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Electrical and optical properties of molybdenum trioxide thin films

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Abstract. Infrared spectra of vacuum-deposited molybdenum trioxide thin films have been studied. The variation of electrical conductivity with temperature for different thicknesses of films has been investigated. Electrical conductivity of the films as a function of time of UV irradiation was found to increase initially, then decreased rapidly and reached a steady value. It increased and reached a steady value with time when irradiation was cut-off.

Keywords. Molybdenum trioxide; thin films; IR spectra; activation energy; UV irradiation.

1. Introduction

Molybdenum trioxide (MoO_3) is a transition metal oxide having a number of electrical and optical properties. Lampert (1984) reviewed numerous inorganic and organic electrochromic materials in the context of developing a film-based optical shutter for energy-efficient windows. Thin films of MoO_3 can be used in electronic information displays and colour memory devices. The last decade saw extensive electrical and optical investigation of electrochromic materials (Yoshimura *et al* 1983; Donnadieu and Davazoglou 1986; Davazoglou and Donnadieu 1987; Davazoglou *et al* 1987).

Coloured centres in thin films of MoO_3 can be formed by UV light irradiation. Deb and Chopoorian (1966) reported that the colour centres formed as a result of free electrons being trapped at oxygen ion vacancies. The mechanism behind this colouration is not yet well understood. In this paper we report IR spectra, activation energy of MoO_3 films and variation of its electrical conductivity during and after UV irradiation.

2. Experimental

The films of MoO_3 were prepared by physical vapour deposition using a thermal evaporation plant (Hind Hivac, model:12 A4) which provided a base pressure of 4×10^{-4} Pa. MoO_3 (99·9% pure) (Goodfellow, UK) was evaporated from a tantalum boat on to the mylar and glass substrates kept above the source. A constant rate of evaporation was maintained which was monitored by a quartz crystal thickness monitor having an accuracy of 1 nm. The value thus obtained by thickness monitor was counterchecked by using the Fizeau fringe technique (Chopra 1969). MoO_3 films on mylar substrate was used for IR studies (IR spectrophotometer, Shimadzu IR 470). Keithley 617 programmable electrometer was used for studying d.c. electrical conductivity by varying temperature of the films on glass substrate having a fixed bias voltage of 0.8 V. The d.c. electrical conductivity of the film on a glass substrate was also measured using an electrometer by applying a fixed bias voltage of 0.8 V to the film at room temperature during and after UV irradiation.

3. Results and Discussion

The transmission spectra of MoO_3 film formed on mylar (polyethylene terephthalate) substrate were recorded in IR (4000 to 400 cm^{-1}) region by an infrared spectrophotometer with a similar uncoated mylar as a reference. Most of the molecular vibrational frequencies were present in this region. Figure 1 gives the IR spectra of MoO_3 film of thickness 134 nm on a mylar sheet. The notable features of the MoO_3 spectra are the weak transmission bands observed at 580 and 780 cm^{-1} and the strong transmission bands at 468, 890 and 1000 cm^{-1}. These values are in agreement with the reported peaks at 468, 620, 810, 890 and 1020 cm^{-1} (Eda 1989; Anwar *et al* 1990).

Figure 2 shows the temperature dependence of d.c. electrical conductivity (σ) of the films when a fixed bias voltage of 0.8 V is applied for three different thicknesses 165, 187 and 208 nm respectively. Assuming an Arrhenius-type relation,

$$\sigma = \sigma_0 \exp(-\Delta E/kT),$$

where σ_0 is the pre-exponential factor and k, the Boltzmann constant and ΔE, the thermal activation energy. The plot $\ln \sigma$ vs $(10^3/T)$ exhibits two straight line regions of different activation energies of conductivity for the same MoO_3 sample. The value of activation energy ΔE_1 in the lower temperature region as well as activation energy ΔE_2 in the higher temperature region show slight change with thickness of the film.

The variation of d.c. electrical conductivity as a function of irradiation time of MoO_3 thin film of thickness 208 nm is shown in figure 3. Here the d.c. electrical conductivity was measured while increasing the irradiation time. It was seen that the conductivity increased initially, and then decreased much faster. After 30 min, it reached almost a steady value. Due to colouration, the films changed from greenish-blue to dark blue in colour. Figure 4 gives the variation of conductivity as a function

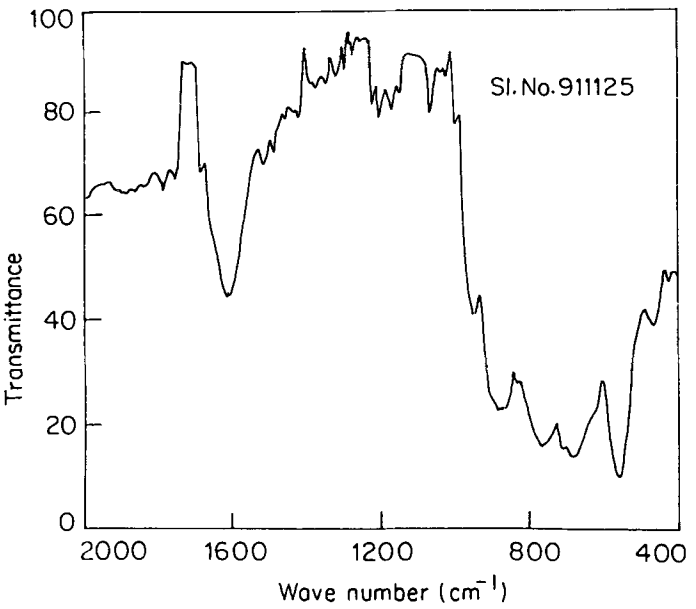

Figure 1. Infrared spectra of MoO_3 thin films of thickness 134 nm.

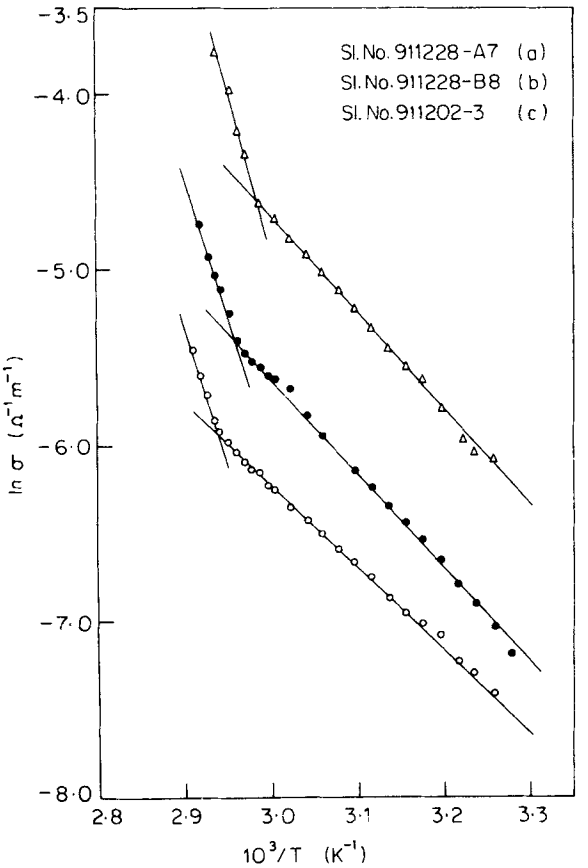

Figure 2. Temperature variation of d.c. electrical conductivity of MoO_3 films of thicknesses (**a**) 165 nm, (**b**) 187 nm and (**c**) 208 nm.

Table 1. Activation energies ΔE_1 and ΔE_2 obtained for different thicknesses and MoO_3 films.

Sample No.	Thickness (nm)	ΔE_1 (305–338 K) (eV)	ΔE_2 (338–348 K) (eV)
911228-A7	165	0·46	1·35
911228-B8	187	0·43	1·32
911202-3	208	0·41	1·29

of time after terminating the irradiation. It was found that conductivity increased much faster at the beginning and reached a steady value.

The conductivity of transition metal oxides was due to the hopping of small polarons (Austin and Mott 1969). When we irradiated MoO_3 thin film with UV light, initially its conductivity increased. As a result of irradiation of the film, the phonons took the energy which resulted in the electron-phonon interaction, so that the effective mass of the polaron increased. Since the effective mass increased, the resistivity also

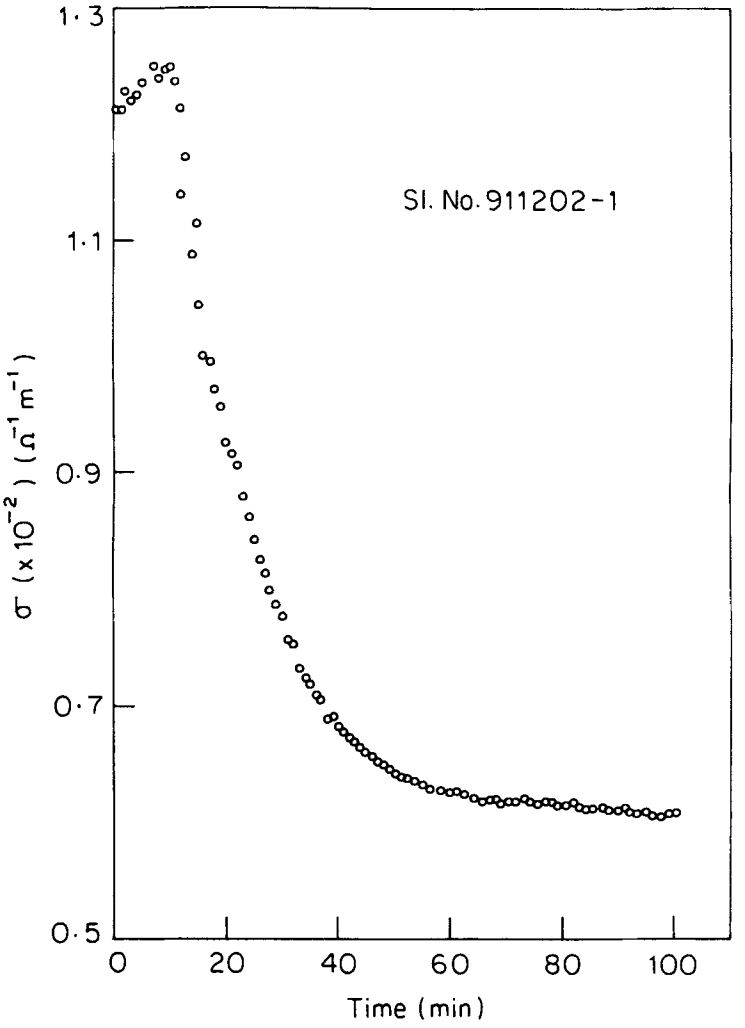

Figure 3. Variation of d.c. electrical conductivity as a function of time while UV irradiating MoO_3 films of thickness 208 nm.

increased, which in turn decreased its conductivity. After some time the electron-phonon interaction reached an equilibrium. As a consequence, a steady value of conductivity was reached. From figure 3 it is seen that cutting-off the irradiation terminated electron-phonon interaction. The conductivity rapidly increased and reached a steady value. This suggests that the electrical properties of MoO_3 are sensitive to high energy electromagnetic radiation and time of exposure.

4. Conclusion

From IR spectrum it is clear that the film formed was MoO_3. The film was capable of colouring by UV irradiation. Activation energy of conductivity for MoO_3 thin film varied with thickness of the film. The d.c. electrical conductivity of MoO_3 film

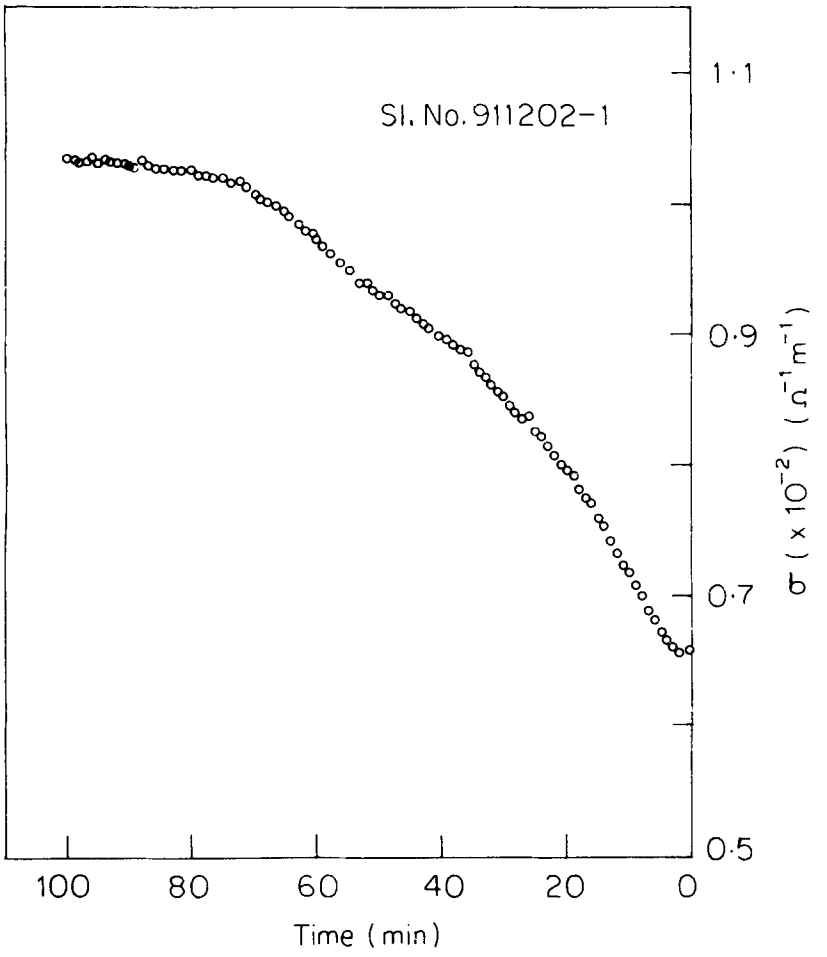

Figure 4. Variation of d.c. electrical conductivity as a function of time after terminating UV irradiation of MoO_3 film of thickness 208 nm.

initially increased and then decreased and finally reached a steady value during UV irradiation. It increased rapidly and reached a steady value when the irradiation was stopped.

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