

Short Communication

Optical and electrical properties of $(V_2O_5)_{1-x}-(MoO_3)_x$ thin films[†]

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Abstract

Thin films of $(V_2O_5)_{1-x}-(MoO_3)_x$ ($0 \leq x \leq 1$) were prepared by electron beam evaporation technique in an oxygen partial pressure of 2×10^{-4} mbar and at a substrate temperature of 423 K. The optical absorption data in the range 300–1500 nm suggests that the optical bandgap increases with increase in the composition of x and shows a curvilinear behaviour. Electrical conductivity decreased with increase in the composition of x . The temperature dependence of electrical conductivity obeys $T^{-1/4}$ law.

Keywords: $(V_2O_5)_{1-x}-(MoO_3)_x$ thin films, optical properties and electrical properties.

1. Introduction

In recent years there has been considerable interest in variable transmittance electrochromic devices¹ based on lithium intercalation in transition metal oxides. An electrochemical material can reverse its optical properties following a redox reaction due to an applied voltage. Optical modulation is controlled by direction and magnitude of the charge transferred. Among the various transition metal oxides, vanadium pentoxide² is an interesting material for various scientific and technological applications. The variability in optical properties makes it suitable for multicolor electrochromic display device applications. Alternatively, V_2O_5 can be used in conjunction with molybdenum/tungsten oxides^{3,4} for charge-balanced devices for display in informatics, variable reflection mirrors, smart windows in energy-efficient architecture and surfaces with tunable emittance for temperature control of space vehicles. In the present investigation, thin films of $(V_2O_5)_{1-x}-(MoO_3)_x$ ($0 \leq x \leq 1$) were prepared, by electron beam evaporation technique, on Corning 7059 glass substrates maintained at 423 K in an oxygen partial pressure of 2×10^{-4} mbar. The optical and electrical properties of these thin-film oxide bronzes were studied with respect to their composition x .

2. Experimental

Thin films of $(V_2O_5)_{1-x}-(MoO_3)_x$ ($0 \leq x \leq 1$) were prepared, by electron beam evaporation technique, on chemically and ultrasonically cleaned Corning 7059 glass substrates maintained at 423 K in an oxygen partial pressure of 2×10^{-4} mbar using Balzers BA 510E high-vacuum coating unit. Pure V_2O_5 and MoO_3 powders obtained from Merck, Germany, were thoroughly mixed in

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required proportions and calcinated at about 773 K for 8 h and grounded once again. Later, these were made into pellets of 2 cm diameter and 5 mm thick and calcinated once again for 10 h at 873 K. The pellets were kept in a water-cooled copper crucible. An electron beam with an approximate power density of 1.5 kWcm^{-2} was deflected and scanned over the surface of the pellet during evaporation. The deposition rate, 4 nm s^{-1} , was controlled by a quartz crystal thickness monitor. The thickness of the films investigated was about $1 \mu\text{m}$. The optical properties were studied in the range 300–1500 nm using Hitachi U 3400 UV-VIS-NIR double beam spectrophotometer. The electrical conductivity of these films was studied using standard four-probe technique.

3. Results and discussion

Electron beam-evaporated $(\text{V}_2\text{O}_5)_{1-x}(\text{MoO}_3)_x$ ($0 \leq x \leq 1$) films were found to be uniform, pinhole free and well adherent to the substrate surface. Their broad and diffused X-ray diffraction pattern indicated the amorphous nature of the films. The wavelength dependence of the optical transmission spectra of the films is shown in Figs 1 and 2. The optical absorption coefficient was evaluated using the relation

$$\alpha = 1/t \ln [T/(1-R)^2] \quad (1)$$

where T is the transmittance, R , the reflectance and t , the thickness of the film. The variation of $\ln \alpha$ with incident photon energy of the films was found to be linear in the absorption region near the fundamental absorption edge. This indicates that the absorption coefficient near the fundamental absorption edge is an exponential dependent on the incident photon energy and obeys the empirical Urbach rule⁵

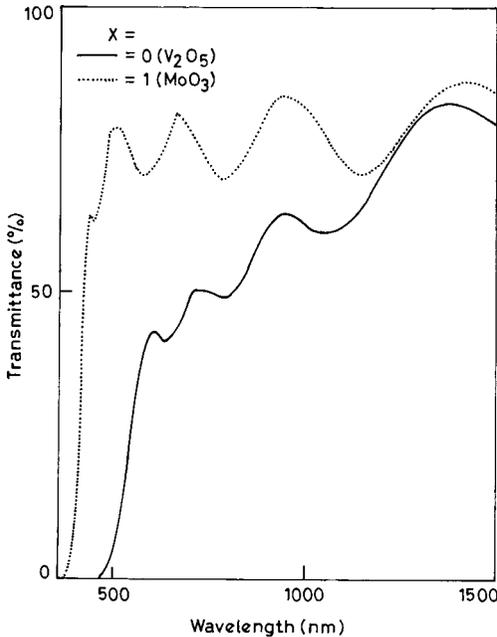


FIG. 1. Optical transmittance spectra of V_2O_5 and MoO_3 films formed at $T_s = 423 \text{ K}$.

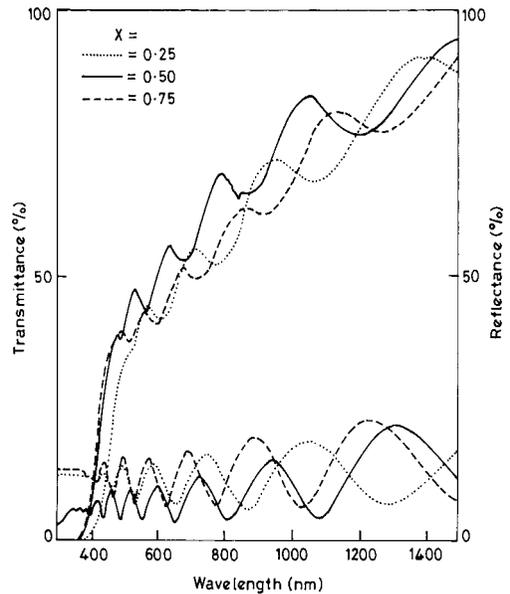


FIG. 2. Optical transmittance spectra of $(\text{V}_2\text{O}_5)_{1-x}(\text{MoO}_3)_x$ ($0 < x < 1$) films formed at $T_s = 423 \text{ K}$.

$$\alpha = \alpha_0 \exp [h\nu / E_c] \quad (2)$$

where α is the absorption coefficient, α_0 , a constant and E_c , energy. The E_c is often interpreted as the width of the localized states associated with the amorphous state in the bandgap of the material. This exponential behaviour of the absorption coefficient with photon energy in our samples may arise from the electronic transitions between localized states, which have tailed off in the bandgap. The density of these states falls off exponentially with energy, which is in consistence with the theory of Tauc.⁶ However, Dow and Redfield⁷ believe that the exponential dependence of absorption coefficient on energy may arise from the random fluctuations of the internal fields associated with the structural disorder in many amorphous materials. The width of the localized states (band tail energy or Urbach energy) (E_c), is estimated from the slopes of $\ln \alpha$ vs $h\nu$ plots of $(V_2O_5)_{1-x}-(MoO_3)_x$ films. The evaluated Urbach energy values were found to be in the range 0.4–0.31 eV. These results are consistent with the reported values of amorphous V_2O_5 thin film bronzes.^{8,9} The Urbach energy values were found to be slightly decreasing with increase in the composition of x from 0.0 to 1.0.

For an incident photon energy greater than the bandgap and above the exponential tail, the optical absorption follows a power law:

$$\alpha h\nu = B (h\nu - E_g)^n \quad (3)$$

where B is constant, E_g , the bandgap of the material and n , the exponent. The exponent n determines the type of electronic transitions causing the absorption and can take the values 1/2, 3/2, 2 and 3 for direct allowed, direct forbidden, indirect allowed and indirect forbidden transitions, respectively. The value of optical energy for different compositions has been calculated by extrapolating the straight line parts of the curves $(\alpha h\nu)^{1/n} = 0$. The value of optical bandgap for V_2O_5 ($x = 0$) for indirect allowed ($n = 2$) and direct forbidden ($n = 3/2$) transitions is found to be 2.1 and 2.3 eV, respectively. However, the fundamental absorption edge in our V_2O_5 thin films was found to give a better fit for the exponent $n = 3/2$ representing transfer of electronic charge from O (2p) to V (3d) band following a process of direct forbidden transitions. This is in consistence with the values reported by several authors.^{10,11} The optical bandgap evaluated for MoO_3 thin films ($x = 1$) for direct allowed ($n = 1/2$) and indirect allowed ($n = 2$) transition is found to be 3.16 and 2.76 eV, respectively, which are in good agreement with the reported values.¹²

The optical transmission spectra of $(V_2O_5)_{1-x}-(MoO_3)_x$ films where $x = 0.25, 0.5$ and 0.75 are shown in Fig. 2. The shift in the fundamental absorption edge towards lower wavelength side was clearly observed with increasing x from 0.0 to 1.0. For the films in the intermediate composition range the absorption data gave a better fit for the exponent $n = 2$ suggesting indirect transition. The plots of $(\alpha h\nu)^{1/2}$ vs $h\nu$ are shown in Fig 3. The estimated optical bandgaps from the plot of $(\alpha h\nu)^{1/2}$ vs $h\nu$ were 2.2 (for $x = 0.25$), 2.45 (for $x = 0.5$) and 2.6 eV(for $x = 0.75$). The optical bandgap in general (considering the indirect transitions) increased with increasing x from 0.0 to 1.0.

The room-temperature electrical conductivity of $(V_2O_5)_{1-x}-(MoO_3)_x$ ($0 \leq x \leq 1$) films was studied by four-probe technique. The variation of electrical conductivity with composition is shown in Fig. 4. The electrical conductivity of V_2O_5 films ($x = 0$) was about $6 \times 10^{-3} \text{ ohm}^{-1}\text{cm}^{-1}$. It

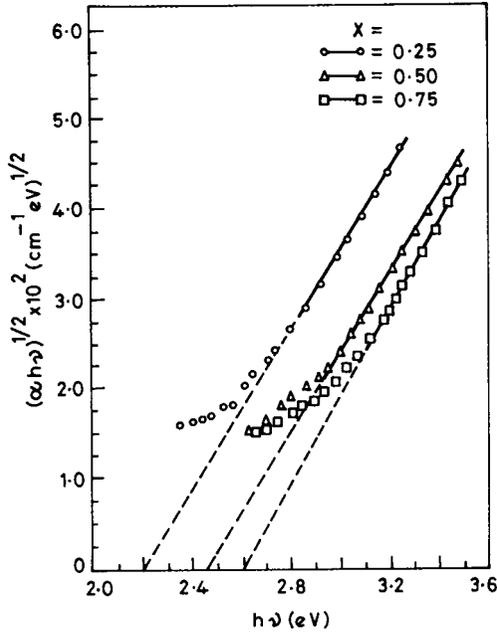


FIG. 3. Plots of $(\alpha h\nu)^{1/2}$ vs $h\nu$ for $(V_2O_5)_{1-x}-(MoO_3)_x$ ($0 < x < 1$) films.

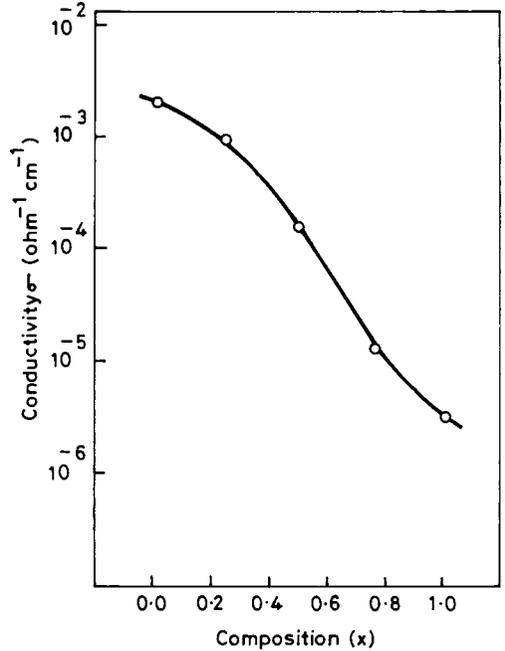


FIG. 4. Variation of DC conductivity with composition for $(V_2O_5)_{1-x}-(MoO_3)_x$ ($0 \leq x \leq 1$) films.

decreased with increase in the composition of x from 0.0 to 1.0. The number of V^{4+} ions is induced by the presence of Mo^{6+} ions and decrease with increase in the MoO_3 content. The interference of the nonperiodic coulmbic field produced by Mo^{6+} will dominate with increase in molybdenum content in V_2O_5 . In turn, this interference may lead to decrease in the number of V^{4+} ions when compared with the number of Mo^{6+} ions which is responsible for decrease in electrical conductivity with increase in Mo concentration of $(V_2O_5)_{1-x}-(MoO_3)_x$ thin films. The interference of the Coulomb fields may not be significant at lower concentration of molybdenum in $(V_2O_5)_{1-x}-(MoO_3)_x$ solid solution. The distance between Mo^{6+} ions may also be large which shows the weak dependence of conductivity on the composition at lower concentrations.^{13,14} The d band in V_2O_5 - MoO_3 may have an appreciable electron density at lower concentrations which further decreases as molybdenum concentration increases. The variation in DC electrical conductivity of $(V_2O_5)_{1-x}-(MoO_3)_x$ films was studied in the temperature range 300–500 K. It is observed that the DC electrical conductivity is temperature dependent.

Figure 5 shows the plots of $\log \sigma$ vs $T^{-1/4}$. The $T^{-1/4}$ behaviour of the electrical conductivity is explained by the temperature dependence of individual transition rates, assisted by multiphonon interactions. The weak dependence of conductivity on temperature may be attributed to the freezing out of the multiphonon process as T decreases.¹⁵ The observed nonactivated temperature dependence of DC conductivity can be a manifestation of multiphonon hopping between the localized states. Triberis and Friedman^{16,17} have reported the temperature dependence of conductivity for small polaron hopping for many disordered amorphous oxide systems. They have also applied percolation theory¹⁸ to the high temperature multiphonon-assisted small polaron hopping regime.

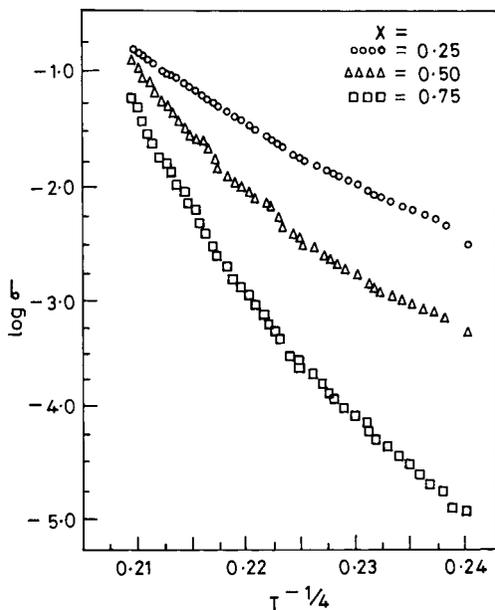


FIG. 5. Plots of $\log \sigma$ vs $T^{-1/4}$ for $(V_2O_5)_{1-x}-(MoO_3)_x$ ($0 < x < 1$) films.

The most interesting result is the observation of $T^{-1/4}$ -dependent conductivity on the few phonon at low temperature and multiphonon at high temperature. We have also observed in our samples that the conductivity obeys $T^{-1/4}$ law. It is also observed that the activation energy decreases with decrease in temperature.

4. Conclusions

Thin films of $(V_2O_5)_{1-x}-(MoO_3)_x$ ($0 \leq x \leq 1$) were prepared by electron beam evaporation technique in an oxygen partial pressure of 2×10^{-4} mbar and at a substrate temperature of 423 K. The optical absorption data for V_2O_5 (when $x = 0$) films showed a better fit for the exponent $n = 3/2$ suggesting direct forbidden transition with an evaluated bandgap of 2.3 eV, whereas for MoO_3 (where $x = 1$) films the data gave a better fit to the exponent $n = 1/2$ suggesting direct allowed transition with an evaluated bandgap of 3.16 eV. In the intermediate composition, i.e. for $x = 0.25$, 0.50 and 0.75, the absorption data showed a better fit for the exponent $n = 2$ suggesting indirect transition with an evaluated bandgaps of 2.2, 2.45 and 2.6, respectively. The optical bandgap increased with increasing x from 0.0 to 1.0 and showed a curvilinear behaviour. The electrical conductivity decreased with increase in the composition of x . The temperature dependence of electrical conductivity obeys $T^{-1/4}$ law.

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