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Electrical conduction through MIM structures of evaporated V_2O_5 and V_2O_5/B_2O_3 amorphous thin films

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The electrical conduction through vacuum-evaporated thin films of V_2O_5 and V_2O_5/B_2O_3 in MIM structures has been investigated. The high-field behaviour of both types of film is in accordance with the Poole–Frenkel type of mechanism. The increase in B_2O_3 content in co-evaporated V_2O_5/B_2O_3 films results in a decrease in the conductivity of the composite films. This is attributed to the expansion of the resultant film structure due to the network-forming effect of B_2O_3. The co-evaporated thin films of V_2O_5/B_2O_3 with a molar content of B_2O_3 larger than 40% are observed to be unstable because of their hygroscopic nature.

1. Introduction

The semiconducting properties of amorphous transition metal oxides arise from hopping of unpaired electrons between transition metal ions in two different valence states [1]. Two types of localization processes occur in such materials. The first type is the result of strong interaction of unpaired electrons with the polar network leading to the formation of small polarons [2]. A polaron (an electron and its accompanying distortion) whose dimension is comparable to the lattice spacing is designated as a small polaron [3]. The second type of localization, known as Anderson localization [4], occurs due to structural disorder.

Morin [5] showed that the width of the 3d band decreases in the 3d oxide series from scandium to vanadium and it approaches zero for chromium oxide. Depending upon the width of the 3d band, conduction in these materials is attributed either to electrons in the 3d band of the transition metal or to electron transitions between cations of different valencies. The intermediate position of vanadium oxide in the series of 3d transition metal oxides has stimulated interest in their properties.

Heamers *et al.* [6] found the conduction through V_2O_5 single crystals to be due to variable range hopping between defect levels situated in the neighbourhood of the Fermi level. Koffyberg and Benko [7] showed that the activation energy for the d.c. electronic conductivity of amorphous V_2O_5 and some glasses containing V_2O_5 obeys the relation as given by Killias [8]. Sanchez *et al.* [9, 10] observed that the electrical properties of amorphous V_2O_5 obtained by splat cooling appear to be consistent with the small-polaron model of nearest neighbour hopping. Nadkarni and Shirodkar [11] have proposed that the electrical properties (d.c. as well as a.c.) of the $Al/V_2O_5/Al$ structure could be explained by considering the crystallite–crystallite interfacial Schottky-type barrier which exists because of granular nature of these films. No extensive work has been published on amorphous thin films of V_2O_5 prepared by the evaporation technique.

Most of the semiconducting glasses based on V_2O_5 contain so-called network formers such as P_2O_5 and B_2O_3. Many authors [12–18] have investigated the electronic conduction processes through V_2O_5-based glass systems. In a glass containing V_2O_5 and P_2O_5, as the oxygen ions adjacent to the vanadium ions may also have phosphorus ions as near neighbours, so the network forming may effect the conductivity [12]. Sharma *et al.* [19] were the first to investigate V_2O_5–B_2O_3 glass. They observed a decrease in electrical conductivity with increasing B_2O_3 content. Culea and Nicula [20] also studied the electrical properties of V_2O_5–B_2O_3 glasses and proposed a small polaron model for the conduction.

The transition metal ions can enter a semiconducting glass in several oxidation states. Glasses based on V_2O_5 are known to have both V^{5+} and V^{4+} ions present. For these glasses, the conduction process has been described as the motion of an electron from a V^{4+} site to a V^{5+} site where the extra electron is bound to the vanadium by the lattice polarization it induces, i.e. forms a small polaron. The electrical conductivity in such semiconducting glasses is critically dependent on the ratio of low to high oxidation states of transition metal ions present in the glass [13]. The d.c. conductivity at higher temperatures is found to be well described by

$$\sigma = \sigma_0 \exp(-W/kT) \qquad (1)$$

but below room temperature, W (the activation energy), ceases to be constant and decreases gradually as the temperature drops [14].

Here the electrical conduction through amorphous thin films of V_2O_5 and V_2O_5/B_2O_3 prepared by the thermal evaporation technique has been investigated.

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2. Experimental procedure

The samples for electrical measurements were deposited on 3 in. × 1 in. (~7.62 cm × 2.54 cm) Corning 7059 borosilicate glass slides. In order to prepare MIM sandwiches, a metal strip was evaporated as the base electrode followed by mixed oxides from separate sources as insulator using the co-evaporation technique of Hogarth and Wright [21], and finally evaporating metal for the top electrodes. The rates of evaporation and film thickness could be controlled. Six devices, each having an effective area 0.1 cm^2, were made on each substrate.

All electrical measurements were taken in a subsidiary vacuum system capable of producing a vacuum of 10^{-6} torr (1.33×10^{-4} Pa) and equipped with the necessary facilities. The device was firmly attached to the base of copper by pressure contacts, and electrical connections were made to the devices by means of copper strips joined with silver paste. A stainless steel tank incorporated into the top plate was used for low-temperature measurements by pouring liquid nitrogen into it. An insulated resistive wire made of molybdenum ribbon was inserted in the holes at the copper base and used as a heater element. The temperature measurements were made by attaching a chromel/alumel thermocouple to the substrate which was connected to a Comark electronic thermometer type 1601 Cr/A. The d.c. voltage–current characteristics were measured in a conventional manner. The circulating current was recorded by a Keithley 610C solid state electrometer.

3. Results

The $I(V)$ characteristics for evaporated V_2O_5 (300 nm) thin films is shown in Fig. 1. For low fields, the films show ohmic type of conduction whereas at higher fields they show non-ohmic behaviour. Fig. 2 shows the plot of $\log I$ against $V^{1/2}$ for the same sample as in Fig. 1. In order to calculate activation energy, electrical conductivity was plotted against inverse temperature as shown in Fig. 3 for the same sample as in Fig. 1. It can be seen that for low temperatures the activation energy is lower than at higher temperature indicating a different type of conduction process, compared to that at higher temperature.

Fig. 4 shows the $I(V)$ characteristics for 70% V_2O_5/30% B_2O_3 (300 nm) thin films prepared by the co-evaporation technique. The films show an exponential type of behaviour at higher field, whereas for lower fields their behaviour follow Ohm's law. The data of Fig. 4 replotted as $\log I$ against $V^{1/2}$ for the same sample as in Fig. 4 can be seen in Fig. 5. Fig. 6

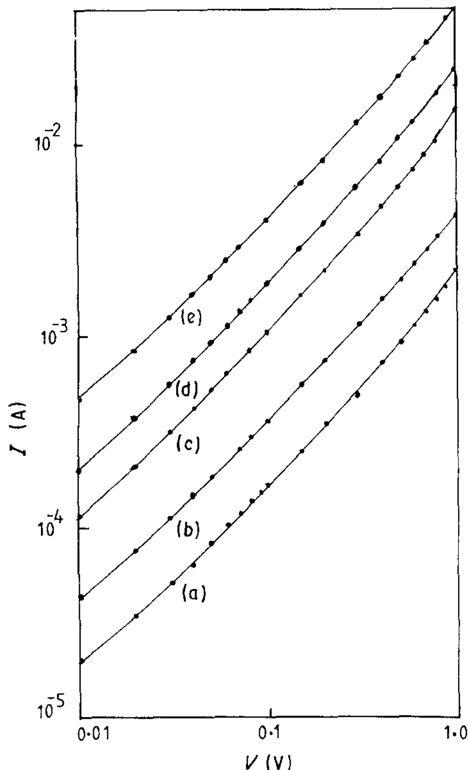


Figure 1 $I(V)$ characteristics for evaporated V_2O_5 (300 nm) thin films at different temperatures: (a) 193 K, (b) 233 K, (c) 269 K, (d) 295 K, (e) 323 K.

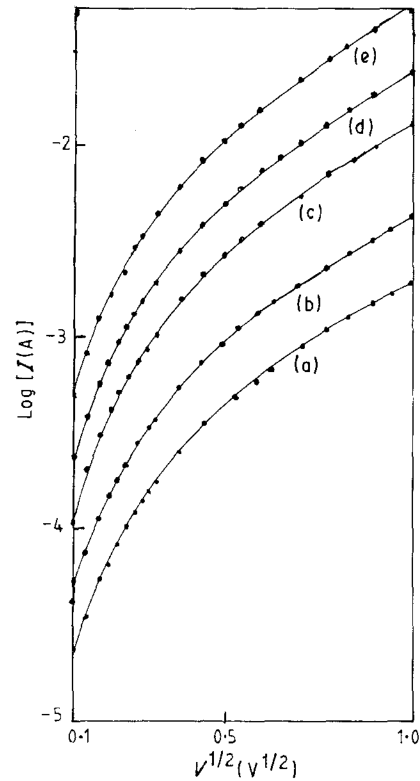


Figure 2 Data of Fig. 1 replotted as $\log I$ against $V^{1/2}$.

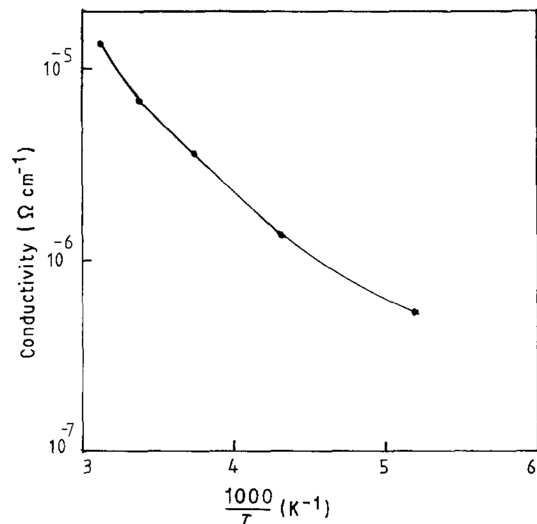


Figure 3 Conductivity plotted against inverse temperature for the same sample as in Fig. 1 at an applied voltage of 0.7 V.

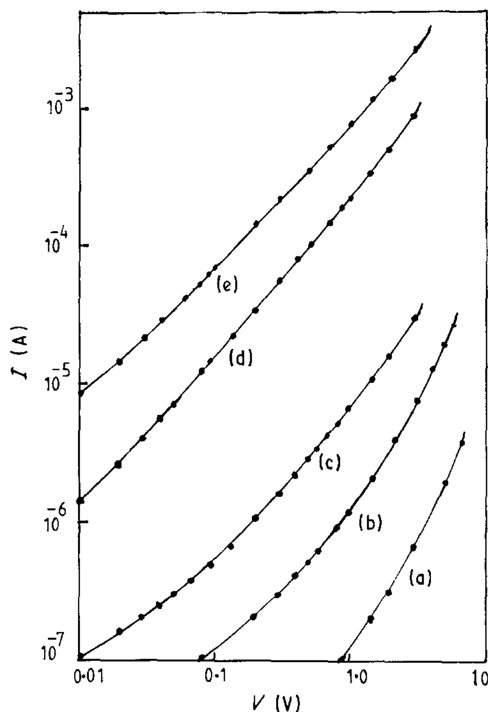
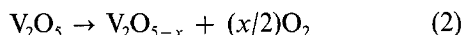


Figure 4 $I(V)$ characteristics for evaporated V_2O_5/B_2O_3 (300 nm) thin films at different temperatures: (a) 193 K, (b) 223 K, (c) 253 K, (d) 293 K, (e) 327 K.

represents the plots of log conductivity against the inverse temperature.

4. Discussion

Vanadium pentoxide is an oxygen-deficient semiconductor. The molten V_2O_5 at the temperature just above the melting point dissociates according to the reaction



$$V_2O_5 \rightarrow V_2O_{5-x} + (x/2)O_2 \qquad (2)$$

where x increases with the increasing temperature.

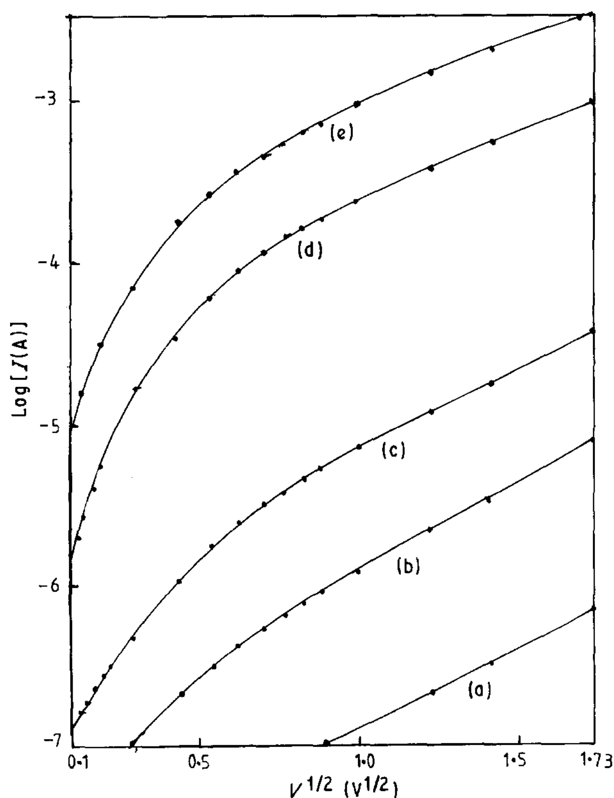


Figure 5 Data of Fig. 4 replotted as $\log I$ against $V^{1/2}$.

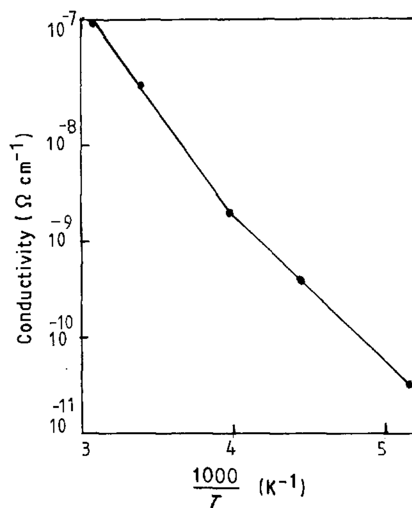
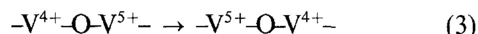


Figure 6 Conductivity plotted against inverse temperature for the same sample as in Fig. 4 at an applied voltage of 0.7 V.

For every oxygen atom evolved, two electrons are left behind. Among the many possibilities of electron behaviour, two were examined carefully: (a) the electrons are singly trapped at separate V^{5+} centres yielding two V^{4+} centres, and (b) the two electrons are trapped at one V^{5+} centre to yield one V^{3+} centre. The type (a) reaction is believed to be the most probable [22] because of the low energies involved.

Conduction in low-mobility transition metal oxides was originally considered to take place by a hopping mechanism [23]. Therefore, for V_2O_5 an electron on a V^{4+} centre will move to a V^{5+} centre, the overall mechanism being formally represented by



$$-V^{4+}-O-V^{5+}- \rightarrow -V^{5+}-O-V^{4+}- \qquad (3)$$

The localization of an electron on a V^{4+} centre causes polarization of the surrounding lattice resulting in polaron formation.

Thus it is inferred that V^{4+} and V^{5+} are the two centres responsible for the electrical conduction through amorphous thin films of V_2O_5. It is reported by Dmitrieva *et al.* [24] that V_2O_5 contains V^{4+} ions and their concentration is proportional to the conductivity. The presence of V^{4+} ions in V_2O_5 is also supported by electron spin resonance (ESR) investigations [25]. It can be assumed that in evaporated V_2O_5 amorphous thin films V^{4+} ions are present whose existence has been confirmed by our ESR investigations. The conduction process in the present samples may be governed by the hopping of electrons between V^{4+} and V^{5+} ions. Under the application of an electric field the barrier between V^{4+} and V^{5+} centres may be lowered and the transfer of charge between V^{4+} and V^{5+} centres may be increased.

The behaviour of the present samples as shown in Fig. 2 shows that the conduction process for higher fields indicates a barrier-lowering type of behaviour (Schottky or Poole–Frenkel effect) as

$$I \propto \exp(\beta E^{1/2}/kT) \qquad (4)$$

where E is the applied field, k is the Boltzmann constant, T is absolute temperature and β is the barrier-lowering coefficient. In order to decide whether the conduction mechanism is Schottky or Poole–Frenkel

type, the experimental value of β can be compared with those of β_S or β_{PF}, respectively. The experimental value of β can be calculated with the help of Equation (1), i.e. from the curve between $\log I$ and $V^{1/2}$ for higher fields. The theoretical value of β is given by the expression

$$\beta = (e^3/n\pi\varepsilon_0\varepsilon_r)^{1/2} \quad (5)$$

where ε_r is the high-frequency dielectric constant, $n = 1$ for Poole–Frenkel effect and $n = 4$ for the Schottky effect, and the other constants have their usual meanings. The experimental value of β at room temperature for V_2O_5 (300 nm) thin films as calculated from the slope of the curve in Fig. 2 for higher values of fields is found to be 2.1×10^{-5} eV m$^{1/2}$ V$^{-1/2}$. The theoretical value of β_{PF} as determined through Equation 2 for high-frequency (900 kHz) dielectric constant (11.8) at room temperature is 2.2×10^{-5} eV m$^{1/2}$ V$^{-1/2}$ whereas the value of β_S (theoretical) under the same conditions is 1.1×10^{-5} eV m$^{1/2}$ V$^{-1/2}$. It is clear that the experimental value of β_{PF} is comparable with theoretical value of β where the experimental value of the β_S is twice the theoretical value of β. It is also observed that the experimental value of β is almost independent of temperature. Therefore, we propose that the conduction process through the MIM structure of evaporated V_2O_5 thin films follows the Poole–Frenkel type of hopping of electrons from V^{4+} centres to V^{5+} centres. The activation energy of the evaporated thin films of simple V_2O_5 has been calculated from the slope of the curve in Fig. 4 and is found to be 0.18 eV, which is consistent with the value as determined by Bullot *et al.* [26] for amorphous V_2O_5 layers deposited from gels.

In the case of co-evaporated thin films of V_2O_5 and B_2O_3, the network former oxide (B_2O_3) expands the V_2O_5 structure and the resulting V_2O_5/B_2O_3 films become more disordered compared to those for simple V_2O_5 under similar conditions. It is possible that the oxygen ions adjacent to vanadium ions may have boron ions as near neighbours, so the network forming may effect the conductivity as reported by Denton *et al.* [11] in the case of V_2O_5–P_2O_5 glasses. During the co-evaporation of V_2O_5/B_2O_3, the B_2O_3 may cause some structural changes in the composite films and an Anderson-type localization process may occur. Because of such a localization, the conductivity of co-evaporated V_2O_5/B_2O_3 thin films will decrease compared to that for the evaporated thin films of simple V_2O_5. This agrees with our experimental results as is clear from Figs 1 and 4. By co-evaporating B_2O_3 with SiO_x, Hogarth and Wright [21] observed that co-evaporated SiO_x/B_2O_3 film showed better dielectric properties than simple evaporated SiO_x films. Vardhan *et al.* [27] have also observed that the addition of B_2O_3 to SiO results in an increase in the dielectric constant of SiO films. They have suggested that some structural changes brought about by B_2O_3 in SiO–B_2O_3 composite films could be responsible for such a change in the dielectric constant. Mikoda *et al.* [28] reported that the addition of B_2O_3 to glasses containing PbF_2 reduced the dielectric loss by suppression of crystallization.

The $I(V)$ characteristics for co-evaporated 70% V_2O_5/30% B_2O_3 (300 nm) thin films as shown in Fig. 4, indicated a non-linear type of behaviour (almost exponential) for higher fields. When the data of Fig. 4 are replotted as $\log I$ against $V^{1/2}$, a straight line is obtained for higher fields which is an indication of Schottky or Poole–Frenkel type of conduction mechanism. So it can be concluded that the conduction mechanism through composite thin films of V_2O_5/B_2O_3 in MIM structure also follows the same relationship as in Equation 4. The experimental value of β for 70% V_2O_5/30% B_2O_3 (300 nm) thin films as determined with the help of Fig. 5 and Equation (1) is found to be 1.35×10^{-5} eV m$^{1/2}$ V$^{-1/2}$. In addition, the theoretical value of the barrier-lowering coefficient in the case of the Poole–Frenkel effect (β_{PF}) for the higher frequency (40 kHz) dielectric constant (28.5) is 1.42×10^{-5} eV m$^{1/2}$ V$^{-1/2}$ and that for the Schottky effect is 7.1×10^{-6} eV m$^{1/2}$ V$^{-1/2}$. From comparison of the experimental value of β with those values calculated for the Poole–Frenkel coefficient and the Schottky coefficient, respectively, we again favour a Poole–Frenkel type of conduction mechanism through co-evaporated 70% V_2O_5/30% B_2O_3 thin (300 nm) films. A similar behaviour has been observed previously for other compositions of co-evaporated V_2O_5/B_2O_3 films. It is worthwhile to mention that the co-evaporated thin films with a molar content of B_2O_3 greater than 40% were unstable because of their hygroscopic behaviour. A similar behaviour has also been observed by Sharma *et al.* [19] for V_2O_5–B_2O_3 glasses. This suggests that during the co-evaporation of V_2O_5/B_2O_3, the effect of B_2O_3 may result in the expansion of the structure and the insulating behaviour of co-evaporated V_2O_5/B_2O_3 thin films may be enhanced, compared to that for simple V_2O_5. Thus the effect of applied field on the lowering of the barrier height in the case of co-evaporated V_2O_5/B_2O_3 films will be less than that for simple V_2O_5 thin films. This is consistent with the increase in the optical band gap of V_2O_5/B_2O_3 with increasing B_2O_3 content which will be reported elsewhere. Therefore the co-evaporated V_2O_5/B_2O_3 thin films should be more insulating than simple V_2O_5 thin films, a conclusion which is in agreement with the present experimental observations. Our results also agree with the observations made by other authors [19, 21, 28, 29].

5. Conclusion

The conduction process through an MIM structure of evaporated V_2O_5 and of co-evaporated thin films of V_2O_5/B_2O_3 obeys the Poole–Frenkel type of hopping of electrons from V^{4+} to V^{5+} centres. The conductivity of co-evaporated V_2O_5/B_2O_3 films shows a decrease with increasing B_2O_3, but the films with B_2O_3 contents higher than 40% are found to be unstable. The electrical characteristics of V_2O_5/B_2O_3 films are consistent with their optical behaviour.

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