

CHAPTER VI

ELECTRICAL AND OPTICAL STUDIES OF MIXED OXIDE

SYSTEMS OF  $\text{MoO}_3$  AND  $\text{V}_2\text{O}_5$  THIN FILMS.



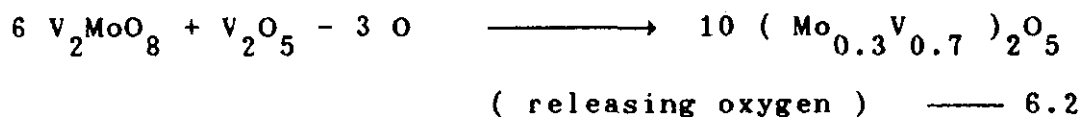
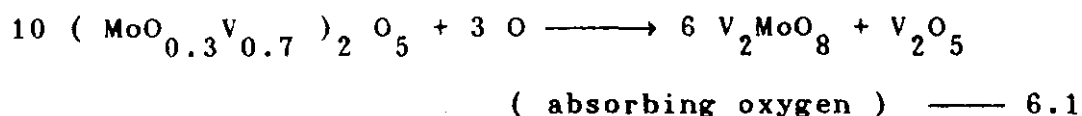
### 6.1. Introduction.

Electronic conduction in amorphous solids has received considerable attention in recent years because of its importance in electronic devices. The dielectric films are important in the manufacture of semiconductor devices and integrated circuits. Charge transport measurements in semiconductors and insulators have been of considerable interest recently, because they can provide information about electronic structure of amorphous material. When two suitable oxides are mixed together appropriate impurities may be regarded as being added. The study of electrical conductivity of mixed thin films of  $\text{MoO}_3\text{-V}_2\text{O}_5$  has been made and reported here. Bursill<sup>1</sup> reports that  $\text{MoO}_3$  decomposes to lower oxides when heated. In evaporated  $\text{MoO}_3$  films, the predominant defects are oxygen vacancies in large concentrations<sup>2</sup>.

Anwar and Hogarth<sup>3</sup> have studied various properties of mixed oxide systems of  $\text{MoO}_3\text{-In}_2\text{O}_3$  and  $\text{MoO}_3\text{-SiO}$  thin films. Neena Chopra et al.<sup>4</sup> have reported electrical and optical properties of amorphous films of  $\text{V}_2\text{O}_5\text{-TeO}_2$  system by varying molar percentage composition



of each oxide . Khan and Hogarth<sup>5,6</sup> have investigated electrical and optical properties of  $V_2O_5-B_2O_3$  mixed oxide amorphous thin films. Kang et al.<sup>7</sup> have studied mixed oxide system of  $V_2O_5-MoO_3$ . Several authors<sup>8,9</sup> have reported the type of reaction of  $V_2O_5-MoO_3$  as follows:



ie,

6.1) During absorption of atomic oxygen the  $V_2O_5$  and  $V_2MoO_8$  phases coexist;

6.2) Under desorption of oxygen the  $( Mo_{0.3}V_{0.7} )_2 O_5$  phase is formed.

These are the reversible solid state reactions in the case of  $MoO_3-V_2O_5$  mixed oxide system.

The study of optical properties of evaporated thin films of  $MoO_3-V_2O_5$  system has been made. The optical absorption is a useful method for the investi-



gation of optically induced transition and for the provision of information about the band structure. 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 theory proposed by Davis and Mott<sup>10</sup> and Tauc et al.<sup>11</sup> for amorphous materials.

## 6.2 Experiment

Analytical reagent grade  $\text{MoO}_3$  and  $\text{V}_2\text{O}_5$  powder of various molar concentrations have been taken in an agate mortar and ground well to get fine powder of the mixed oxide, which is then pelletised. These pellets have been used for EBG evaporation in a vacuum coating unit at a pressure of  $8 \times 10^{-5}$  mbar on to cleaned glass and mylar substrates. The substrates have been kept at a temperature of  $100^\circ\text{C}$ . Thickness of the films has been monitored on a thickness monitor and accurately measured by Tolansky method. Films of 90%  $\text{MoO}_3$ : 10%  $\text{V}_2\text{O}_5$ , 75%  $\text{MoO}_3$ : 25%  $\text{V}_2\text{O}_5$ , 60%  $\text{MoO}_3$ : 40%  $\text{V}_2\text{O}_5$ , 50%  $\text{MoO}_3$ : 50%  $\text{V}_2\text{O}_5$  have been used for optical and electrical investigations. In



the case of optical studies UV-visible and IR spectra have been taken. In the case of electrical studies coplanar electrical conductivity variation of these films have been made using the Keithley electrometer.

### 6.3. Results and discussion

The electrical studies have been made for the films of different percentage of molar concentrations of the  $\text{MoO}_3\text{-V}_2\text{O}_5$  systems. Figure 6.1 gives the plot of  $\ln\sigma$  vs  $10^3/T$  of 90%  $\text{MoO}_3$ :10%  $\text{V}_2\text{O}_5$ , 75%  $\text{MoO}_3$ :25%  $\text{V}_2\text{O}_5$  and 60%  $\text{MoO}_3$ :40%  $\text{V}_2\text{O}_5$ , 50%  $\text{MoO}_3$ :50%  $\text{V}_2\text{O}_5$  films of almost the same thickness (190- 210 nm). The increase in conductivity and decrease in activation energy when the molar percentage of  $\text{V}_2\text{O}_5$  is increased in  $\text{MoO}_3$  is attributed to the increasing concentration of oxygen vacancies and vanadium interstitials.

The value of activation energy in the low temperature region is due to the electronic hopping process which dominates low temperature conduction in the samples. The straight line part of the curve in the high temperature region corresponds to activation



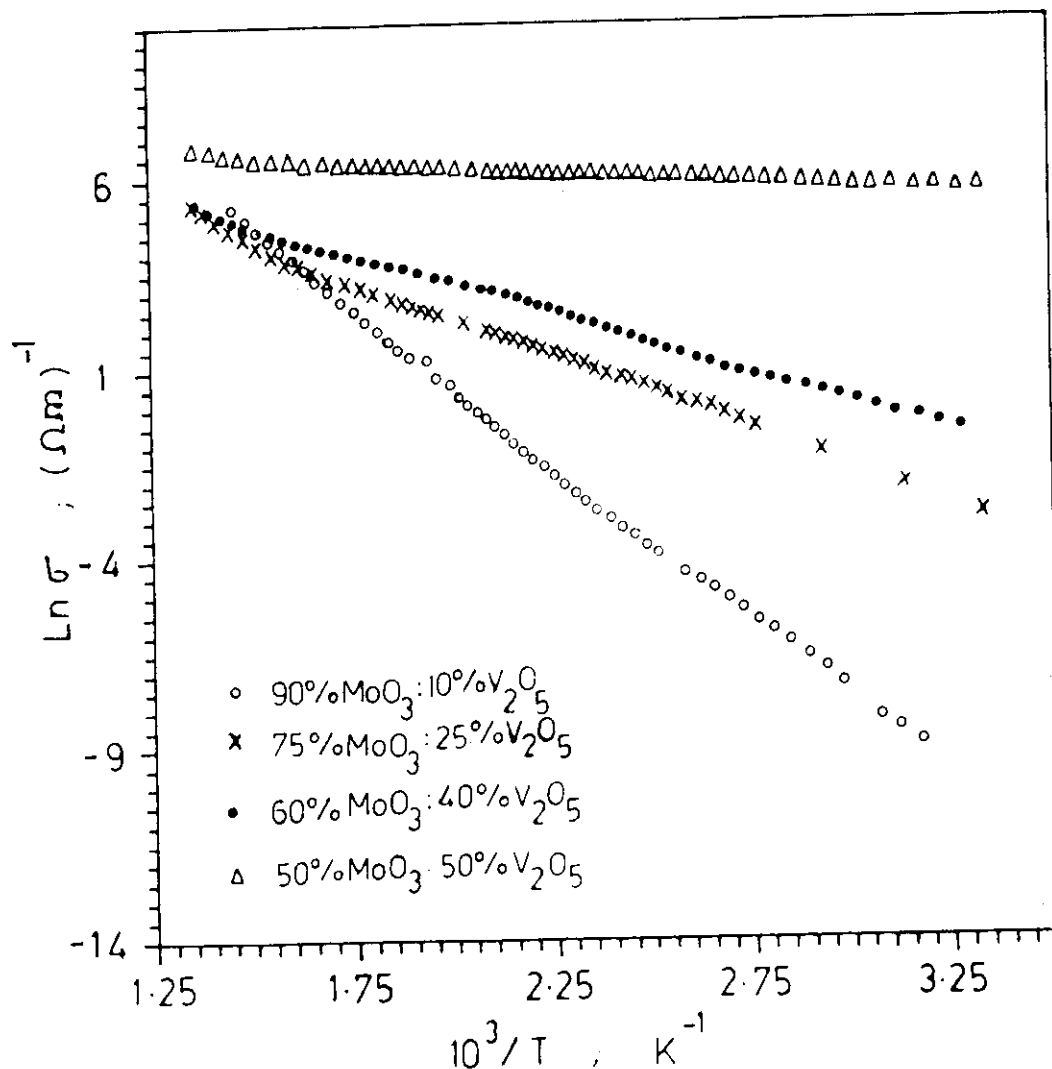


Fig.6.1. Plot of  $\log \sigma$  vs  $1000/T$  for  $\text{MoO}_3\text{-V}_2\text{O}_5$  system in different molar concentrations. Thickness of the films is between 190-200 nm.

energy. The conduction at high temperature is believed to be a transition from hopping conduction to a free band conduction. The gradual transition from hopping to free band conduction may be due to overlapping of localised levels and free bands.

In amorphous materials both free band and hopping conduction may take place as in crystalline materials<sup>12</sup>. These conduction mechanisms may be separated experimentally by operating in the appropriate temperature ranges.

Table 6.1. Activation energy of mixed systems of  $\text{MoO}_3$  and  $\text{V}_2\text{O}_5$  in various molar concentrations.

Sample	90% $\text{MoO}_3$ : 10% $\text{V}_2\text{O}_5$	75% $\text{MoO}_3$ : 25% $\text{V}_2\text{O}_5$	60% $\text{MoO}_3$ : 40% $\text{V}_2\text{O}_5$	50% $\text{MoO}_3$ : 50% $\text{V}_2\text{O}_5$
Activation energy(eV)	0.716	0.338	0.263	0.029

As the value of  $\text{V}_2\text{O}_5$  is increased in  $\text{MoO}_3$  its activation energy decreases, which is shown in the table 6.1. In other words, when the content of  $\text{V}_2\text{O}_5$  is



increased, the conductivity increases. This is explained in the following manner. When the content of  $V_2O_5$  increases the concentration of trapping centres of  $MoO_3$  decreases and the conductivity of the mixed film increases.

The transmittance spectra for  $MoO_3-V_2O_5$  system taken using UV-visible spectrophotometer are shown in figure 6.2. Data from figure 6.2 are used for plotting  $(\alpha h\nu)^{1/n}$  vs  $(h\nu)$  in accordance with equation 4.12 (chapter IV, section 4.4.2) where  $n = 2, 3, 1/2$ , and  $3/2$  in accordance with the transition is allowed or forbidden.  $n=2$  gives maximum points on the best fit line which is shown in figure 6.3. The optical band gaps have been evaluated by extrapolation of the plot to  $(\alpha h\nu)^{1/2} = 0$  and are collected in table 6.2. When the molar percentage of  $V_2O_5$  is increased in the mixed system there is an overall disorder in the system. Vanadium ions may be incorporated in an  $MoO_3$  lattice. The presence of interstitial vanadium ions in the  $MoO_3$  lattice may cause a decrease in the optical band gap. This result supports the idea that in  $MoO_3-V_2O_5$  films,





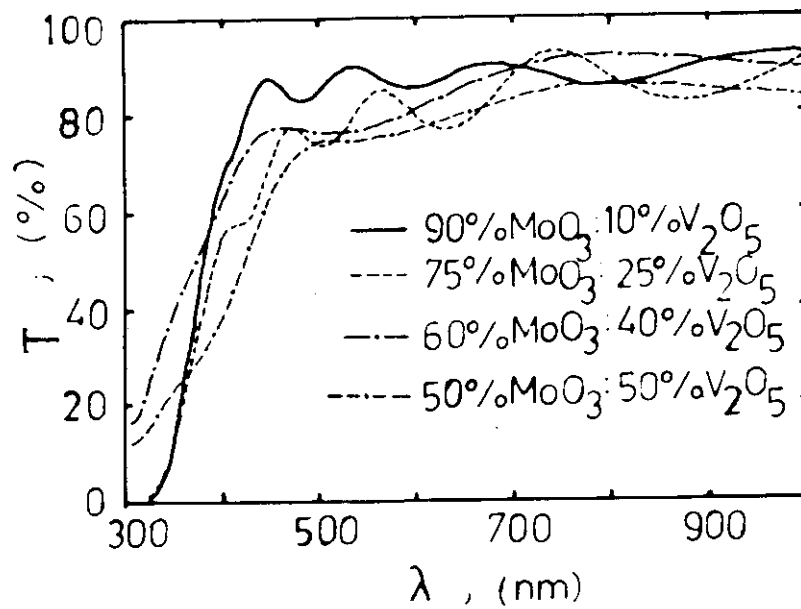


Fig.6.2. Transmittance spectra of  $\text{MoO}_3\text{-V}_2\text{O}_5$  mixed system in different molar concentrations as a function of wavelength. Thickness of the film is between 190-210nm.

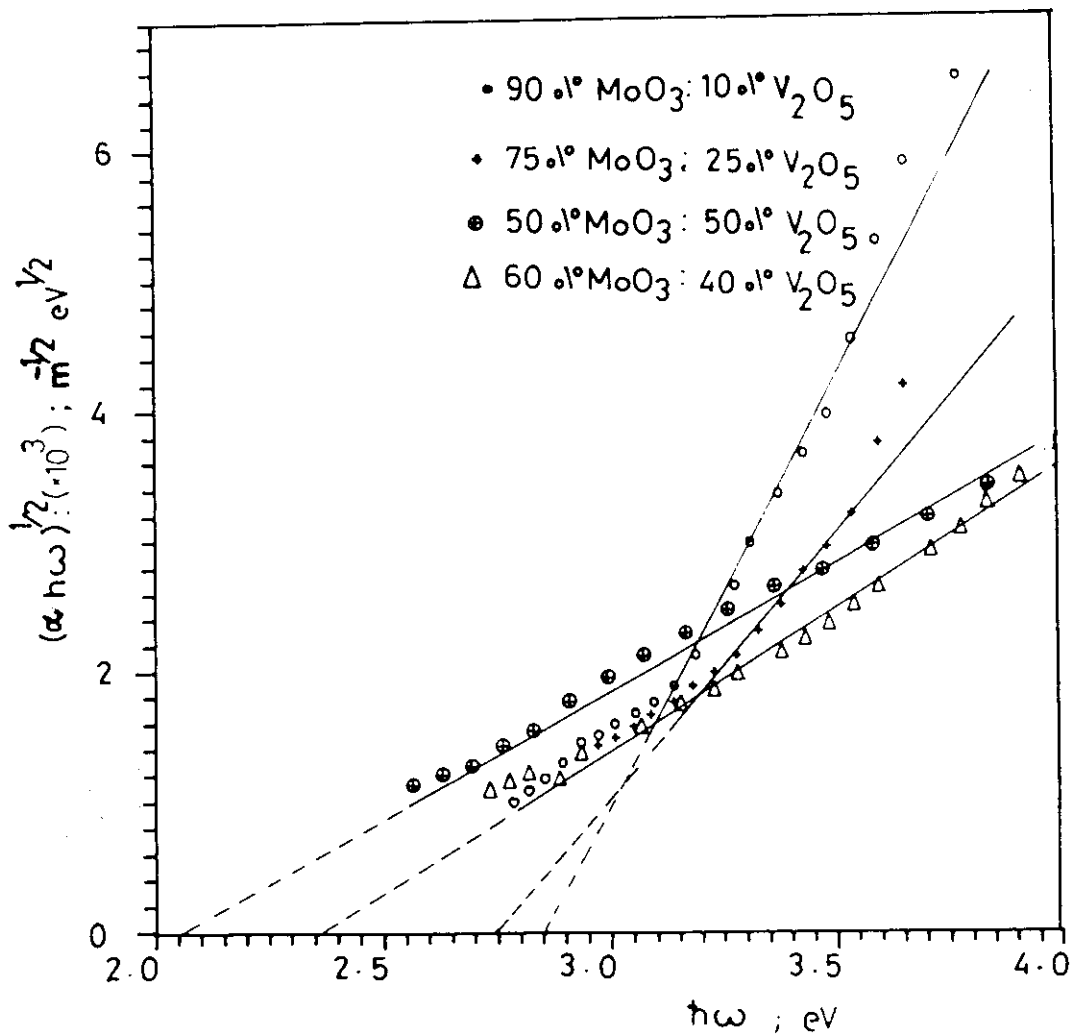


Fig.6.3. Plot of  $(\alpha h\omega)^{1/2}$  vs.  $(h\omega)$  for different molar concentrations of MoO<sub>3</sub> and V<sub>2</sub>O<sub>5</sub> mixed system. The thickness of the film is 190-210nm.

indirect transitions occur with much stronger absorption because the  $k$  vector is not uniquely defined in disordered materials.

The value of refractive index ( $n$ ) and extinction coefficient ( $k$ ) for different wavelengths ( $\lambda$ ) are calculated using the equations 4.9 and 4.4 (Chapter IV, section 4.2) respectively. Figure 6.4 shows the variation of  $n$  and  $k$  with  $\lambda$  of  $\text{MoO}_3\text{-V}_2\text{O}_5$  mixed system.  $n$  decreases exponentially with  $\lambda$  is in agreement with that in the cases of  $\text{MoO}_3$  and  $\text{V}_2\text{O}_5$  separately.

Table 6.2 The optical band gap of mixed oxide systems of  $\text{MoO}_3$  and  $\text{V}_2\text{O}_5$  in various molar concentration.

Sample	90% $\text{MoO}_3$ : 10% $\text{V}_2\text{O}_5$	75% $\text{MoO}_3$ : 25% $\text{V}_2\text{O}_5$	60% $\text{MoO}_3$ : 40% $\text{V}_2\text{O}_5$	50% $\text{MoO}_3$ : 50% $\text{V}_2\text{O}_5$
Optical band gap (eV)	2.856	2.748	2.354	2.123

IR spectra of the films of various concentration of the mixed oxide coated on mylar are shown in figure 6.5. IR spectra of  $\text{MoO}_3\text{-V}_2\text{O}_5$  system



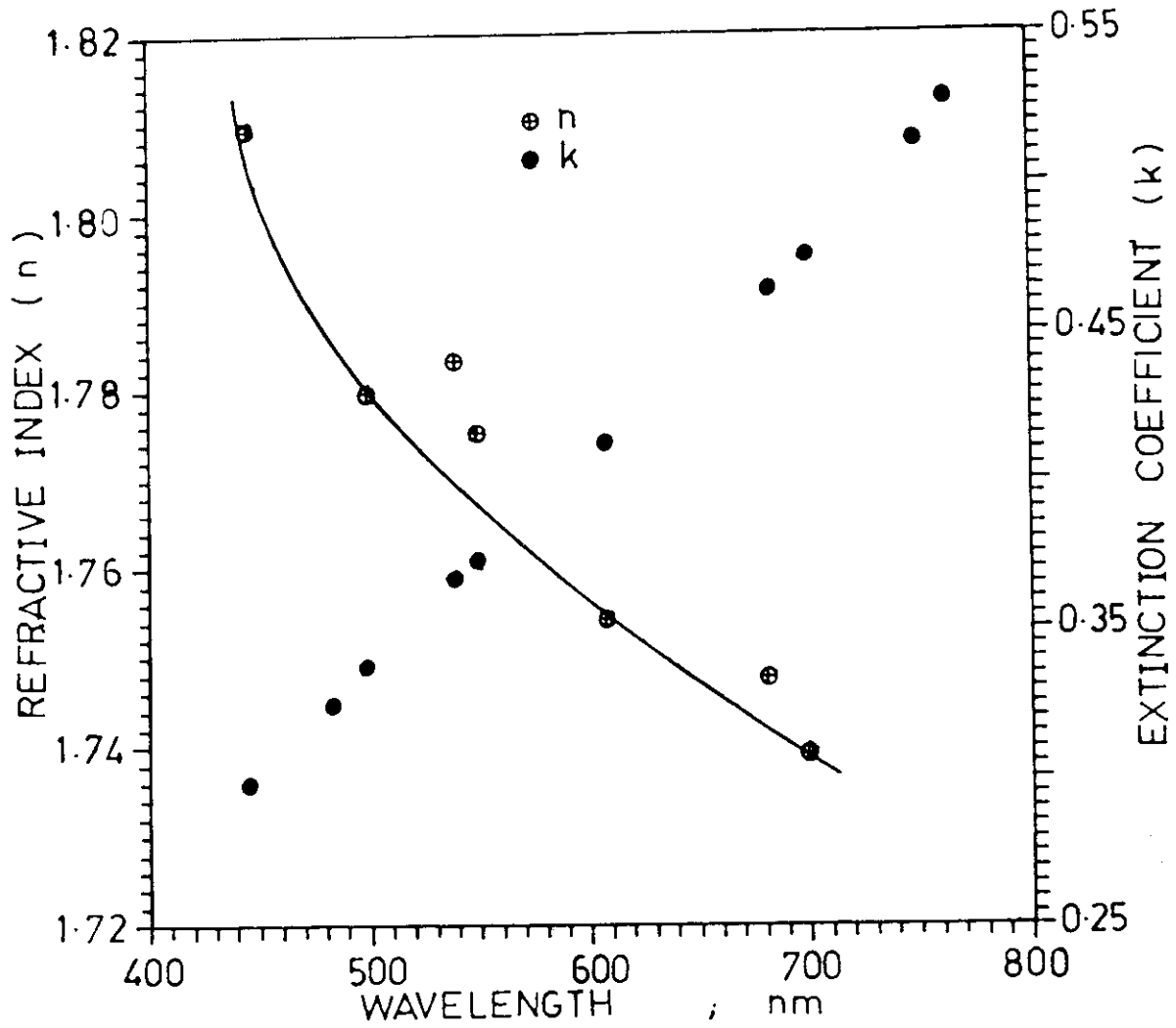


Fig.6.4. Plot of  $n$  and  $k$  vs. wavelength ( $\lambda$ ) for 90% $\text{MoO}_3$ :  
10%  $\text{V}_2\text{O}_5$  mixed system of thickness 194nm.

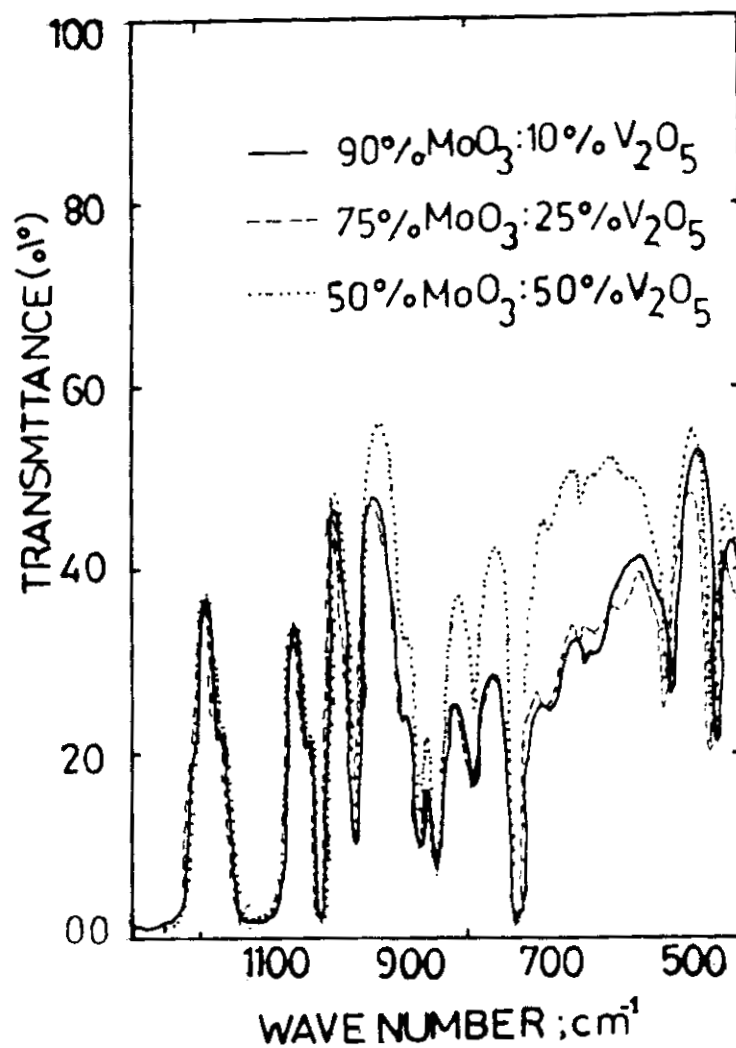


Fig.6.5. IR spectra of MoO<sub>3</sub>-V<sub>2</sub>O<sub>5</sub> mixed systems in different molar concentrations and thickness of the range of 190-210.

shows that changes in property with composition may be due either to the incorporation of vanadium ion in  $\text{MoO}_3$  lattice or to the change in  $\text{V}_2\text{O}_5$  composition. The bands at 554 and 576  $\text{cm}^{-1}$  are not present in pure  $\text{MoO}_3$  sample; but appear in the sample containing  $\text{V}_2\text{O}_5$ . The shift in band towards lower frequency can be explained by assuming that when the molar percentage of  $\text{V}_2\text{O}_5$  is increased in the mixed system of  $\text{MoO}_3-\text{V}_2\text{O}_5$ , some vanadium ions are incorporated in a molybdenum lattice, which may cause a shift in the band to lower frequency.

#### 6.4 Conclusion.

From the present work the optical absorption edge of amorphous  $\text{MoO}_3-\text{V}_2\text{O}_5$  film is observed to be governed by direct forbidden transition. The optical band gap varies with the variation of molar concentration of the mixed oxide. The activation energy varies with the variation of molar concentration of the mixed oxide.



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## CHAPTER VII

### DESIGN AND FABRICATION OF ELECTROCHROMIC WINDOWS USING MOLYBDENUM TRIOXIDE AND VANADIUM PENTOXIDE





## 7.1. Introduction

Electrochromic (EC) window changes its transmittance electronically. There are various types of dynamic adjustable optical windows which are usually called "smart window". The optical modulation occurs through the reversible formation of an intermediate compound by the insertion or extraction of ions and electrons. The general configurations of EC windows can be represented as<sup>1</sup>

i) lamination type :

<substrate / TCO / EC / ELT / CE / TCO / substrate>

ii) all-solid type :

<substrate / TCO / EC / ELT / CE / TCO>

where TCO is the transparent conducting oxide, EC the electrochromic layer, ELT is an electrolyte and CE is counter electrode layer required for ion storage. In the lamination type two substrates are laminated by electrolyte. In the all-solid type, five layers are formed on a single substrate. Transmittance is changed due to the application of voltage between the two TCOs.



$\text{MoO}_3$  and a combination of  $\text{MoO}_3$  and  $\text{V}_2\text{O}_5$  based EC systems are described.

## 7.2. Operating principle.

Smart window comprises of two transparent conducting layers, required for applying the electric field. Also the intervening materials serve as active electrochromic layer, ion conductor, and ion storage mechanism.

The ions needed in the electrochromic reaction are provided by the ion storage and are injected into, or withdrawn from, the electrochromic layer via the ion conductor<sup>2,3</sup>. For liquid electrolyte devices the electrolyte can serve both for storage and conduction of ions, while in all-solid-state devices the ion conductor has to be an appropriate dielectric and the ion storage is another electrochromic layer. One may also combine the conductor and ion storage media into one layer. It



is possible to include the ion storage medium and instead rely on a replenishment of  $H^+$  ions originating from the dissociation of water molecules diffusing in from an ambience with controlled humidity<sup>4-7</sup>. This requires a substantial atomic permeability of the outer electrode.

The transparent electrode at the glass interface is a high-performance transparent infrared-reflector<sup>8-10</sup>, such as films of the doped oxide semiconductors  $In_2O_3:Sn$ ,  $SnO_2:F$ ,  $SnO_2:Sb$  or  $Cd_2SnO_4$ . The outer electrode is of different kinds: for liquid electrolytes it is a bulk material which is sufficiently small so that the overall transparency is not severely affected, while for an all-solid-state device it is a transparent infrared-reflector which is produced without deterioration of the electrochromic property for the underlying layers.

The radiative properties of smart windows are switchable between different states. The nature of this switching is different depending on the basic requirement of the window. The main goal of a window is



to achieve control of the energy flowing through the window aperture.

Figure 7.1 illustrates idealized case for energy control. For this it is important that the solar spectrum extends over the 0.3-3  $\mu\text{m}$  range, while the eye is sensitive only in the 0.4-0.7  $\mu\text{m}$  interval. The relevant spectra are shown by the shaded area in figure 7.1. Almost 50% of the total solar energy comes as infrared radiation. Hence it is possible to change the energy without affecting the luminous transparency. The changed infrared transmittance can be achieved in two ways: by modulating the infrared reflectance (upper part of figure 7.1) or by modulating the infrared absorbance (lower part of figure 7.1).

The thermal properties of the windows are governed by reflectance in the 3-100  $\mu\text{m}$  range. The all-solid-state concept, which is preferable in a window, includes an extended outer transparent conductor which provides low thermal emittance. In many cases this is the desired property. If instead a high thermal emittance is required, this can be obtained by applying

