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Effect of cerium oxide addition on the optical absorption edge of tungsten trioxide

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Thin films of WO_3/CeO_2 deposited by vacuum co-evaporation (10^{-6} torr) on to Corning 7059 glass slides at room temperature have been shown to be amorphous in structure. The optical absorption spectra of amorphous WO_3/CeO_2 thin films have been measured at room temperature. The optical absorption edge of WO_3/CeO_2 and WO_3 thin films above 10^5 cm^{-1} follows the Davis and Mott equation for the non-direct optical transitions. The optical absorption coefficient, α, below this obeys the Urbach exponential relation. The value of the optical band gap of amorphous WO_3 thin films is in good agreement with that found by Deb. The shift of the optical gap to lower energies and that of the Urbach energies to higher energies as the content of CeO_2 is increased, indicate that both parameters are strongly dependent on the concentration of Ce^{4+} present in the structure. Thus, the increase of Ce^{4+} is thought to lead to strong potential fluctuations which cause an increase in the density of localized states in the gap.

1. Introduction

Tungsten trioxide, WO_3 which is the base material in the present work, is one of the transition metal oxides which has attracted the interest of many workers over the years because of its semiconducting and ferroelectric behaviour [1]. Sienko [2] has shown that WO_3 forms tungsten bronzes when metal ions are incorporated in its lattice. Mansingh *et al.* [3] have studied the electrical properties of WO_3, while Deb [4] has reported some details of the optical properties of amorphous WO_3 thin films. The optical absorption coefficient calculated by Deb is higher than 10^3 cm^{-1}. His results show that in the range 10^3–10^5 cm^{-1} the optical absorption coefficient follows an exponential form. Our measurements on optical absorption edges of most amorphous WO_3 thin films in the same range show a similar behaviour.

The optical absorption edge of cerium oxide, CeO_2, and the mixed oxide films of CeO_2 and SiO has been investigated by Hogarth and Al-Dhhan [5]. The shape of the absorption edge of amorphous CeO_2 thin films found by these authors is fairly abrupt, much more like that of crystalline materials. They also found that the optical absorption edge of mixed films of SiO/CeO_2 is dominated by the presence of the rare-earth Ce^{4+} ions. Furthermore, they suggested that the fundamental optical transition in glassy materials containing lanthanide ions would be dominated by the presence of the rare-earth ions. It was therefore of interest to see whether this dominance is restricted only to glassy materials or it may be extended to other classes of materials such as transition metal oxides.

2. Experimental procedure

Simple WO_3 films and mixed oxide films of WO_3 and CeO_2 of thicknesses in the range 104–294 nm were prepared by the co-evaporation technique of Hogarth and Wright [6] in a vacuum of about 10^{-6} torr (1 torr = 133.322 Pa). The films for optical measurements were deposited on clean Corning glass 7059 substrates, whereas the film for electron microscope study was deposited on carbon-coated mica. The substrates were held at room temperature. The optical transmittance measurements were made using a Perkin-Elmer Model Lambda 3 double-beam spectrophotometer. The effects of the substrate on the optical characteristics were minimized by placing another cleaned uncoated substrate in the path of the reference beam. The thickness of the film for the electron microscope study was about 10 nm.

3. Results and discussion

Figs 1 and 2 show that the electron diffraction patterns of WO_3/CeO_2 thin films prepared by co-evaporation are amorphous in structure at room temperature and after annealing. This would suggest that the internal structure is thermally stable. However, the electron micrograph after annealing shown in Fig. 2 indicates clearly that the surface is affected by the increase of temperature. This could be due to the high concentration of metal ions in the structure, that is, their valence requirement is easily satisfied as the temperature is raised, leading to the formation of groups of metal ions as well as their migration to the surface as is shown in Fig. 2.

The optical transmission of amorphous WO_3/CeO_2 thin films of various compositions and for different thicknesses is illustrated in Fig. 3. It is observed that the fundamental absorption edge is sharp, very much like that of crystalline materials. It is also observed

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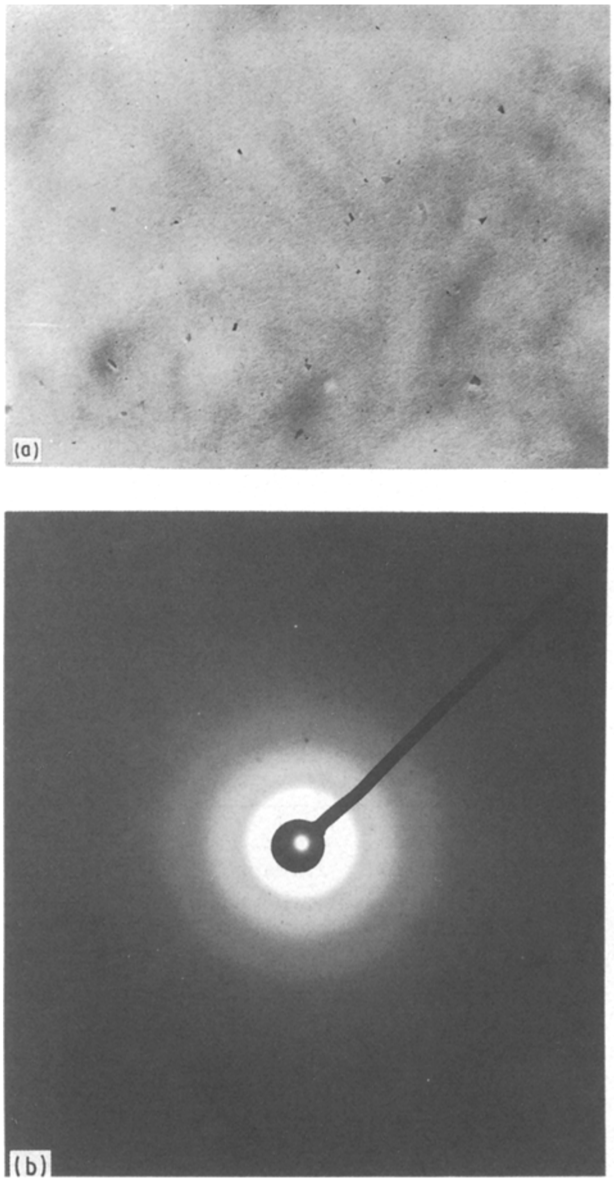

Figure 1 (a) Electron micrograph and (b) diffraction pattern of a WO_3/CeO_2 thin film at room temperature.

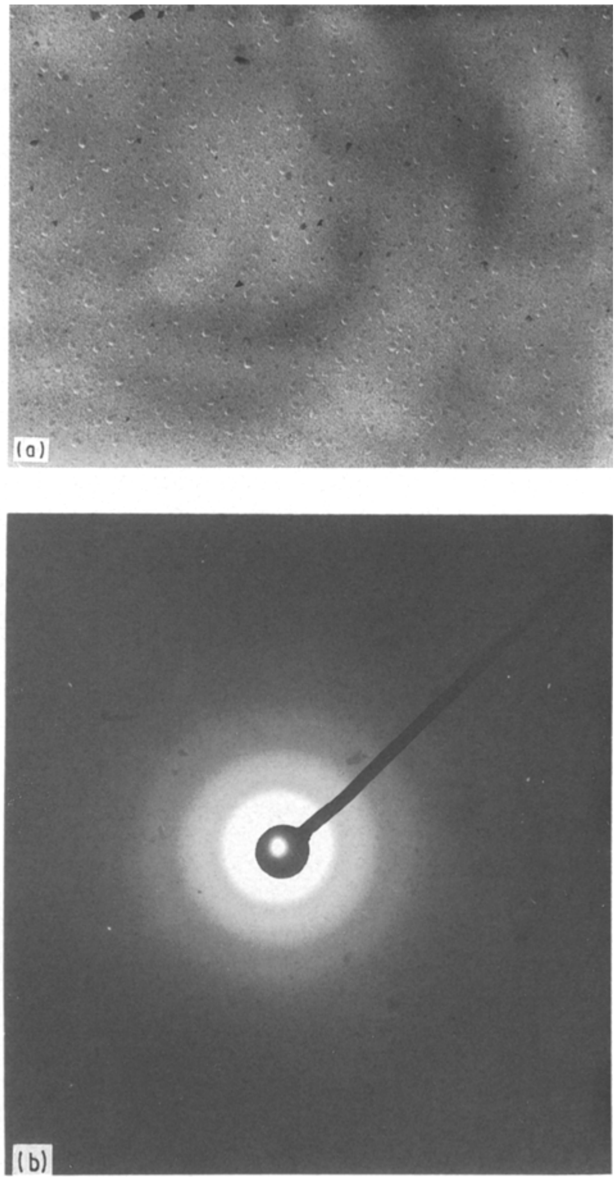

Figure 2 (a) Electron micrograph and (b) diffraction pattern of a WO_3/CeO_2 thin film after annealing.

that the position of the absorption edges moves towards longer wavelengths with the increase of CeO_2 content. As the content of cerium oxide is further increased the positions of the absorption edge return towards shorter wavelengths.

The absorption coefficients, $\alpha(\omega)$ for the films shown in Figs 4 and 5 have been calculated ignoring reflection and assuming the relation

$$\alpha(\omega) = (1/t)\ln(I_0/I) \qquad (1)$$

to be applied, where I is the intensity of the transmitted light through the film, I_0 is the intensity of the incident light, and t is the thickness of the film.

The observed structure in the absorption spectrum shows that the main absorption occurs when the absorption coefficient reaches a value around 10^5 cm^{-1}. In a band model for amorphous materials, this first absorption edge is interpreted as being due to non-direct transitions. This model is based on the assumption that there is little chance for electrons to be transferred from one localized state at the top of the valence band to another at the bottom of the conduction band. Therefore, Davis and Mott [7] neglected all transitions in which both the initial and final states are localized and derived Equation 2. If in amorphous WO_3/CeO_2 thin films we assume that transitions of electrons occur between localized and extended states as described by Davis and Mott, then the spectral dependence of the absorption coefficient will follow the square-law dependence given by them.

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

where E_{opt} is the optical energy gap, $\hbar\omega$ is the incident photon energy and B is a constant.

Fig. 4 shows the plots of $(\alpha\hbar\omega)^{1/2}$ as a function of photon energy. It is seen that the plots are linear for higher energies which is in a good agreement with Equation 2 indicating that the transitions involved are non-direct.

The values of E_{opt} and E_{t} for different compositions and thicknesses are recorded in Table I.

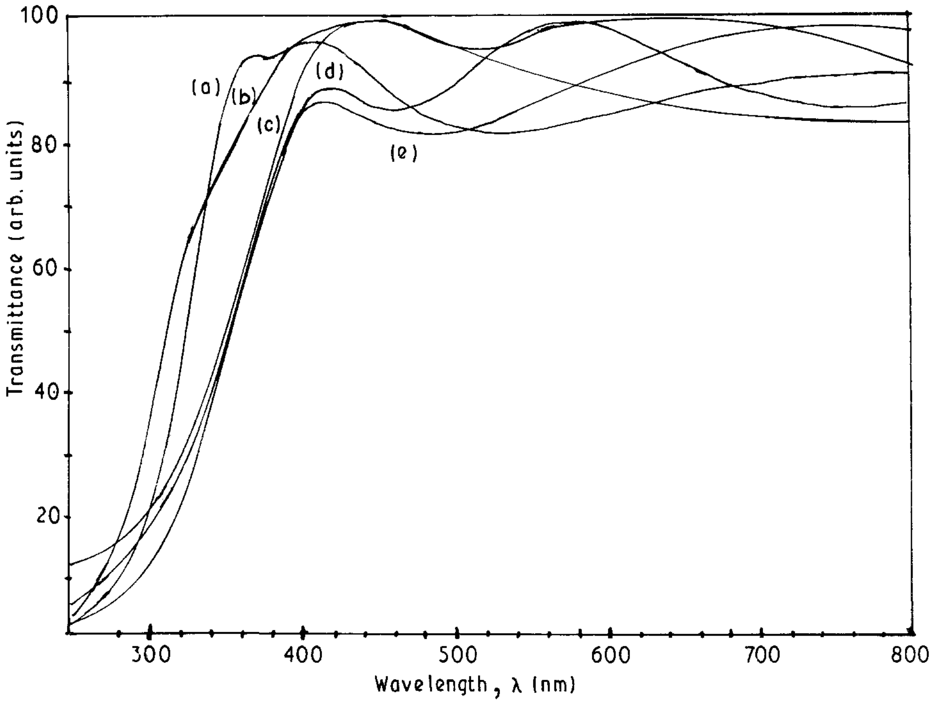

Figure 3 Optical transmittance as function of wavelength for different compositions of WO_3/CeO_2 thin films. (a) 100% WO_3 (294 nm thick), (b) 97% WO_3 (193 nm thick), (c) 48% WO_3 (104 nm thick), (d) 81% WO_3 (294 nm thick), (e) 81% WO_3 (176 nm thick).

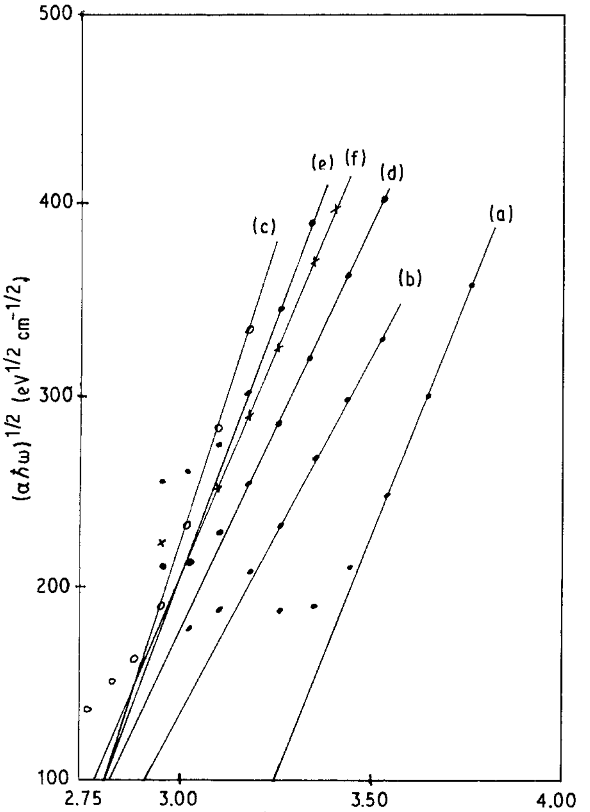

Figure 4 $(\alpha\hbar\omega)^{1/2}$ versus photon energy for different compositions of WO_3/CeO_2 thin films. (a) 100% WO_3 (294 nm thick), (b) 97% WO_3 (193 nm thick), (c) 48% WO_3 (108 nm thick), (d) 81% WO_3 (294 nm thick), (e) 81% WO_3 (176 nm thick), (f) 72% WO_3 (182 nm thick).

Fig. 5 shows the plot of logα versus $\hbar\omega$. The optical absorption edge where a linear region is observed is governed by a similar relation to that of Urbach [8]

$$\alpha(\omega) \propto \exp(\hbar\omega/E_t) \tag{3}$$

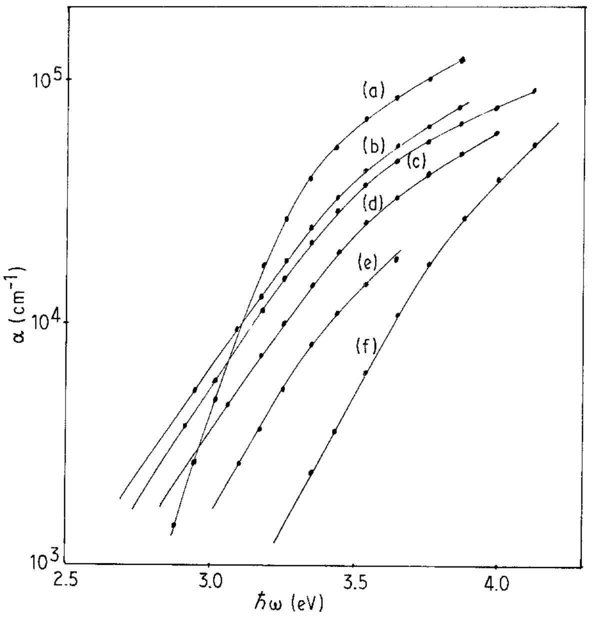

Figure 5 Log α versus photon energy for the same compositions of WO_3/CeO_2 thin films as in Fig. 4, but for t (nm): (a) 104, (b) 176, (c) 182, (d) 294, (e) 193, (f) 294.

where α is the absorption coefficient, $\hbar\omega$ is the incident photon energy and E_t is a constant calculated from Fig. 5 as follows

$$E_t = 1/[A \ln(10)] \tag{4}$$

where A is the slope of the curve shown in Fig. 5.

The values of E_t for different compositions and thicknesses at room temperature are presented in Table I, from which it is observed that the optical energy gap is independent of the thickness for the same compositions, but there is a systematic shift of E_{opt} towards lower energies and of E_t towards higher energies as the content of CeO_2 is increased. This is in

TABLE I Values of E_{opt} and E_t at room temperature for various compositions and thicknesses of WO_3/CeO_2 thin films

WO_3 content (mol %)	E_{opt}(eV)	E_t(eV)	t(nm)
100	3.25	0.20	294
97	2.91	0.20	193
81	2.81	0.26	294
81	2.81	0.26	176
72	2.78	0.24	182
48	2.81	0.10	104

a good agreement with the models of Cohen *et al.* [9] and of Davis and Mott [7] which suggest that the extent of the localized states near the mobility edge increases with increasing disorder in the amorphous structure. As the content of CeO_2 is further increased, E_{opt} and E_t tend to shift back to higher and lower energies, respectively. This effect is similar to a phenomenon associated with an impurity band in a crystalline semiconductor. The localized impurity states will overlap as the concentration of the impurity is increased. However, according to Mott [10] the effect of the impurities may be neglected in the amorphous state, but they contribute only to the disorder. Therefore by analogy, it may be assumed that CeO_2 contributes to the disorder and thereby creates localized states in the gap. As the content of CeO_2 is increased some of the localized states overlap and hence their effective density is reduced just as in the case of the impurity states. Thus the value of E_t decreases and E_{opt} returns to higher energies. This effect has been also observed in other mixed oxide thin films [11–13].

Another possible explanation is that the valence and conduction bands are assumed to be formed by the base material WO_3. The presence of CeO_2 (very low concentration as compared to WO_3), as well as other forms of defects such as impurities, voids and dangling bonds, introduce localized states in the gap. The density of the localized states increases with increasing CeO_2 content, hence the optical gap of WO_3 which is 3.25 eV (calculated in the present work) decreases to a minimum value. This value is smaller than that of the optical gap of CeO_2 which is 3.1 eV as measured by Hogarth and Al-Dhhan [5] but the optical gap returns to higher energies with further increase of CeO_2 until it reaches the value 3.1 eV corresponding to 100% CeO_2. The values of the constant B given by Equation 2 are of the order of $10^5\ \mathrm{cm}^{-1}\ \mathrm{eV}^{-1}$ which is in good agreement with the theoretical value [7].

Tauc [14] assumed that E_t could be the band tail of the localized states in the gap. However, the values of E_t are too high to be in good agreement with this assumption. Thus an alternative possibility is that the exponential tail could be due simply to a transition from band-to-band optical transitions to absorption levels in the gap. These levels could be excitons and in this case they are completely quenched and broadened due to the strength of the internal electric fields which are caused by the random distribution of Ce^{4+} in the structure [15]. This leads to an exponential form of the absorption edge below $10^5\ \mathrm{cm}^{-1}$ without an absorption peak.

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