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The effect of composition and substrate temperature on the optical energy gap of SiO_x/SnO amorphous thin films

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The fundamental absorption edge of co-evaporated SiO_x/SnO thin films of various compositions has been investigated. The results have been analysed by assuming optical absorption by non-direct electronic transitions. The optical energy gap is seen to decrease with increase in the molar content of SnO which increases the level of disorder of the complex system. The effect of substrate temperature during deposition on the optical absorption is also studied. The optical energy gap increases with the substrate temperature. This is attributed to the annealing of some of the dangling bonds and hence to an increase in the order of the system. The Urbach tail is related to the broadening of the absorption edge as a result of charged defects present in the films and related to the Franz–Keldysh effect.

1. Introduction

Electrons in solids can be excited by the process of absorption of light of suitable energy and these excited electrons in turn may interact with the lattice vibrations. Such electron–lattice interactions have proved to be one of the most important problems of spectroscopy. Measurements of the absorption edge and its shape provide valuable information in this regard. Materials having similar chemical composition may differ in their optical absorption so far as their structure is concerned. It is observed that non-metallic crystalline materials have much steeper absorption edges compared to those of amorphous materials of the same chemical compositions. For the evaluation of optical energy gap of any material of interest, the relationship between absorption coefficient and the energy of an incident photon needs to be fitted to a theoretical expression. Generally, there are two such theoretical explanations put forward so far, one by Urbach [1] and the other by Tauc *et al.* [2] and discussed in more detail by Davis and Mott [3].

While studying the absorption edge in silver bromide, Urbach [1] discovered that the absorption coefficient depends exponentially on the energy of incident photons following a relationship of the form

$$\alpha(\omega) = \alpha_0 \exp - \delta[(\hbar\omega_0 - \hbar\omega)/kT] \qquad (1)$$

where $\alpha(\omega)$ is the absorption coefficient, $\hbar\omega$ is photon energy, $\hbar\omega_0$ and α_0 are constants, T is the absolute temperature and k is Boltzmann's constant. The quantity kT/δ is related to the steepness of the absorption curve and is interpreted as the width of tails of localized states in the band gap (also known as the Urbach energy) [1–4].

Lubchenko and Dudkin [5] tested the validity of the Urbach rule while considering the absorption edge in potassium iodide. Tauc *et al.* [2] proposed that the position and shape of the absorption edge in the high absorption region could be represented by an equation of the type

$$\alpha(\omega) = B(\hbar\omega - E_{\text{opt}})^2/\hbar\omega \qquad (2)$$

where B is a constant and E_{opt} is the optical gap of the material. The quantity $\alpha(\omega)$ in this case is considered to be the absorption coefficient for non-direct transitions. Davis and Mott [3] generalized the validity of the Tauc rule and suggested that for absorption coefficient $\alpha(\omega) < 10^4\,\text{cm}^{-1}$, there is usually an Urbach tail and for further high absorption where $\alpha(\omega) > 10^4\,\text{cm}^{-1}$, the absorption edge is of the form

$$\alpha(\omega) = B[(\hbar\omega - E_{\text{opt}})]^n/\hbar\omega \qquad (3)$$

where the quantities in the above equation have their usual meanings. The index n can take the values 1, 2, 3, 1/2, 3/2 indicating the type of electron transition in k-space. For $n = 2$ the Davis and Mott formula takes the form as proposed by Tauc *et al.* [2]. Mott and Davis [6] have examined various conditions of absorption by direct and indirect transitions in k-space. Under the assumption of k not being a good quantum number for amorphous semiconductors, they estimated the absorption coefficient for indirect transitions from localized states in the valence band to the extended states in the conduction band to be given by Equation 2. Moridi and Hogarth [7] applied the Tauc equation to evaluate the optical gap in copper–calcium–phosphate glasses. The Tauc rule is also observed in many amorphous non-metallic materials [6]. Particularly at the higher values of absorption, the absorption edge is suggested as being due to non-direct transitions with fairly constant matrix elements and a relaxed k-conservation rule. From the density-of-states model, the gap states near the band edges are increased as the

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degree of disorder in the amorphous structure is increased. The value of optical energy gap in such materials is important as part of the evaluation of their band structure.

Some researchers [8–13] have studied optical properties of various co-evaporated thin films and have noticed a decrease in the optical gap of SiO with the addition of TiO, BaO, GeO and Ge, and argued that the change in the optical gap was due to an increase in disorder of the complex system with the addition of the above materials to SiO. It is known that during the evaporation of dielectric thin films, some dangling bonds are created and these act as structural defects which are responsible for localized states in the forbidden gap. The annealing of films has the effect of reducing the number of unpaired electrons on the dangling bonds. Al-Ani and Hogarth [9] and Arshak and Hogarth [13] have reported an increase in the optical gap as the films were annealed.

It is assumed that in mixed dielectric films of composition AO/BO as long as they remain amorphous the randomly distributed contents of A, B and O will determine the properties of the films. Hogarth and Wright [14] found differences when mixed thin films were prepared from a given oxide with SiO or SiO_2. Islam and Hogarth [15] reported a decrease in the optical energy gap with the increase in the content of SnO_2 in SiO/SnO_2 mixed oxide films. It is thus of interest to verify how the starting material in a given system such as SiO/SnO or SiO/SnO_2 may effect the properties of composite layers. We have investigated the optical absorption of SiO_x/SnO complex amorphous thin films as the molar contents of SnO in the mixed oxide system are varied. The effects of substrate temperature on the optical gap for a given composition and thickness of SiO_x/SnO thin film system are also studied.

2. Experimental details

Thin film complexes of SiO_x/SnO were deposited from analytical reagent grade materials on to pre-cleaned 7059 Corning glass substrates held at an elevated temperature of about 373 K in a Speedivac Coating Unit model 19A/122 at a pressure of the order of 10^{-6} torr. The co-evaporation technique used here has already been established and described by Hogarth and Wright [14]. Silicon monoxide and tin monoxide were evaporated from tantalum and tungsten boats, respectively. The evaporation parameters such as composition and thickness of the complex assembly were monitored by means of a quartz crystal monitoring system which was calibrated for each material. The total thickness of co-evaporated oxide thin films was measured by multiple beam interferometry making use of Fizeau fringes of equal thickness. In order to see the effect of substrate temperature on the optical absorption edge of a given composition and thickness, the substrate temperature was varied from 292 to 563 K in steps during the evaporation cycles.

The measurements of fundamental absorption edges of different samples were made using a Perkin-Elmer Lambda 9 Spectrophotometer. The instrument was equipped with two beams, one used as source beam and the other as reference beam. This enabled us to obtain the absorption spectrum of co-evaporated oxide thin films by cancelling the effect of the glass substrate on placing another uncoated Corning 7059 glass substrate across the reference beam. The ultraviolet range of wavelength from 250 to 900 nm was covered. The structure of the SiO_x/SnO thin films was studied with the help of a JEM7 electron microscope with a magnification of × 38 000. The films are amorphous as shown in Fig. 1.

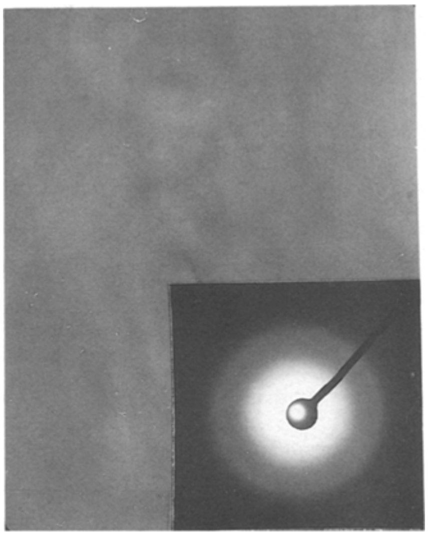

Figure 1 Electron micrograph and diffraction pattern of an 80% SiO_x/20% SnO (300 nm) thin film.

3. Results

The transmission spectra of complex oxide SiO_x/SnO thin films with different compositions and constant thickness (≈ 300 nm) can be seen in Fig. 2. The absorption edge is less sharp than that for crystalline materials. It is well defined and typical of many amorphous thin films of various materials. The absorption coefficient $\alpha(\omega)$ has been calculated from the relation

$$\alpha(\omega) = 2.303\, A/d \tag{4}$$

where $A = \ln (I_o/I_t)$ is the absorbance where I_o and I_t are the intensities of incident and transmitted light, respectively, and d is the thickness of the dielectric film. For the evaluation of optical energy gap corresponding to different compositions of the complex oxide system, the data of Fig. 2 have been plotted according to the Tauc rule as shown in Fig. 3. The straight parts of these lines which correspond to the higher values of $\alpha(\omega)$ are extrapolated to $(\alpha\hbar\omega)^{1/2} = 0$, to determine the value of E_{opt} according to Equation 2. It is observed that the optical energy gap decreases as the molar contents of SnO in SiO are increased. The

TABLE I The dependence of E_{opt} and E_e on the compositions of SiO_x/SnO (300 nm) co-evaporated thin films

SiO_x/SnO composition	E_{opt} (eV)	E_e (eV)
100% SiO_x	2.20	0.91
95% SiO_x	2.15	0.78
90% SiO_x	1.84	0.54
80% SiO_x	1.72	0.50
100% SnO	1.60	0.41

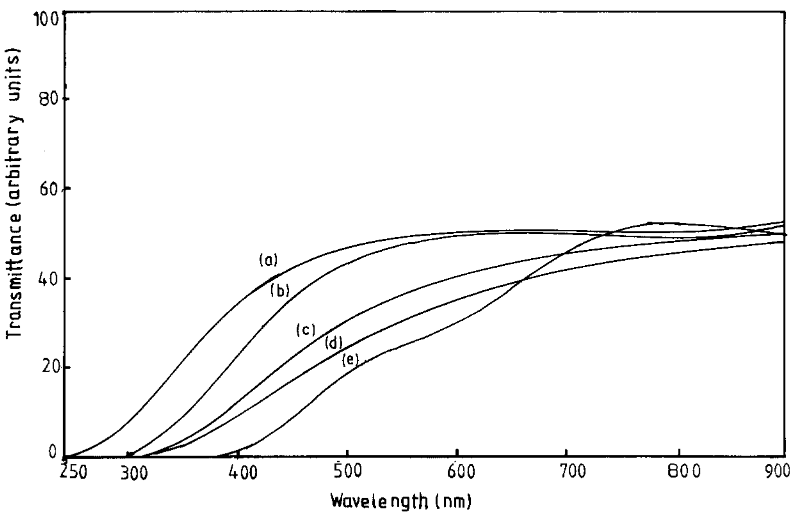

Figure 2 Transmission spectra of SiO_x/SnO (300 nm) thin films of different compositions. (a) 100% SiO_x, (b) 95% SiO_x, (c) 90% SiO_x, (d) 80% SiO_x, (e) 100% SnO.

values of E_{opt} corresponding to different compositions are shown in Table I. Although $\alpha(\omega)$ in our samples is greater than 10^4 cm^{-1}, the validity of some sort of the Urbach law (Equation 1) is observed in the lower absorption region of spectra as shown in Fig. 4. The values of energies related to the Urbach law for various SiO_x/SnO samples are also shown in Table I. As can be seen, these values increase as the molar percentage of SnO is increased.

The effect of substrate temperature on the absorption edge for a given composition and thickness of SiO_x/SnO films is shown graphically in Fig. 5. The data of Fig. 5 drawn by using Equation 2 are represented in Fig. 6. The value of optical energy gap is observed to increase with increase in the substrate temperature during the deposition. Table II shows the different values of optical energy gaps of SiO_x/SnO thin films for different substrate temperatures. In order to gain an insight into the band edges, the data of Fig. 4 have also been plotted following the Urbach law as given in Fig. 7. The widths of the band tails in the forbidden gap decrease to a small extent and the corresponding energies are listed in Table II. Fig. 8 shows the variation of E_{opt} with thickness for 90% SiO/SnO_2 (after Islam and Hogarth [15]) for the comparison of our results.

4. Discussion

The features of optical data corresponding to the higher absorption region can be explained by considering the phonon-assisted transitions associated with the states close to the mobility edge, probably the transitions between the localized states at the top of the valence band to the extended states above the mobility edge in the conduction band. The decrease in the optical gap with the increase of SnO content can be attributed to the increase in the degree of disorder of the SiO_x/SnO system as observed by other authors [7–13]. Evaporated SiO_x thin films are observed to contain a large number of dangling bonds and other structural defects such as E_1' centres which are the O^- vacancies and are, therefore, charged [16–18, 22–23]. The presence of charged defects like E_1' centres and dangling bonds have already been observed by us elsewhere while studying the paramagnetic centres in composite SiO_x/SnO thin films. The exponential part

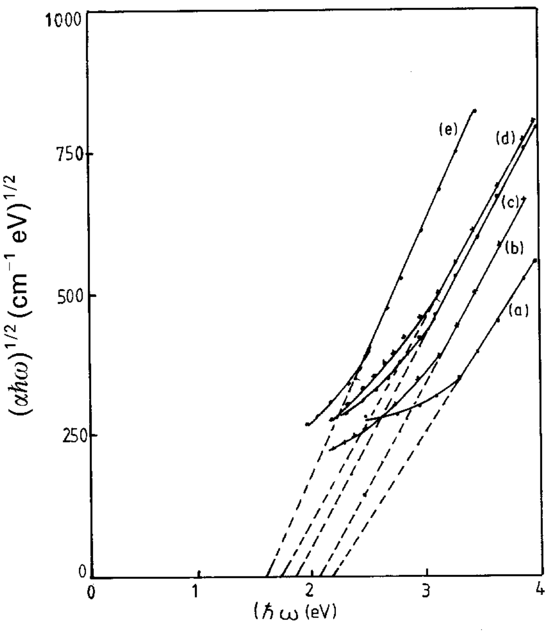

Figure 3 Data of Fig. 2 replotted for indirect transitions.

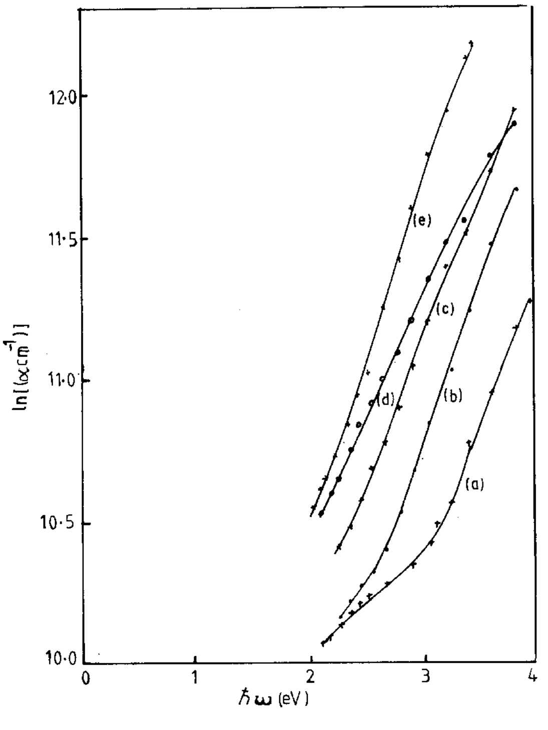

Figure 4 Data of Fig. 2 replotted according to the Urbach law.

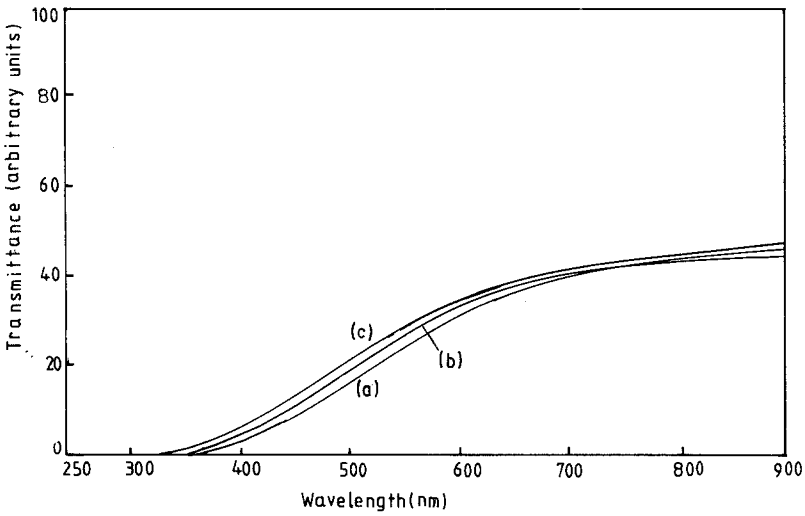

Figure 5 Optical transmission spectra of 70% SiO_x/30% SnO (300 nm) thin films deposited at different substrate temperatures, (a) 292 K, (b) 423 K, (c) 563 K.

of the edge corresponding to the lower absorption region can be considered as the broadening of the high absorption edge because of the interference of the local electric field of charged defects, due to the Franz–Keldysh effect. Similar behaviour has been observed by some other authors [19, 20]. As the contents of SnO are increased, the density of such charged defects is changed and thus affects the broadening of the absorption edge.

White and Weizenkamp [21] studied the effect of substrate temperature on vacuum-deposited thin films of silicon monoxide. They noticed that the effect of high temperature was equivalent to the annealing of films during deposition followed by slow cooling after deposition. It has been observed that during the annealing process, thin films do undergo some atomic re-arrangements, so defects would be removed and by reducing the dangling bond density, would help to redistribute atomic distances and bond angles and thereby increase the optical band gap [10, 13]. A high substrate temperature during the evaporation process is equivalent to the annealing process followed by a cooling process. Therefore, the effect of substrate temperature in our case is to saturate some of the dangling bonds or other structural defects so that the degree of order is increased resulting in an increase in the optical gap. It is interesting to compare the optical energy gap (1.84 eV) related to 90% SiO_x/10% SnO (300 nm) thin film sample in our case with the value of the energy gap (2.01 eV, Fig. 8) as estimated by Islam and Hogarth [15] for a 90% SiO_x/10% SnO_2 (300 nm) thin film sample under similar conditions.

TABLE II The effect of substrate temperature during deposition on E_{opt} and E_e for (70% SiO_x/30% SnO) 300 nm thin films

Substrate temperature (K)	E_{opt} (eV)	E_e (eV)
393	1.69	0.40
423	1.75	0.33
563	1.82	0.30

The observed decrease in E_{opt} related to SnO

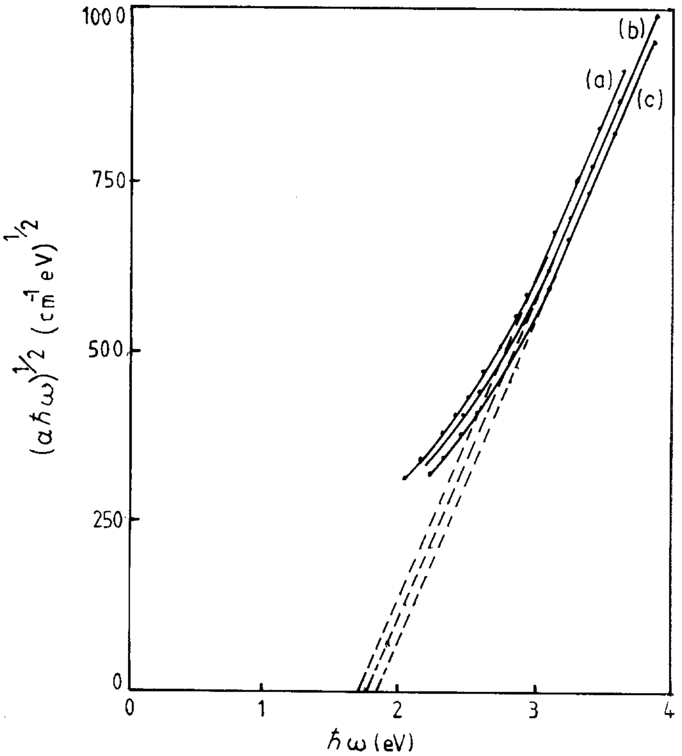

Figure 6 Data of Fig. 5 replotted according to indirect transitions.

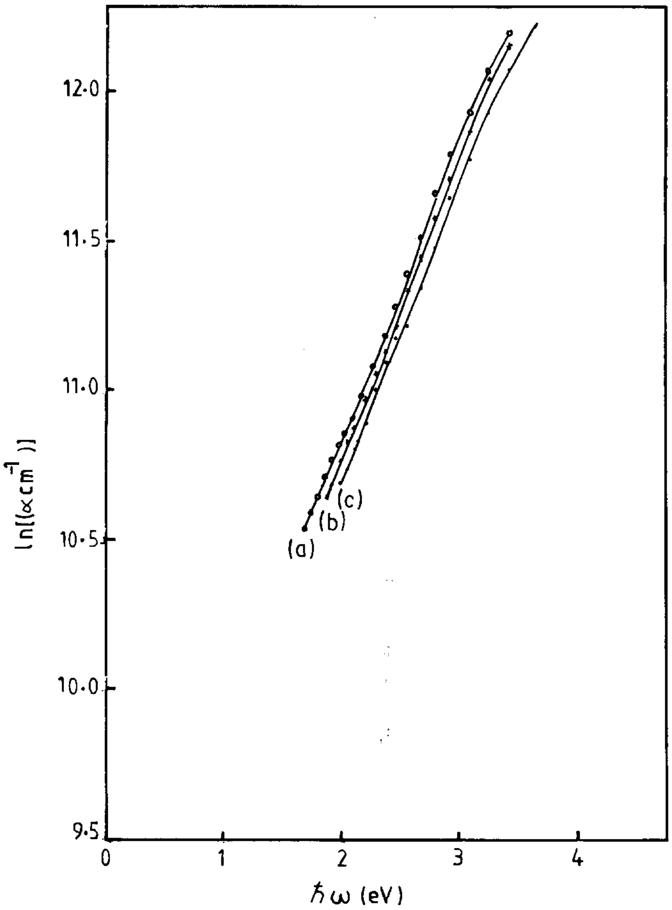

Figure 7 Data of Fig. 5 replotted according to the Urbach law.

content in the present case could be attributed to the fact that on replacing SnO_2 by SnO for the co-evaporation with SiO under similar conditions, the composite oxide (SiO_x/SnO) thin films will be deficient in oxygen content compared to co-evaporated oxide (SiO/SnO_2) thin films. This deficiency in oxygen content will create more disorder in the system and as a result the optical energy gap will decrease if SnO_2 is replaced by SnO in the composite oxide (SiO_x/SnO_x) thin films.

4. Conclusion

The addition of SnO to SiO in complex SiO_x/SnO thin film samples is to increase the level of disorder, so that the optical energy gap of the system is decreased. The effect of high substrate temperature is broadly equivalent to the annealing effect on films deposited on a substrate at a lower temperature. The Urbach tail is attributed to the broadening of the optical absorption edge according to the Franz–Keldysh effect.

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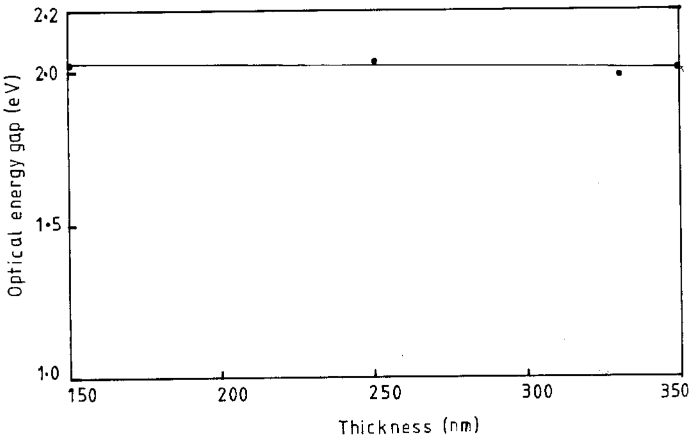

Figure 8 Variation of E_{opt} with the thickness of 90% SiO:10% SnO_2 thin films (after Islam and Hogarth [15]).

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