferometry using Fizeau fringes of equal thickness. Absorption measurements in the wavelength range 190 to 850 nm were carried out using a Perkin–Elmer spectrophotometer Model 402 with a slit width of 250 nm and at a fast speed scan. KBr discs of 2 cm diameter were prepared by hot pressing and thin films of Ge–SiO were then deposited on the discs. The infrared absorption spectrum was measured using a Perkin–Elmer 577 grating infrared double-beam spectrometer. The transmission spectra in the near infrared (between 0.85 and 2.5 μm) were measured using a Beckman spectrophotometer M IV. All the absorption measurements were made at room temperature.

3. Results and discussion

The optical absorption spectra for different compositions of the Ge–SiO system are presented in Figs. 1, 2 and 3 corresponding to three sample thicknesses, l, of 170, 420 and 600 nm, respectively. The absorbance (A) is related to the absorption coefficient $\alpha(\omega)$ as $0.434\,\alpha l$. These data are plotted as $(\alpha\hbar\omega)^{1/2}$ against $\hbar\omega$ in Figs. 4, 5 and 6, respectively. The extrapolations of the linear regions of the optical absorption edges in these figures leads to values of E_{opt} which are listed in Table I.

As the Ge percentage increases in the SiO–Ge system, the disorder increases, the band tailing starts to occur at higher energies in the density-of-states diagram, and the value of E_{opt} reduces accordingly. The summarized data taken from Figs. 4 to 6 are shown as one general curve in Fig. 7. The data in Figs. 1 to 3 are replotted in Figs. 8 to 10 to show the Urbach edge and the corresponding values of E_1 are calculated and also listed in Table I. The values of the constant B in Equation 1 are of the order of 10^5 eV^{-1} cm^{-1} in good agreement with the theoretical value [4].

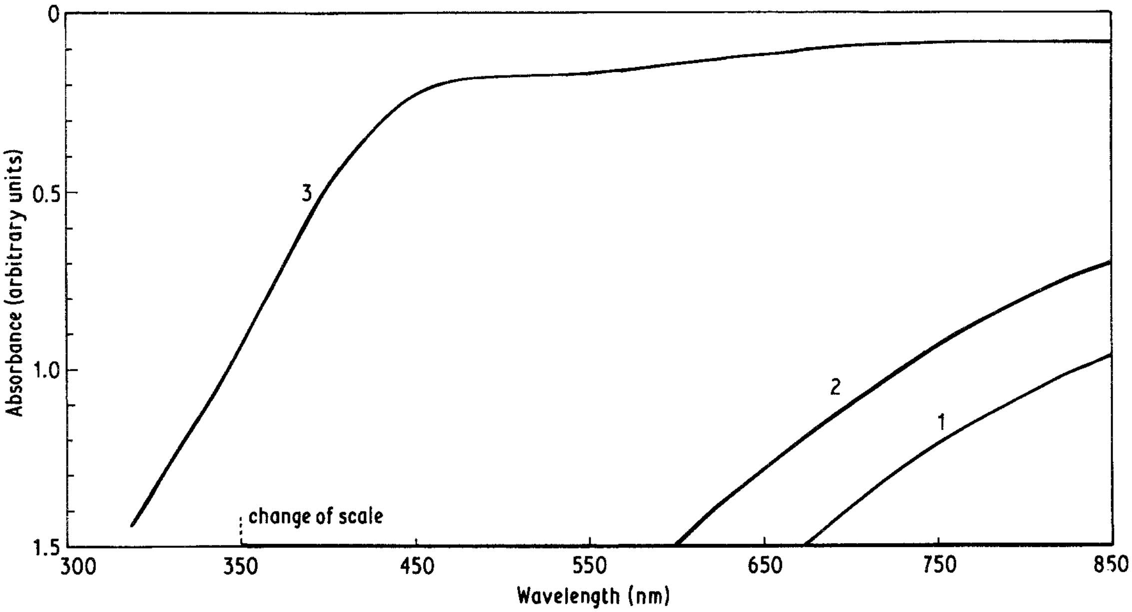

Figure 1 Optical absorption spectra of Ge/SiO thin films of thickness 170 nm (compositions as in Table I).

The refractive index n_f has been estimated from the condition of the maxima of interference fringes and for normal incidence

$$2n_f l = m\lambda \tag{3}$$

where m is the order of the fringe. Fig. 11 shows the variation of n_f with λ for some SiO–Ge samples. In many dielectrics, the refractive index decreases with the decrease in the layer thickness. The dependence [13, 14] on the wavelength of the refractive index of thin SiO–Ge films seems to vary with both thickness and mixing ratio. In the absence of ellipsometric or other reliable measurements on this system, a close comparison cannot be drawn.

The infrared spectra of SiO and mixed layers of Ge with SiO are shown in Fig. 12. The main features of these spectra are as follows:

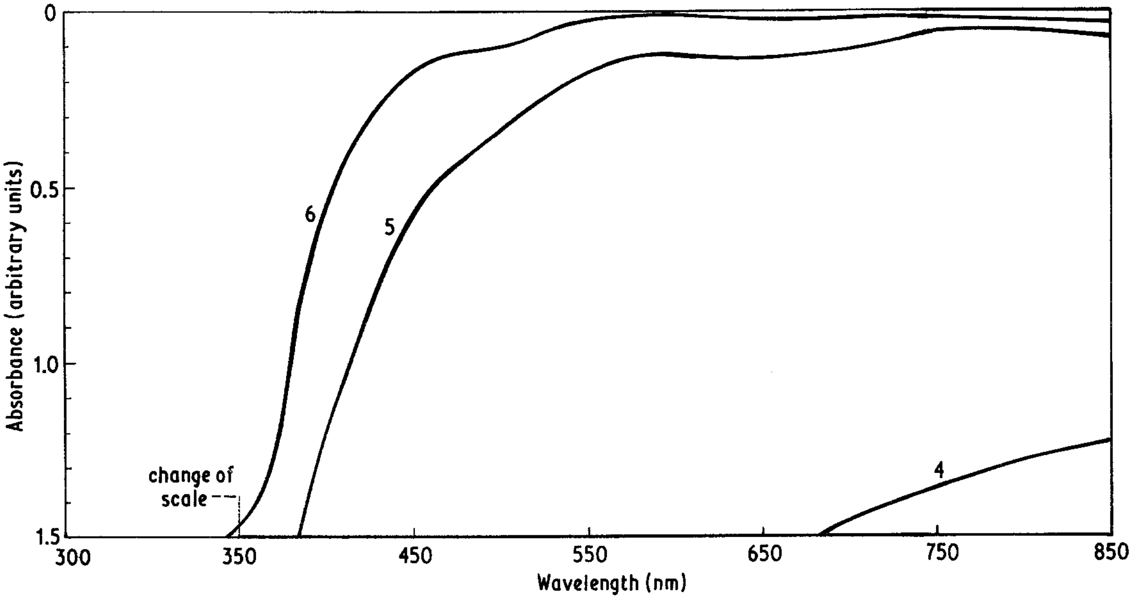

Figure 2 Optical absorption spectra of Ge/SiO thin films of thickness 420 nm (compositions as in Table I).

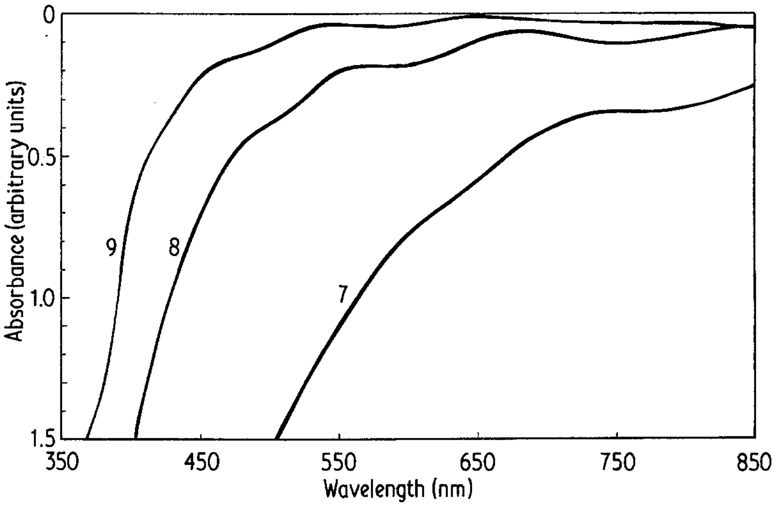

Figure 3 Optical absorption spectra of Ge–SiO thin films of thickness 600 nm (compositions as in Table I).

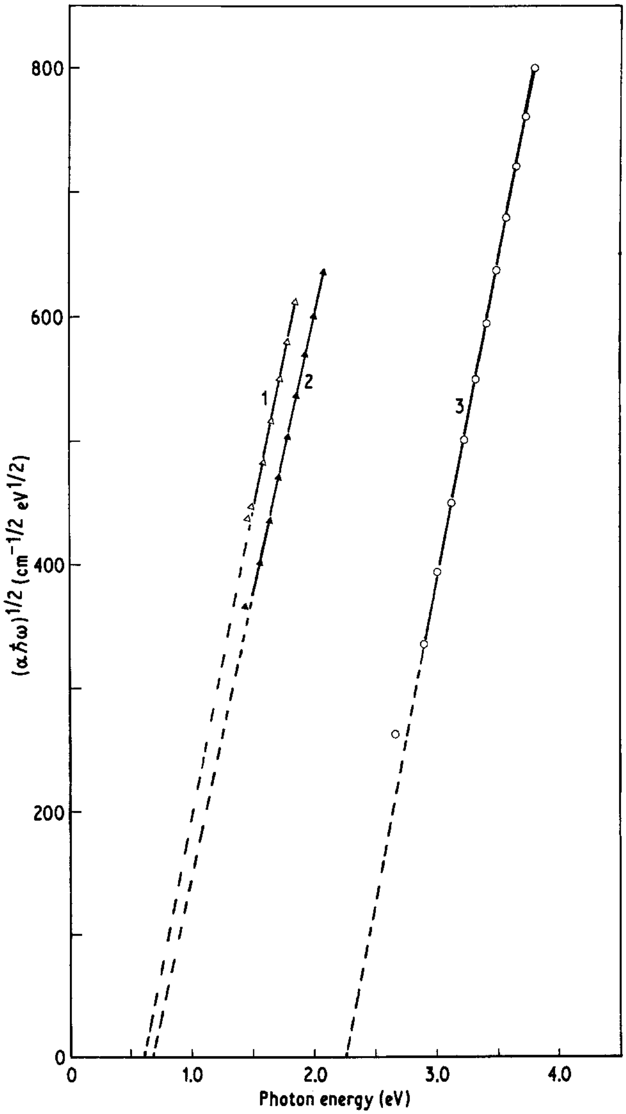

Figure 4 Data of Figure 1 replotted in terms of theory for non-direct transitions.

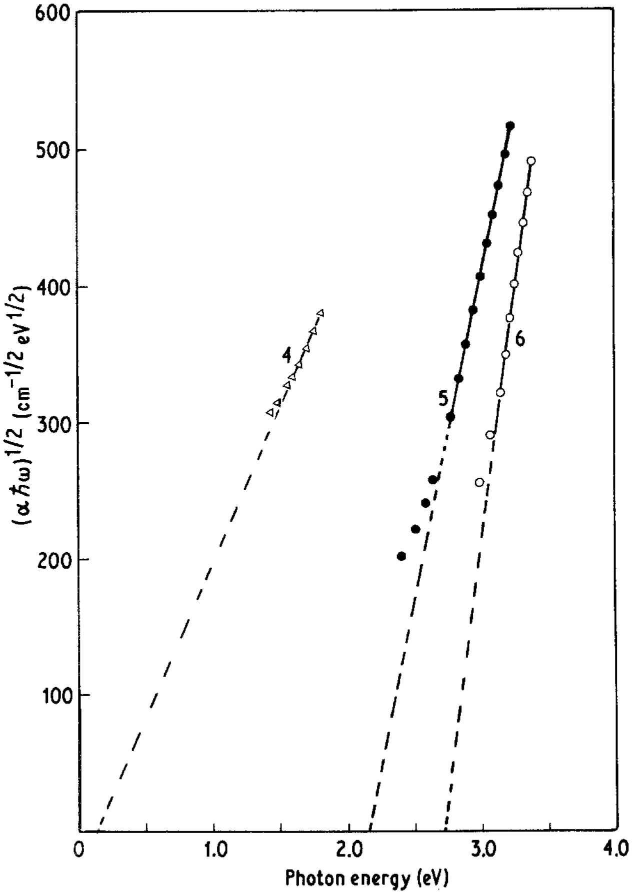

Figure 5 Data of Fig. 2 replotted in terms of the theory for non-direct transitions.

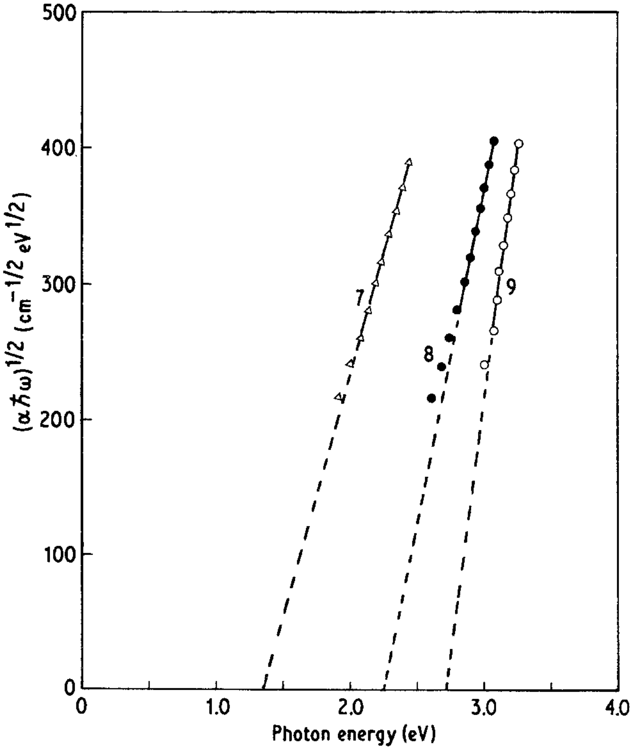

Figure 6 Data of Fig. 3 re-plotted in terms of theory for non-direct transitions.

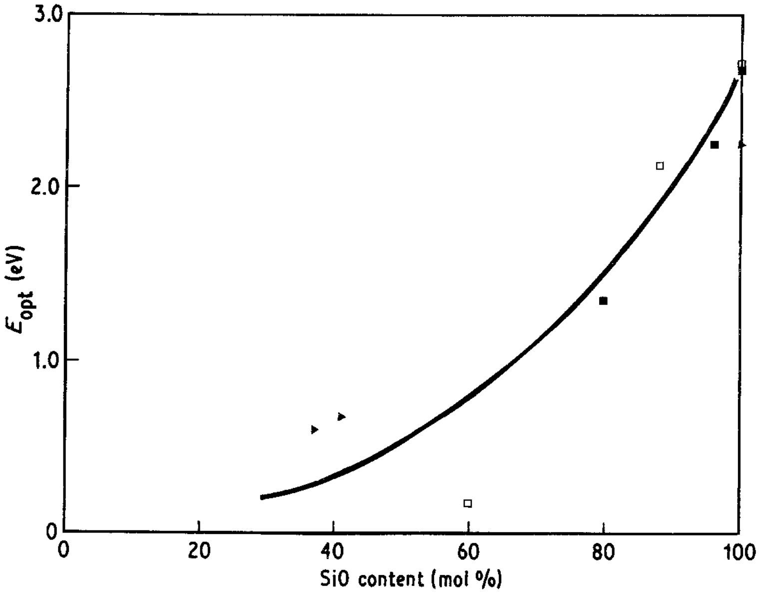

Figure 7 Summarized results for E_{opt} as a function of SiO content. (Data taken from Figs. 4, 5 and 6; ▼ 170 nm, □ 420 nm, ■ 600 nm.)

(a) The main absorption band at ~ 1000 cm^{-1} is characteristic of a true SiO film (Spectrum 3 in Fig. 12).

(b) The absorption peak intensity of the mixed layers (Spectra 1 and 2 in Fig. 12) increases as the thickness of the samples increases and moves slightly to a higher frequency region.

(c) The appearance of a moderate peak (shoulder) at ~ 870 cm^{-1} indicates that a chemical interaction between the two materials has occurred, and the evaporated film cannot be treated as a simple physical mixture. This is similar to the case of evaporated SiO–V_2O_5 complex oxide films [15].

Investigations of the ageing process in thin films are of interest because of their applications in opto-electronic systems [16]. Films aged at room temperature are often known to show different characteristics from those of freshly evaporated films [17, 18]. In this note we have measured the optical absorption in films aged over a three-month

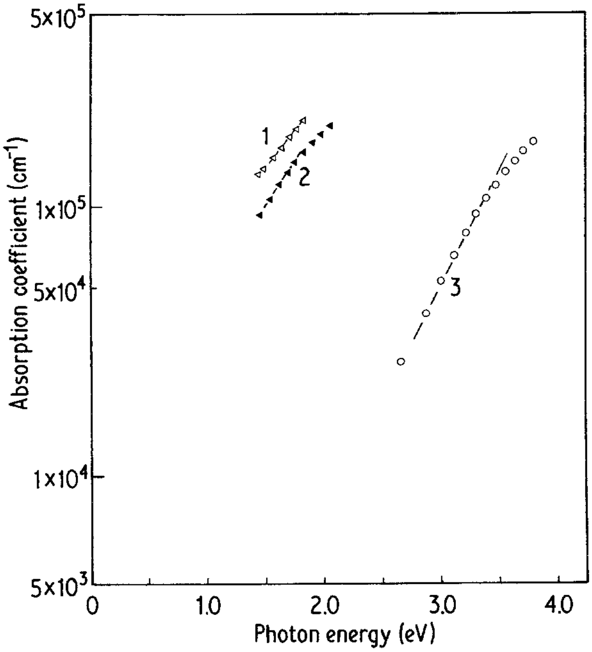

Figure 8 Data of Fig. 1 plotted in accordance with the Urbach law.

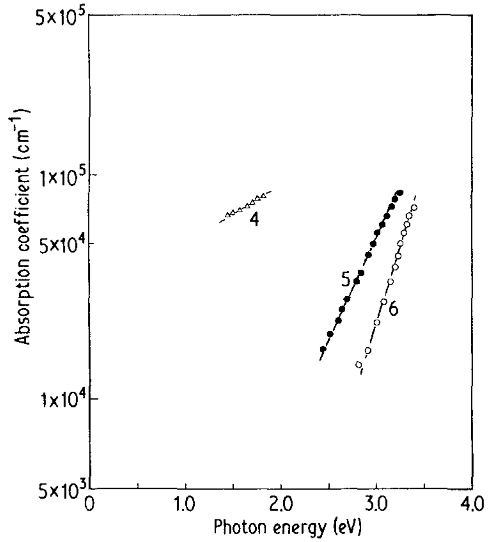

Figure 9 Data of Fig. 2 plotted in accordance with the Urbach law.

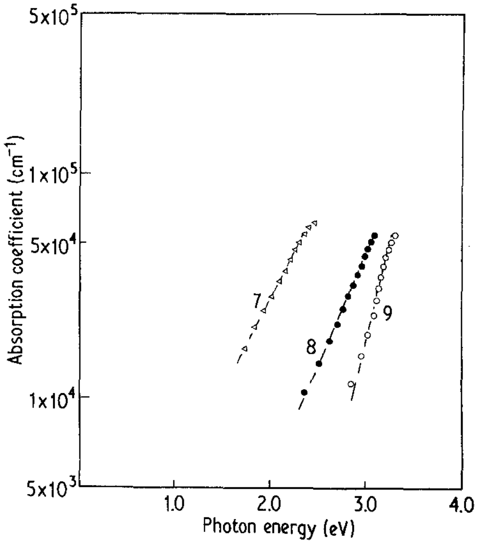

Figure 10 Data of Fig. 3 plotted in accordance with the Urbach law.

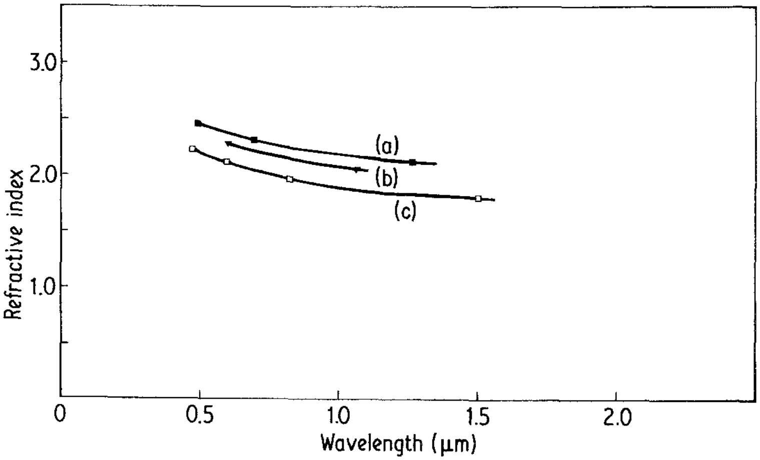

Figure 11 Variation of refractive index with wavelength for three Ge–SiO thin films. (a) 300 nm thick, 77 mol% SiO; (b) 260 nm, 91 mol% SiO, (c) 420 nm, 88 mol% SiO.

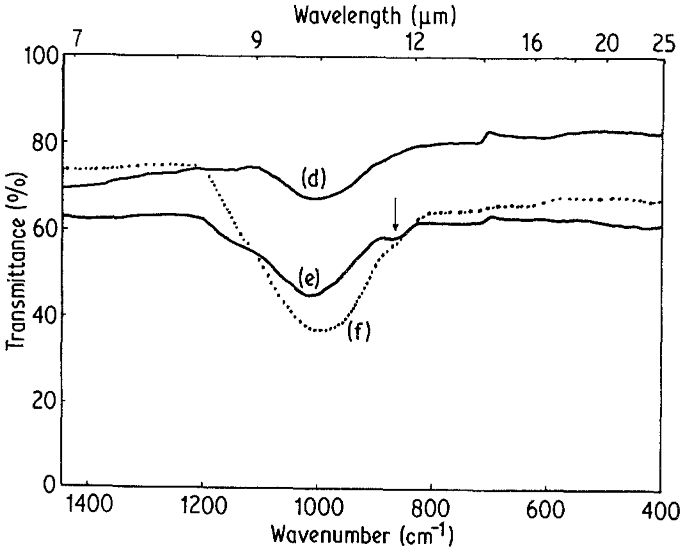

Figure 12 Absorption spectra of three SiO–Ge thin films. (d) 170 nm thick, 37 mol% SiO; (e) 290 nm, 74 mol% SiO; (f) 740 nm, 100 mol% SiO. The shoulder in curve (e) is associated with bonds in the mixed film.

period and surprisingly they showed nearly the same basic optical properties as those of fresh films. This demonstrates the durability of these compound films based on SiO.

4. Conclusion

In this note we have demonstrated that mixed and amorphous thin oxide films of Ge with SiO made by a co-evaporation process can be achieved with a structure and physical properties similar to those in glasses. The optical constants of these films have been measured and estimated. Their optical absorption edges have also been confirmed and different values of E_{opt} are reported for the different compositions. A simple study of the infrared absorption of a typical sample on these films has been presented. Finally the mixed systems of other oxides in amorphous form can also be obtained and the properties of such new materials we believe will be of both theoretical and technological interest.

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