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Optical absorption in co-evaporated V_2O_5–TeO_2 thin films

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The electron diffraction pattern shows that co-evaporated V_2O_5–TeO_2 thin film samples are amorphous at room temperature and become polycrystalline at temperatures higher than about 513 K. This behaviour is similar to that of amorphous V_2O_5 thin films. The optical absorption edge of amorphous thin films of V_2O_5–TeO_2 is studied in the wavelength range 200 to 900 nm and the FTIR spectra are studied in the wave number range 400 to 4000 cm^{-1}. The FTIR spectra of amorphous V_2O_5 thin film are found to be similar to those of amorphous V_2O_5–TeO_2 thin films. This suggests that the coordination number of the vanadium ion in V_2O_5–TeO_2 is the same as that in crystalline V_2O_5, and thus the optical absorption edge of amorphous V_2O_5–TeO_2 thin films can be described by direct forbidden transitions.

1. Introduction

In all band models of amorphous semiconductors, the localized states due to the lack of the long-range order, are close to the band edges rather than deep in the bands. Most of the workers [1, 2] agreed that the states are localized below E_C and above E_V which are sharply defined energies called the mobility edges [1]. These localized states play an important role in determining the optical absorption edge and their contribution to the optical transitions may be seen through the following arguments. Davis and Mott [3] derived an equation for the optical absorption coefficient $\alpha(\omega)$ as a function of photon energy $\hbar\omega$

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

where n is an exponent, ω the angular frequency of the incident radiation, B a constant and E_{opt} is defined as the optical energy gap of the material and corresponds to the smallest energy separating the localized states that are close to one of the two bands and the extended states of the other (see the model of Davis and Mott [3]).

A similar equation with $n = 2$ was derived by Tauc *et al.* [4]. The definition given to E_{opt} by these authors is, however, different from that given by Davis and Mott. Tauc *et al.* defined it as the energy separating the localized states above E_v and those below E_c.

Equation 1 with $n = 2$ offers the best fit to the optical absorption data in most amorphous semiconductors. There are, however, special cases where the index n is different from 2. For instance Davis and Mott [3] gave the value $n = 1$ in amorphous selenium and many other workers found $n = 3/2$ in vanadate glasses. It is thought that this value is due to the fact that the coordination environment of V^{5+} in crystalline V_2O_5 is not affected by the disorder. Indeed nuclear magnetic resonance studies show that the coordination number of the vanadium ions in the glass is the same as for the vanadium ions in crystalline V_2O_5 [5, 6] and that their site symmetry is similar to that in the crystal. As a consequence, one would expect similar electronic transitions in both non-crystalline and crystalline V_2O_5. In fact, it was found in the latter (V_2O_5 single crystal) that the absorption coefficient fits the condition for direct forbidden transitions

$$\alpha\hbar\omega = B(\hbar\omega - E_{opt})^{3/2} \qquad (2)$$

much better than it fits the condition for direct allowed transitions [7, 8] given by

$$\alpha = B(\hbar\omega - E_{opt})^{1/2} \qquad (3)$$

Al-Ani and Hogarth [9] have also used Equation 2 to determine the optical gap of V_2O_5–SiO amorphous thin films and they found that it gives a better fit to their optical absorption data. In addition the optical absorption properties of V_2O_5–P_2O_5 glasses show that the fundamental absorption arises from direct forbidden transitions (Equation 2) and occurs at about 2.4 eV at room temperature [10].

Equations 2 and 3, give very different plots for the optical absorption data. The choice between equations 1 (with $n = 2$) and 2 becomes difficult in the case where both of them give straight lines. The aim of this paper, therefore, is to compare Equations 1 (with $n = 2$) and 2 with the help of the FTIR studies, so that we can choose the appropriate equation for the calculation of the optical energy gap.

2. Experimental work

The optical absorption measurements of co-evaporated V_2O_5–TeO_2 thin films in vacuum of 10^{-6} torr, were made in two spectral regions; the ultraviolet and the infrared region (4000 to 400 cm^{-1}). Corning 7059 glass substrates were used for the UV, and monocrystalline silicon wafers were used as substrates for the FTIR measurements. The optical measurements in

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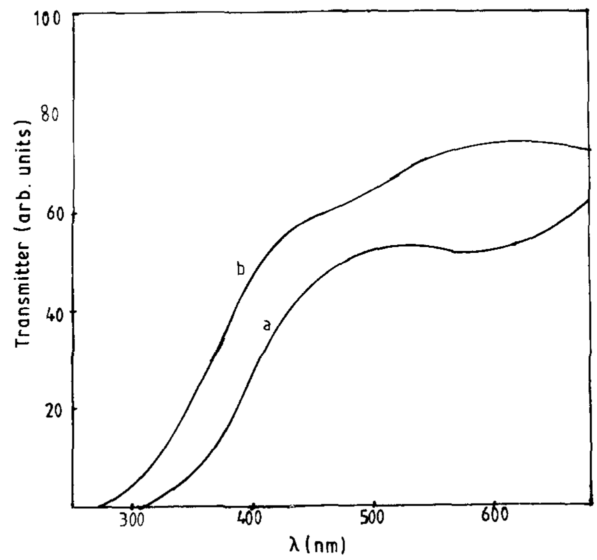

Figure 1 Optical transmittance as function of wavelength for V_2O_5–TeO_2 thin films (about 200 nm thick). (a) 68%V_2O_5 and (b) 51%V_2O_5.

the ultraviolet and visible regions were made using a Perkin-Elmer (Model Lambda 3) double beam spectrophotometer and the infrared measurements were made using a Perkin-Elmer (Model 1710 FTIR) double beam spectrophotometer. The effects of the substrate on the UV and FTIR characteristics were minimized by placing another cleaned uncoated substrate in the path of the reference beam. The structure of layers of about 40 nm thickness was investigated in an electron microscope (JEO model JEM7) by electron diffraction and microscopy. For this purpose the thin film of V_2O_5–TeO_2 was deposited on a carbon-coated mica substrate held at room temperature.

3. Results and discussion

Curves of the optical transmittance as a function of wavelength for different compositions of V_2O_5–TeO_2 co-evaporated layers are presented in Fig. 1. It is seen that the transmittance is very low indicating

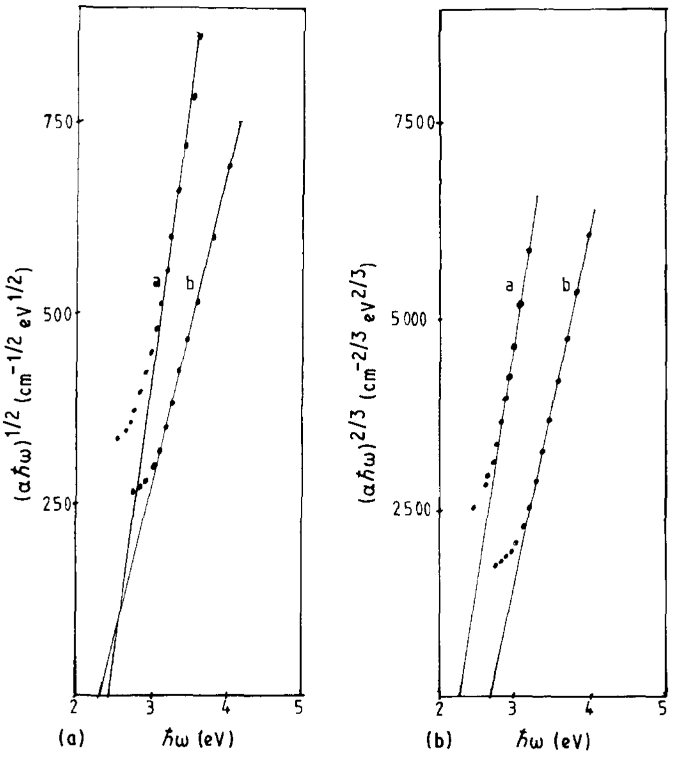

Figure 2 (a) $(\alpha\hbar\omega)^{1/2}$ and (b) $(\alpha\hbar\omega)^{2/3}$ plotted against $\hbar\omega$ for V_2O_5–TeO_2 thin films (about 200 nm thick). (a) 68% V_2O_5 and (b) 51%V_2O_5.

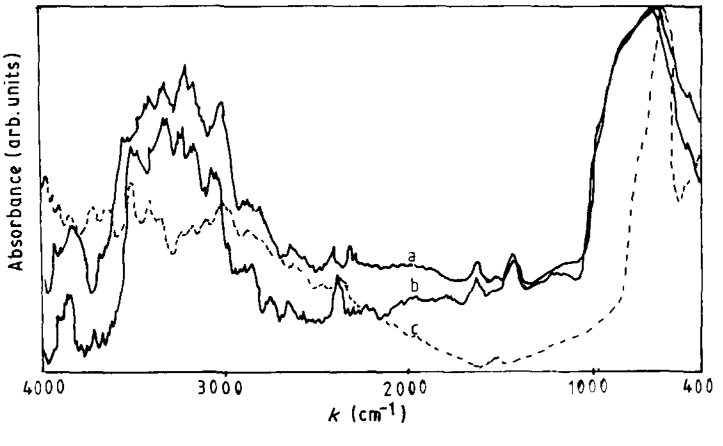

Figure 3 FTIR absorbance plotted against wave number for (a) V_2O_5–TeO_2, (b) V_2O_5 and (c) TeO_2 thin films.

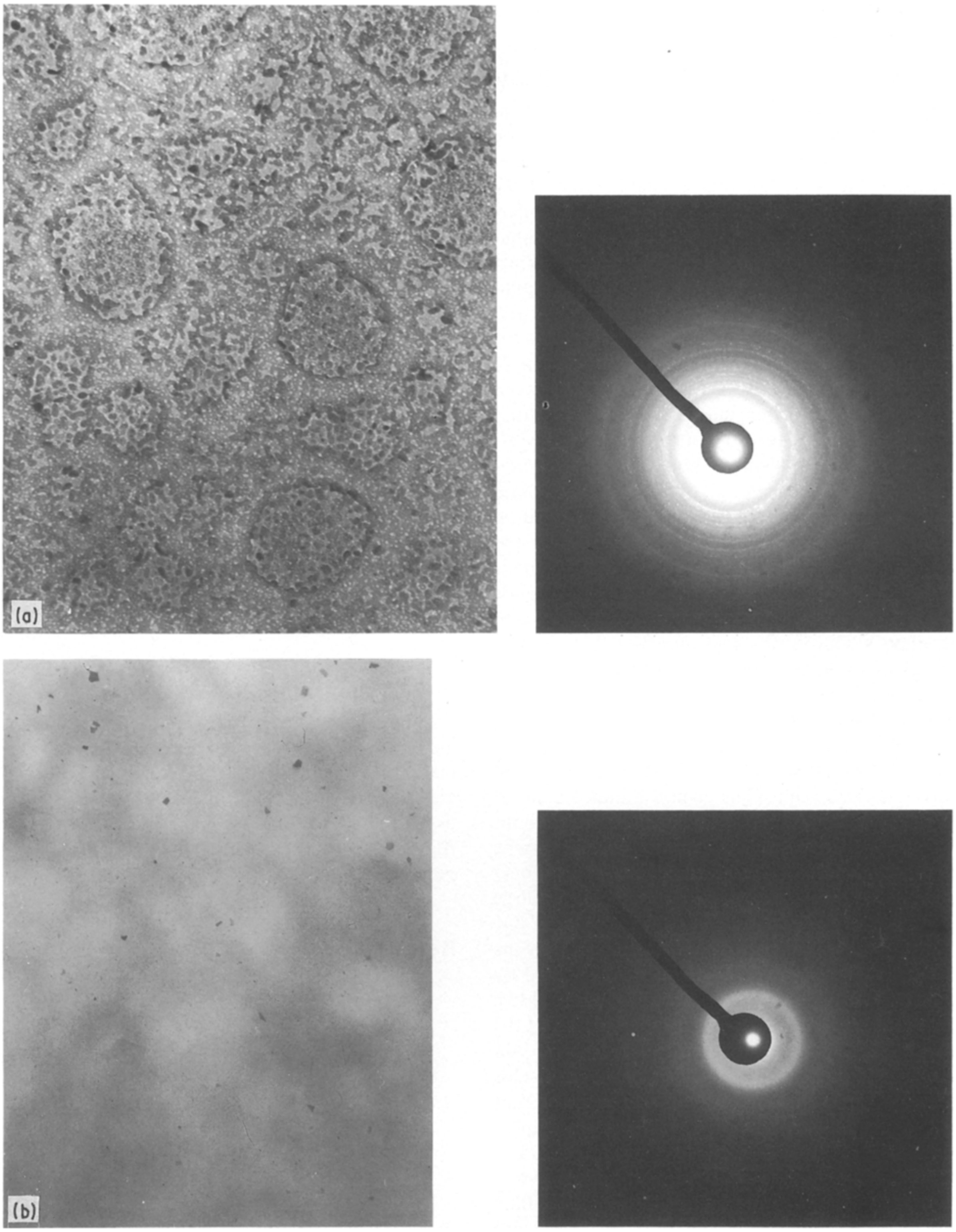

Figure 4 Electron micrograph and diffraction patterns of V_2O_5–TeO_2 thin film at (a) high temperature and (b) room temperature.

that the optical absorption coefficient is very high ($\alpha > 10^3\,\mathrm{cm}^{-1}$).

The absorption coefficient $\alpha(\omega)$ was calculated from

$$\alpha(\omega) = (1/t)\ln(I_0/I). \qquad (4)$$

where I_0 and I are the intensities of the incident and the transmitted light respectively and t the thickness of the specimen.

Fig. 2 shows the plots of $(\alpha\hbar\omega)^{2/3}$ and $(\alpha\hbar\omega)^{1/2}$ against photon energy. It is seen that both plots give straight lines, hence it is difficult to see which equation is the best to fit our data. The values of E_{opt} for 68% V_2O_5–32%TeO_2 corresponding to $n = 2$ and $n = 3/2$ are 2.27 and 2.40 eV, respectively, and those for 51% V_2O_5–49%TeO_2 corresponding to $n = 2$ and $n = 3/2$ are 2.70 and 2.30 eV, respectively. The FTIR results are shown in Fig. 3 and the electron diffraction patterns as well as the electron micrographs are shown in Fig. 4.

The results reported by Bodo' and Hevesi [8] on the optical absorption edge of crystalline V_2O_5 indicate that the ions responsible for direct forbidden transitions [7] are V^{5+} which exist in sixfold coordination in crystalline V_2O_5. Thus if the coordination of these cations remains the same in the amorphous state then the infrared will give the same band as in crystalline V_2O_5. In fact it has been shown that the infrared spectra are the same for both crystalline and glassy vanadate [11]. Similar results were found by Anderson and Compton [10]. Furthermore they found that the absorption coefficient fits the condition for direct forbidden transitions given by Equation 2. It should be noted that the equations for direct forbidden and direct allowed transitions give very different plots for the optical absorption data, and hence the choice of the type of transitions is clear. The choice between Equation 2 for direct forbidden transitions and that given by Davis and Mott [3] for the non-direct transitions, is, however, difficult without infrared measurements since both equations give roughly straight lines to the optical data (Fig. 2). Recent results reported on infrared spectra of V_2O_5 [12] also show that the infrared spectra of orthorhombic and amorphous V_2O_5 are very similar, that is, the absorption bands are at the same wave number for both amorphous and crystalline V_2O_5. It was also observed that the line width is much larger in the amorphous than in the crystalline samples.

An absorption peak at about 650 cm^{-1} was reported by Al-Ani and Hogarth [9] for amorphous V_2O_5 thin films. It was also found that the spectra of amorphous TeO_2 thin films exhibit a minor band at 715 cm^{-1} and one pronounced peak at about 600 cm^{-1}. It was suggested that these bands may be attributed to symmetrical vibrations of the Te–O bond. The present results made on FTIR show a large band at 672 and at 614 cm^{-1} for amorphous V_2O_5 and TeO_2 thin films respectively (Fig. 3). These results are in fairly good agreement with those obtained by Al-Ani and Hogarth [9] and Hilton and Jones [13]. On the other hand, Anderson and Compton [10] reported one strong band at about 1010 cm^{-1} in V_2O_5–P_2O_5 glasses due possibly to V–O bond. This peak corresponds to that found in crystalline V_2O_5 at about 1038 cm^{-1}. The FTIR spectra of the co-evaporated V_2O_5–TeO_2 thin films show one large band at 665 cm^{-1} and the shape of the absorption spectra is very similar to that of an amorphous V_2O_5 thin film. These particular bands which are observed at 672 and 665 cm^{-1} could be attributed to the V–O stretching vibration modes. Furthermore the disappearance of the peak which is observed in the spectra of TeO_2 thin film is noted. This would indicate that the addition of TeO_2 to V_2O_5 does not substantially affect the FTIR transmission properties of vanadium pentoxide. This would suggest that the site symmetry of the vanadium cations in amorphous V_2O_5–TeO_2 thin films may be similar to that in crystalline V_2O_5. The optical absorption edge could, therefore, be due to the same mechanism of transitions in both amorphous V_2O_5 and V_2O_5–TeO_2 thin films. As a consequence, in the mixed oxides of V_2O_5 and TeO_2, the intercept of the curve given by Equation 2 with the photon energy axis, could give better values for E_{opt} than that given by the Equation 1 (with $n = 2$) for non-direct optical transitions which is applied to most amorphous semiconductors [3]. The shift of the absorption band from 672 to 665 cm^{-1} due to the addition of TeO_2 to V_2O_5 could be attributed to the influence of Te^{4+} on the V–O bond thereby weakening it.

4. Conclusion

According to many workers and to the present work on amorphous V_2O_5–TeO_2 thin film, it seems that in general the optical absorption edge in amorphous as well as in vanadate glasses, is described by the direct forbidden transition equation. The main reason for this is that the coordination number of vanadium ion is maintained from crystalline to amorphous state. This is shown by the similarity between the FTIR spectra of amorphous V_2O_5 and V_2O_5–TeO_2 thin films. The shift of the large band observed in amorphous V_2O_5 to lower wave numbers due to the addition of TeO_2, is attributed to the presence of Te^{4+} which is thought to weaken the V–O bond.

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References

1. M. H. COHEN, H. FRITZSCHE and S. R. OVSHINSKY, *Phys. Rev. Lett.* **22** (1969) 1065.
2. N. F. MOTT, *Phil. Mag.* **17** (1968) 1259.
3. E. A. DAVIS and N. F. MOTT, *ibid.* **22** (1970) 903.
4. J. TAUC, R. GRIGOROVICI and A. VANCU, *Phys. Status Solidi* **15** (1966) 627.
5. P. W. FRANCE and H. O. HOOPER, *Bull. Amer. Phys. Soc.* **13** (1968) 90.
6. F. R. LANDSBERGER and P. J. BRAY, *ibid.* **14** (1969) 30.
7. J. BARDEEN, F. BLATT and L. H. HALL, "Photoconductivity Conference", edited by R. G. Beckenridge, B. R. Russell and E. E. Hahn (Wiley, New York, 1956), p. 146.
8. Z. BODO' and I. HEVESI, *Phys. Status Solidi* **20** (1967) K45
9. S. K. J. AL-ANI and C. A. HOGARTH, *J. Mater. Sci.* **20** (1985) 1185.
10. G. W. ANDERSON and W. D. COMPTON, *J. Chem. Phys.* **52** (1970) 6166.
11. B. V. JANAKIRAMA-RAO, *J. Amer. Ceram. Soc.* **49** (1966) 605.
12. J. LIVAGE and R. COLLONGUES, *Mater. Sci. Eng.* **23** (1976) 297.
13. A. R. HILTON and C. E. JONES, *Phys. Chem. Glasses,* **7** (1966) 112.

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