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The optical absorption edge in amorphous thin films of MoO_3–In_2O_3

M. ANWAR, C. A. HOGARTH
Physics Department, Brunel University, Uxbridge, Middlesex, UK

A study of the effects of changes in composition, film thickness, substrate deposition temperature and annealing on the optical properties of MoO_3–In_2O_3 is presented. The results are found to be compatible with the reduction in the value of optical energy gap of these materials as the molar fraction of In_2O_3 in the MoO_3 thin film increases. This decrease of optical gap may be attributed to the incorporation of In(III) ions in an MoO_3 lattice. The decrease in optical band gap with increasing thickness may be interpreted in terms of the incorporation of oxygen vacancies which are also believed to be the source of conduction electrons in the MoO_3–In_2O_3 complex. The decrease of band gap with increasing substrate temperature may be attributed to the enhanced ordering of the samples and the decrease of band gap with annealing may be attributed to a reduction in the concentration of lattice imperfections.

1. Introduction

The study of the optical properties of evaporated thin films of MoO_3–In_2O_3 prepared by the coevaporation technique [1] helps to elucidate the basic properties of these mixed oxides. Thin amorphous dielectric films based on MoO_3 are well known as insulators but In_2O_3 is an oxide having fairly high electrical conductivity and sometimes used for transparent electrodes. There is thus a reasonable expectation of producing such oxide films in an amorphous state which could be used as intermediate conductors having resistivity in the range normally associated with amorphous semiconductors.

The study of the optical absorption and particularly the absorption edge is a useful method for the investigation of optically induced transitions and for the provision of information about the band structure and energy gap in both crystalline semiconductors and non-crystalline materials. The principle of this technique is that photons with energy greater than the band gap energy will be absorbed. The optical energy gaps of a number of mixed oxide films have been successfully analysed on the basis of the theories proposed by Tauc *et al.* [2] and by Davis and Mott [3] for amorphous materials and for the case of non-direct transitions when the k conservation rule is relaxed.

The width of the tails of localized states at the band edges has been estimated using the Urbach relation [4]. There are two kinds of optical transition at the fundamental edge of the crystalline and non-crystalline semiconductors, direct and indirect transitions, both of which involve the interaction of an electromagnetic wave with an electron in the valence band, which is then raised across the fundamental gap to the conduction band. For the direct optical transition from the valence band to the conduction band it is essential that the wave vector for the electron be unchanged. In the case of indirect transitions interactions with lattice vibrations (phonons) take place and thus the wave vector of the electron can change in the optical transition and the momentum change will be taken or given up by phonons.

In_2O_3 is an n-type semiconducting material with a direct gap of about 3.6 eV and an indirect band gap of about 2.6 eV [5]. In its common form it is a yellow powder but can be prepared as a thin film which is transparent in the visible spectrum.

Anwar *et al.* [6] have studied the optical properties of MoO_3 in thin film form and reported that band gap is decreased with the increase of thickness and substrate deposition temperature. In the present work we report some of the optical properties of MoO_3–In_2O_3 thin films. The substrate temperature, composition, film thickness and annealing effects on the optical energy gap are also reported.

2. Experimental measurements

Thin evaporated layers of MoO_3–In_2O_3 were deposited on clean Corning 7059 glass substrates held at a pressure of about 1.33×10^{-4} Pa in a Balzers BA510 coating unit using the coevaporation technique established by Hogarth and Wright [1]. Molybdenum boats were used for the evaporation of both MoO_3 and In_2O_3. All other techniques used to measure film thickness, cleaning of the substrates, raising the substrate temperature, absorption measurements, transmission electron microscopy and annealing the samples in vacuum are the same as described earlier by Anwar and Hogarth [6].

3. Results

The optical absorption spectra of amorphous thin layers of MoO_3–In_2O_3 have been studied for samples of constant thickness of approximately 300 nm but of different compositions. Some samples were studied at

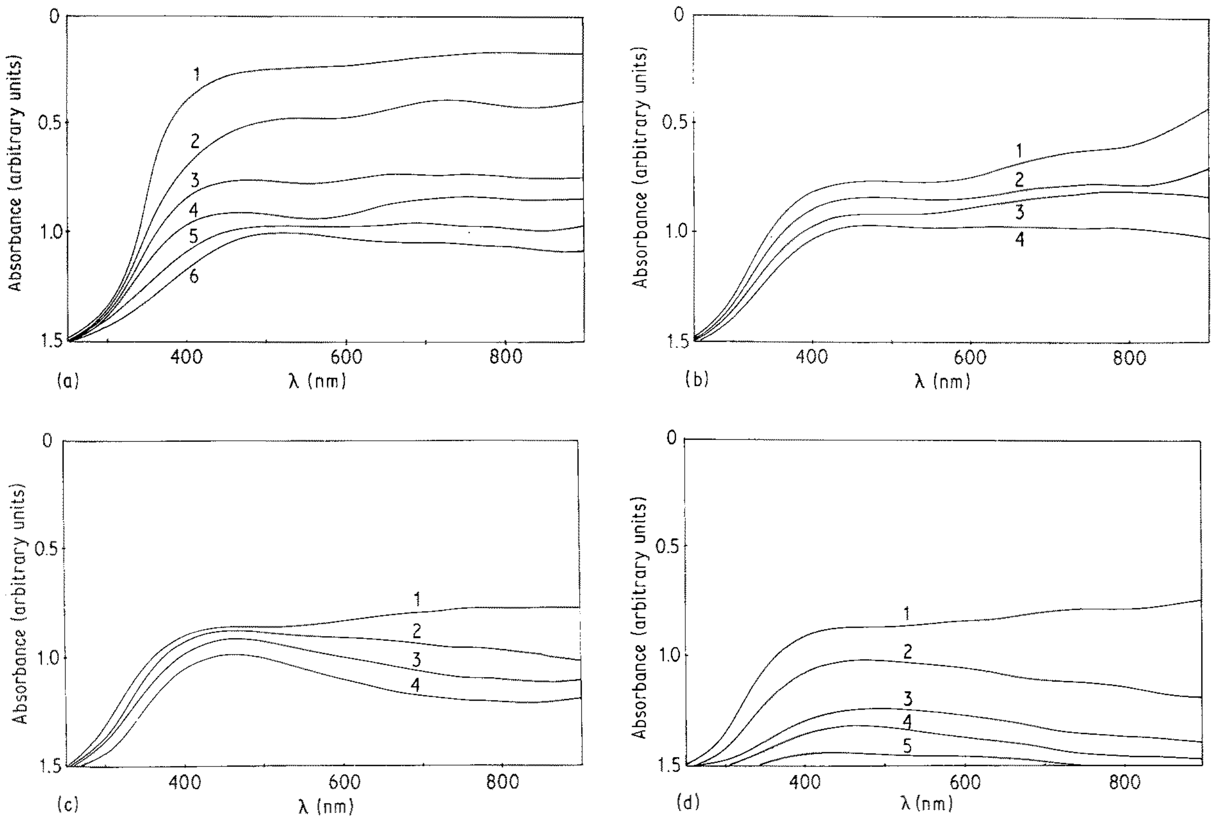

Figure 1 (a) Optical absorbance spectra of 300 nm thick samples as a function of wavelength for MoO_3–In_2O_3 deposited at 20° C, of different compositions, (1) 100%, (2) 95%, (3) 90%, (4) 85%, (5) 80%, (6) 75%, molar% MoO_3. (b) Optical abosrbance spectra of 85 mol% MoO_3–15 mol% In_2O_3 films, deposited at 20° C as a function of wavelength and having thicknesses, (1) 100 nm, (2) 200 nm, (3) 300 nm, (4) 400 nm. (c) Optical absorbance spectra as a function of wavelength for 200 nm thick samples of 85 mol% MoO_3–15 mol% In_2O_3 deposited at substrate temperatures, (1) 20° C, (2) 100° C, (3) 200° C, (4) 270° C. (d) Optical absorbance spectra of 85 mol% MoO_3–15 mol% In_2O_3 as a function of wavelength deposited at 20° C and annealed at different temperatures, (1) as evaporated, (2) 200° C, (3) 300° C, (4) 400° C, (5) 500° C.

fixed composition but different thickness in the range 100 nm to 400 nm, and at different substrate temperatures in the range 20 to 270° C. A few samples were annealed in vacuum for 2 h in the temperature range 200 to 500° C. Fig. 1a shows the variation of absorbance A with wavelength for amorphous thin films of MoO_3–In_2O_3 having constant thickness but varying compositions. This figure shows that the absorption edges move towards the higher wavelength region as the In_2O_3 content increases. The addition of In_2O_3 to MoO_3 causes an increase in the overall disorder of the new system as indicated by an increase in band tailing and a decrease in the optical gap. Fig. 1b shows the absorbance spectra for samples of different thicknesses of MoO_3–In_2O_3 with fixed composition (85 mol% MoO_3–15 mol% In_2O_3). Fig. 1c shows the variation of absorbance with wavelength for 300 nm thick samples 85 mol% MoO_3–15 mol% In_2O_3 at four different substrate temperatures. Four samples 300 nm thick were annealed at four different temperatures in vacuum. Their absorbance as a function of wavelength is shown in Fig. 1d. The optical data in these figures are analysed by an equation related to the absorption by non-direct transitions in k space of the form [2, 3].

$$\alpha(\omega) = \frac{B\,(\hbar\omega - E_{\text{opt}})^2}{\hbar\omega} \tag{1}$$

where $\hbar\omega$ is the energy of the incident photon, E_{opt} is the optical band gap of the material and B is a constant which can be defined as

$$B = \frac{4\pi\sigma_0}{ncE_e} \tag{2}$$

where c is the velocity of light, σ_0 is the value of conductivity extrapolated to $1/T = 0$, n is the refractive index of the material and E_e is the width of the tail of localized states in the band gap.

Figs 2a to 2d show the curves of $(\alpha\hbar\omega)^{1/2}$ as a function of $\hbar\omega$ using the data of Figs 1a to 1d, respectively according to Relation 1 and show good straight lines for higher values of absorption and these satisfy the Relation 1. The extrapolation of the linear regions of these curves to $(\alpha\hbar\omega)^{1/2} = 0$ yields the values of E_{opt}. The values of E_{opt} as determined from the curves of Figs 2a to 2d are listed in Tables I to IV, respectively. Figs 3a to 3d show the Urbach [4] exponential dependence using the data of Figs 1a to 1d

$$\alpha(\omega) = \frac{\alpha_0 \exp \hbar\omega}{E_e} \tag{3}$$

where α_0 is a constant. The values of E_e for all kinds of films of Figs 3a to 3d are estimated and included in Tables I to IV respectively. When the data are replotted from Fig. 1d curve 5 is not replotted since the annealing at 500° C increased the absorption to a very high level and a well defined edge was no longer measured.

Electron diffraction studies demonstrate that freshly evaporated films of 85 mol% MoO_3–15 mol% In_2O_3

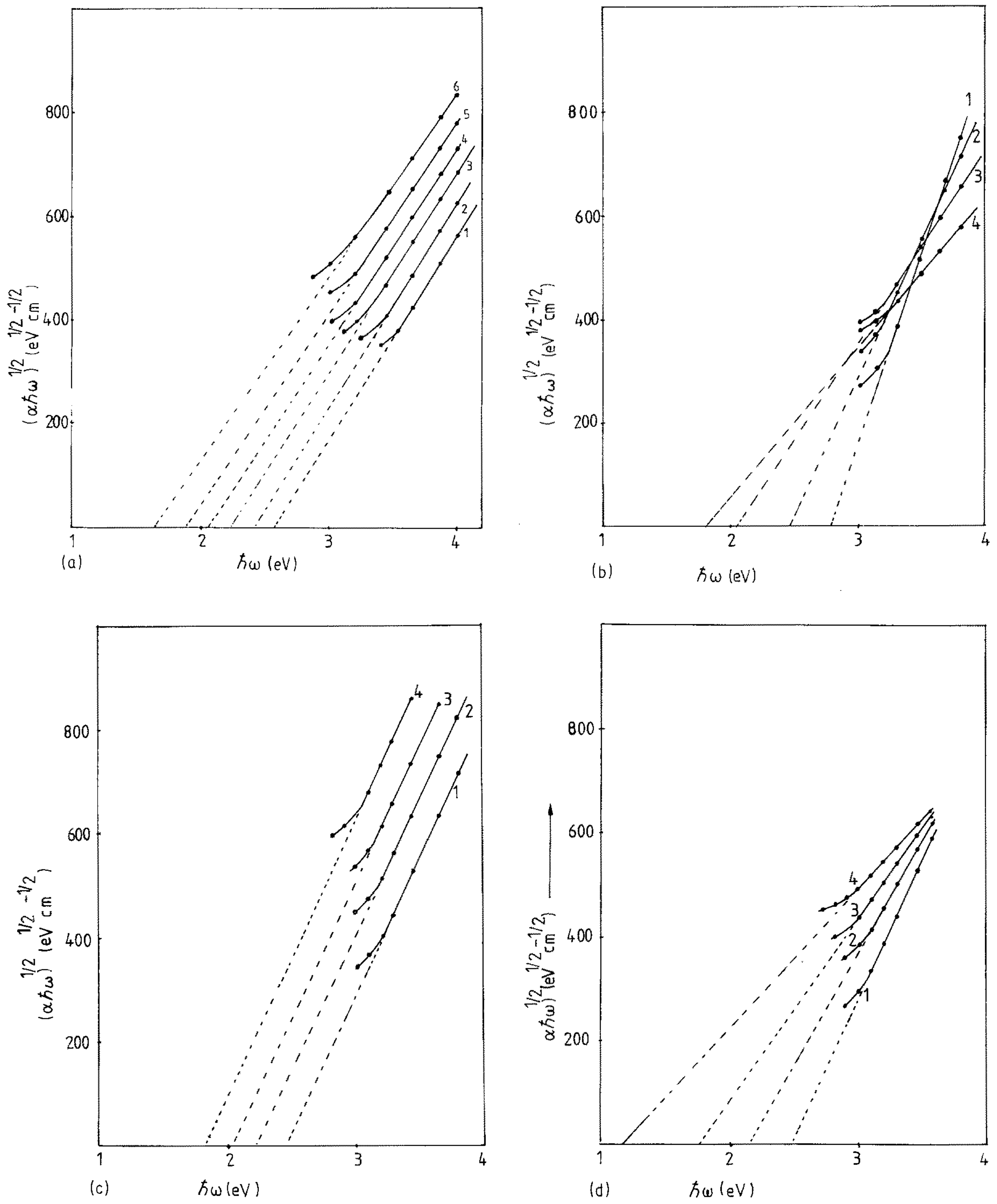

Figure 2 (a) The data of Fig. 1a plotted in accordance with the theory of indirect transitions. (b) The data of Fig. 1b plotted in accordance with the theory of indirect transitions. (c) The data of Fig. 1c plotted in accordance with the theory of indirect transitions. (d)The data of Fig. 1d plotted in accordance with the theory of indirect transitions.

vacuum-deposited at room temperatures are effectively amorphous in structure. The films prepared on substrates at 270° C are polycrystalline. On annealing in vacuum the films become crystalline and many of the defects associated with a fresh film are annealed out.

4. Discussion

In general, the preparation of coevaporated dielectric films introduces extrinsic centres which contribute to the electrical and optical properties. These centres can arise from the presence of impurities introduced during the preparation and by contamination when the sample is exposed to air. Such defects, together with structural defects (e.g. voids) are assumed to give rise to localized states in the band gap.

In order to interpret the observed optical results of MoO_3–In_2O_3 it is necessary to discuss briefly the crystallographic structure of In_2O_3. The crystallographic structure of MoO_3 has already been discussed by Anwar *et al.* [7]. Under normal conditions In_2O_3 crystallizes in the C-type rare earth structure which is very stable [8] and the optical properties of In_2O_3 are governed by defects introduced in the C-type rare earth oxide structure. The structure of In_2O_3 is body-centred cubic with eight atoms per unit cell. X-ray measurements gave a unit cell dimension of 1.01 nm. This structure is closely related to the fluorite structure but in In_2O_3 every fourth anion is missing so that small anion sites constitute interstitial sites in the oxygen sublattice. The energy of formation of oxygen

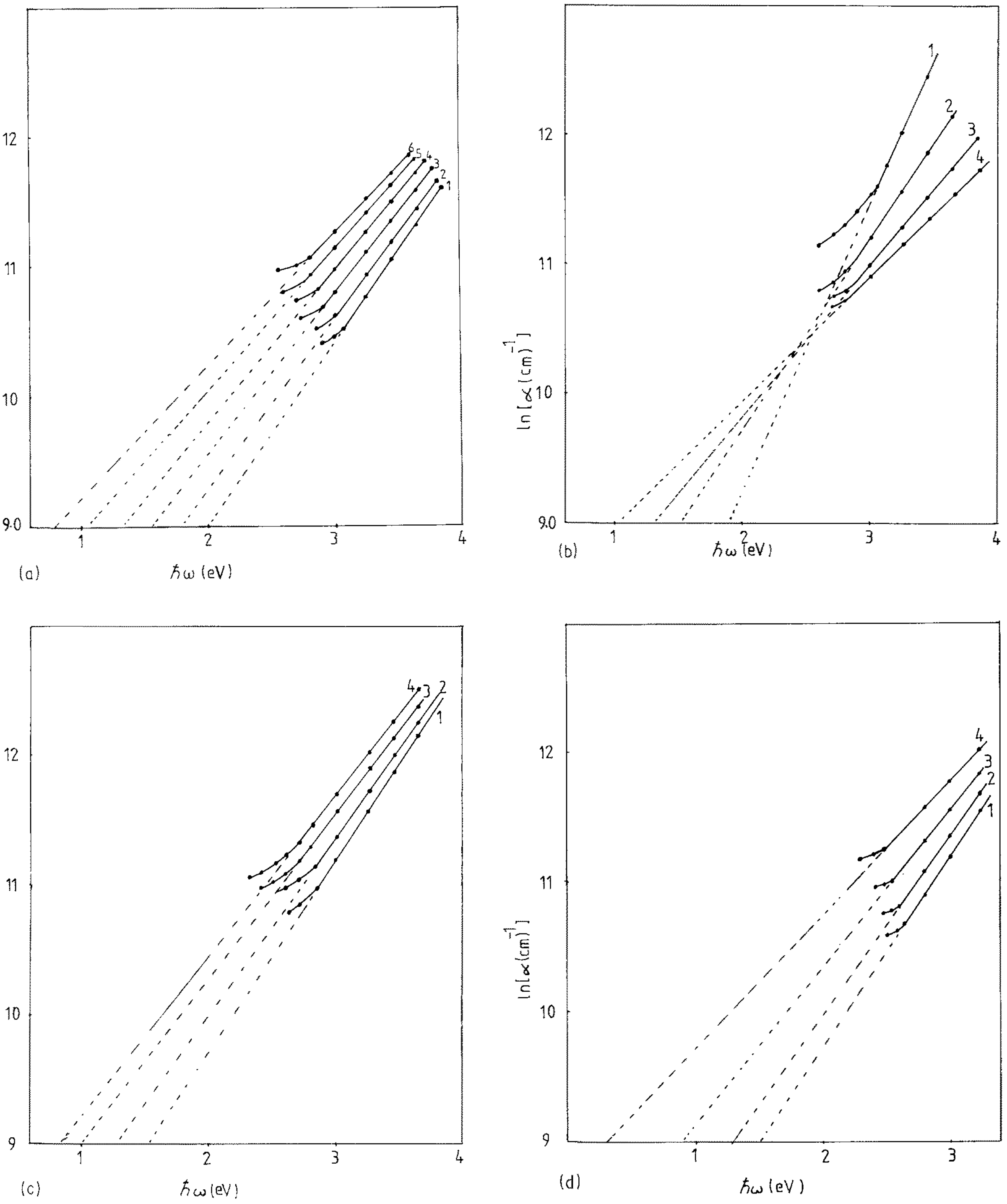

Figure 3 (a) The absorption coefficient as a function of photon energy for films of MoO_3–In_2O_3 (The data are replotted from Fig. 1a). (b) The absorption coefficient as a function of photon energy for films of MoO_3–In_2O_3 (The data are replotted from Fig. 1b). (c) The absorption coefficient as a function of photon energy for films of MoO_3–In_2O_3 (The data are replotted from Fig. 1c). (d) The absorption coefficient as a function of photon energy for films of MoO_3–In_2O_3 (The data are replotted from Fig. 1d).

interstitials in the C-type structure should be small. If the energy of migration is also small, these interstitials will be mobile and oxygen diffusion via interstitials will result. Thus primary ionic defects will be oxygen ion vacancies and interstitials.

Aleshin *et al.* [9] and Molzen [10] have suggested the existence of oxygen vacancies in In_2O_3. These oxygen vacancies act as donor centres. De Wit [8] suggested the presence of In^{3+} ions in the interstitial positions but their concentration is much smaller than the oxygen concentration. He further reported that In_2O_3 is relatively stable and stoichiometric up to 1400° C but Muranaka [11] suggested that amorphous films deposited at room temperature have a slight excess of indium over the stoichiometric composition. Such a non-stoichiometric composition of amorphous films has also been suggested by Noguchi *et al.* [12].

In In_2O_3 the valence band is formed by oxygen 2p states and the conduction band would be composed of empty 5s states. The Fermi energy E_f lies half way between the bands [13]. In the present work the calculated values of optical band gap E_{opt} decrease with the increasing molar percentage of In_2O_3 in MoO_3 and the values of E_{opt} also decrease with the increase of both substrate temperature and film thickness.

These results can be explained in the following

TABLE I Some optical parameters of amorphous MoO_3-In_2O_3 (in mol %) thin films of thickness 300 nm.

Film compositions (mol %)	E_{opt} (eV)	E_e (eV)
100 MoO_3	2.5_8	0.71
95 MoO_3-5 In_2O_3	2.4_2	0.74
90 MoO_3-10 In_2O_3	2.2_2	0.76
85 MoO_3-15 In_2O_3	2.0_6	0.86
80 MoO_3-20 In_2O_3	1.8_0	0.90
75 MoO_3-25 In_2O_3	1.6_2	0.95

manner. When the molar percentage of In_2O_3 is increased in the mixed layers of MoO_3-In_2O_3, there is an increase of overall disorder in the system. In(III) ions may be incorporated in an MoO_3 lattice causing the Mo orbital to be a little less tightly bound. The presence of In(III) ions in an MoO_3 lattice may cause a decrease in the optical band gap. A similar trend was also observed by Arshak [14] for SiO-In_2O_3. This effect may be due to an increase of overall disorder with the addition of In_2O_3 to MoO_3. This is in support of the theory of Mott and Davies [15] which suggests that the extent of localized states near the mobility edge increases with the increase of disorder in an amorphous structure. Additionally as the In_2O_3 content in the MoO_3-In_2O_3 complex increases, deeper band tails of the localized states extend in the gap and cause an increase in the value of E_e and a decrease in the value of E_{opt}.

When the thickness of the samples is increased, the concentration of oxygen vacancies, i.e. positively charged structural defects, is increased in both MoO_3 and In_2O_3. The incorporation of In(III) ions in an MoO_3 lattice may also enhance the electron concentration but the majority of ionic defects are caused by the oxygen vacancies which are believed to be the source of conduction electron states in the MoO_3-In_2O_3 complex. The degree of localization of electrons increases with the increase of cation concentration, thereby increasing the number of donor centres. A large concentration of donor levels will effectively lower the band gap and shift the absorption to the lower wavelengths. The structure of the films and the physical properties have shown to be markedly dependent on the substrate temperature. Anwar *et al.* [6] and Muranaka [11] have suggested that the films of MoO_3 and In_2O_3 prepared on substrates at a temperature of 270° C or higher are crystalline in character, but the present investigation showed that the mixed MoO_3-In_2O_3 complex oxide films are amorphous in character at 270° C substrate temperature. Anwar *et al.* [16] have studied MoO_3 films at higher substrate temperatures and reported the formation of molybdenum species of lower oxidation state (i.e. Mo^{5+}). In In_2O_3 two kinds of ionic defects are produced at higher temperature: oxygen vacancies and indium interstitials (In_i). Rosenberg [17] has suggested the movement of In_i defects while measuring the oxidation state of indium metal at higher substrate temperatures. The decrease in optical band gap with increasing substrate temperature may be due to the increasing concentration of these types of defects and formation molybdenum species of lower oxidation state.

TABLE II Some optical parameters of amorphous 85 mol % MoO_3-15 mol % In_2O_3 thin films deposited at 20° C and having different thicknesses.

Sample thickness (nm)	E_{opt} (eV)	E_e (eV)
100	2.79	0.43
200	2.46	0.66
300	2.06	0.86
400	1.80	1.0

TABLE III Some optical parameters of amorphous 85 mol % MoO_3-15 mol % In_2O_3 thin films of thickness 200 nm deposited at four different substrate temperatures.

Substrate temperature (° C)	E_{opt} (eV)	E_e (eV)
20	2.46	0.66
100	2.22	0.71
200	2.02	0.76
270	1.82	0.80

TABLE IV Some optical parameters of amorphous 85 mol % MoO_3-15 mol % In_2O_3 thin films of thickness 200 nm, annealed at different temperatures.

Annealing temperature (° C)	E_{opt} (eV)	E_e (eV)
As evaporated	2.46	0.66
200	2.14	0.75
300	1.74	0.83
400	1.12	0.97

The complex dielectric film 85 mol % MoO_3-15 mol % In_2O_3 of thickness about 300 nm was found to have a diffuse amorphous structure at room temperature and this structure was retained after annealing at 400° C for 2 h. At higher annealing temperature, up to 500° C, most of the defects are annealed out and a crystalline state is established. The decrease of optical band gap due to increase in annealing temperature may result from a reduction in the concentration of lattice imperfections due to annealing the substrate in vacuum. Our results are consistent with those of other work [18–19].

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