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Electronic conduction in thin amorphous MoO_3/SiO films deposited by co-evaporation

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A study of the effects of changes in composition and temperature on the electrical properties of MoO_3/SiO thin amorphous films is presented. The high-field conduction is probably due to the Poole–Frenkel effect as it is in simple SiO. At low temperature and low field the electron hopping process is dominant but conduction at higher temperatures is a contact-limited process. The decrease in conductivity with increasing concentration of SiO in MoO_3 may be attributed to the increasing number of trapping centres introduced in MoO_3/SiO films during the evaporation process. The increase in conductivity in MoO_3/SiO films with increasing temperature is attributed to the increasing concentration and higher mobility of charge carriers.

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 manufacturing of semiconductor devices and integrated circuits. Charge transport measurements in disordered semiconductors and insulators have been of considerable interest recently because they can provide information about the electronic structure of amorphous materials. There are many theoretical models to explain experimental data on conduction mechanisms, but none as yet is totally satisfactory. When two suitable oxides are mixed together, appropriate impurities may be regarded as being added to amorphous material. The study of the electrical properties of mixed thin films of MoO_3/SiO by the co-evaporation technique established by Hogarth and Wright [1] helps to elucidate the basic properties of these mixed oxides. Thin amorphous dielectric films based on MoO_3 are well known as insulators. Bursill [2] reported that MoO_3 is known to decompose to lower oxides as well as to dissociate when heated or vacuum deposited. In evaporated MoO_3 films the predominant defects are oxygen vacancies in large concentrations [3]. Oxide films sandwiched between metal electrodes and based on glass-forming oxides such as SiO_x ($1 < x < 2$), B_2O_3 and GeO_2 have been extensively studied in this laboratory [4, 5]. The SiO/B_2O_3 thin films show better dielectric properties than simple SiO layers. SiO yields a film containing a mixture of compounds ranging from SiO to SiO_2 as well as free silicon. Furthermore, vacuum deposited films contain large stresses which induce further trapping centres. It follows that thin films of vacuum deposited insulators can contain a very high density of both donor and trap centres. It has been established that SiO does exist in the gas phase [6] whereas on condensation the compound probably disproportionates according to the following reaction.

$$2SiO = Si + SiO_2$$

The condensed material obtained from the experiments to be discussed varied in composition depending on the conditions of preparation. As would be expected, this variation in composition greatly affected the electrical properties of such thin films. The work of Stuart [7], Hirose and Wada [8], Timson and Wickens [9] and Husain [10] confirmed that electrical conduction in insulating films of silicon oxide is bulk limited. Many SiO samples, when evaporated in a sandwich configuration between suitable electrodes, undergo an electroforming effect when voltages in excess of a forming voltage V_f are applied [11]. We have studied the electrical properties of MoO_3 [12] and reported that a change in electrical properties with increase in film thickness is attributed to an increasing concentration of oxygen vacancies. A similar change with increase in substrate temperature is attributed to the inter-electron transfer from an oxygen 2p to a molybdenum 4d orbital that creates the isolated Mo(V) oxidation state. The variation in conductivity with increase in annealing temperature is attributed to a decrease in the density of dangling bonds which tend to connect constituent atoms with their neighbouring ones and to the formation of Mo species of lower oxidation state. Our studies [13–16] on the optical, ESR, IR and XPS properties of the mixed oxide system MoO_3/SiO, suggest that the changes in the above properties with composition may be due either to the incorporation of silicon ions in an MoO_3 lattice or to the change in the SiO_x composition. The changes with increase in film thickness may be due to an increasing concentration of oxygen vacancies, Mo(V) sites and dangling bonds. Those occurring as a result of an increase in substrate temperature may be due to the removal of voids, dissociation of SiO to silicon and oxygen atoms and the formation of molybdenum species of lower oxidation state. The change with increase in annealing temperature may be due either to the incorporation of silicon ions in an MoO_3 lattice or to the removal of voids and a decrease in dangling bond density.

No earlier work on mixed thin amorphous films of MoO_3/SiO is available in the literature apart from recent work performed in this laboratory. In this work

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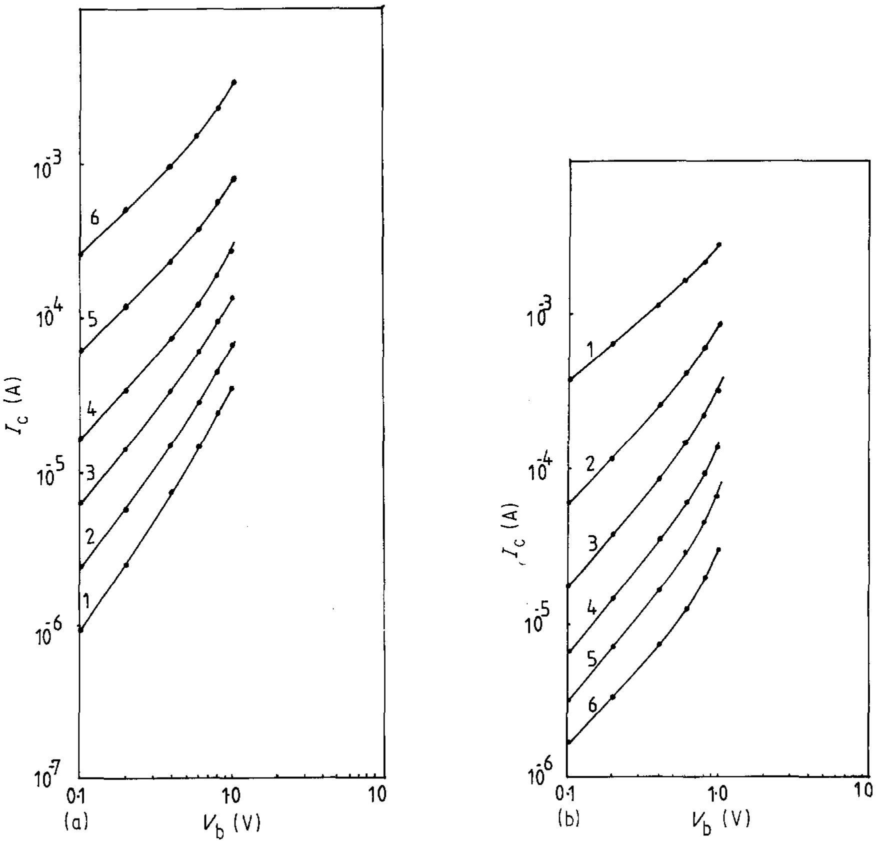

Figure 1 (a) Voltage–current characteristics of a 300 nm thick Al–70 mol % MoO_3/30 mol % SiO–Al assembly at (1) 193 K, (2) 233 K, (3) 273 K, (4) 313 K, (5) 353 K, (6) 393 K. (V_b is applied voltage, I_c is circulating current). (b) Voltage–current characteristics of some 300 nm thick Al–MoO_3/SiO–Al samples at room temperature during measurement having compositions, (1) 100% MoO_3, (2) 90 mol % MoO_3/10 mol % SiO, (3) 80 mol % MoO_3/20 mol % SiO, (4) 70 mol % MoO_3/30 mol % SiO, (5) 60 mol % MoO_3/40 mol % SiO, (6) 50 mol % MoO_3/50 mol % SiO.

we have investigated the d.c. electrical properties of MoO_3/SiO as a function of composition. The effects of temperature on the *V–I* characteristics of the Al–MoO_3/SiO–Al structure are also reported.

2. Experimental work

The thin evaporated layers of MoO_3/SiO used in this study were prepared by the vacuum evaporation of high purity MoO_3 and SiO and were deposited on clean Corning 7059 glass substrates in the form of sandwiches between metal electrodes at a pressure of about 6×10^{-6} torr, in a Balzers BA 510 coating unit, using the co-evaporation technique established by Hogarth and Wright [1]. Molybdenum and tantalum boats were used for the evaporation of MoO_3 and SiO respectively. All other techniques used to measure the film thickness, cleaning of the substrates and d.c. measurements, are similar to those described earlier [12].

3. Results

In this study we have investigated the d.c. electrical properties of MoO_3/SiO films before electroforming. As the forming voltage for SiO is very low, we have studied the samples in the limited applied voltage range 0.1–1.0 V. Figure 1a shows the voltage–current characteristics at different temperatures in the range 193–393 K for a 300 nm thick Al–70 mol % MoO_3/30 mol % SiO–Al sandwich sample. At low fields ohmic behaviour was observed in our samples followed by a non-linear dependence of current on voltage. Figure 1b shows the voltage–current characteristics of 300 nm thick Al–MoO_3/SiO–Al samples at various compositions. The interpretation of these curves based on the assumption of a simple Poole–Frenkel or Schottky effect requires the logarithm of the circulating current to be proportional to $V_b^{1/2}$. The analyses of these results are shown in Figs 2a and b where log I_c is plotted as a function of $V_b^{1/2}$. These plots suggest that mechanism of high field conduction is either Schottky or Poole–Frenkel. Both the phenomena are described by the relation

$$I_c \propto \exp\,(\beta V^{1/2}/kTd^{1/2}) \qquad (1)$$

where I_c is the circulating current, d the thickness, k the Boltzmann constant, T the absolute temperature and β the barrier lowering coefficient. The experimentally determined values of β can be compared with the theoretical values of β_s (Schottky barrier lowering coefficient at metal/insulator interface) or β_{PF} (the Poole–Frenkel barrier lowering coefficient of the donor centres) in order to distinguish between two types of effects. The theoretical values of β_s and β_{PF} are determined from the following relation

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

where ε_0 is the permittivity of free space, ε_r is the relative permittivity of the dielectric material and e is the electronic charge. The difference between the two effects is expressed by $n = 1$ for the Poole–Frenkel effect and $n = 4$ for Schottky emission. The experimental values of β and the estimated relative dielectric

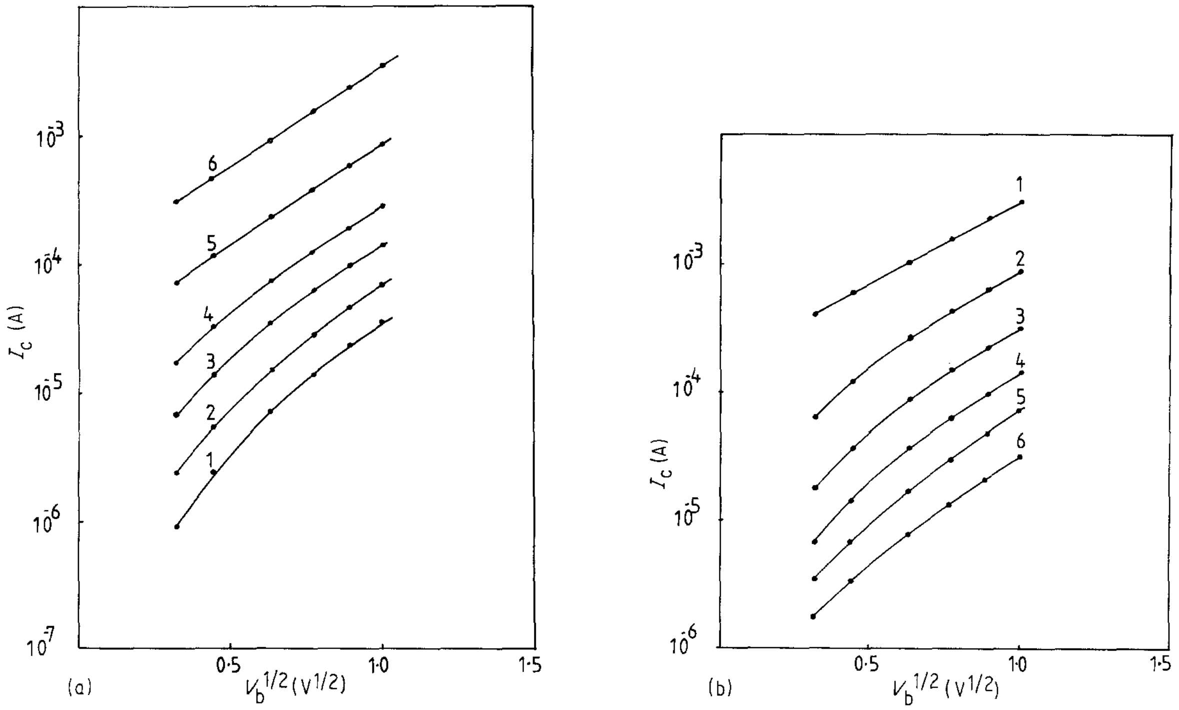

Figure 2 (a) I_c against $V_b^{1/2}$ for a 300 nm thick Al–70 mol % MoO_3/30 mol % SiO–Al assembly (1) 193 K, (2) 233 K, (3) 273 K, (4) 313 K, (5) 353 K, (6) 393 K. (b) I_c against $V_b^{1/2}$ for some 300 nm thick Al–MoO_3/SiO–Al samples at room temperature during measurement having compositions, (1) 100% MoO_3, (2) 90 mol % MoO_3/10 mol % SiO, (3) 80 mol % MgO_3/20 mol % SiO, (4) 70 mol % MoO_3/30 mol % SiO, (5) 60 mol % MoO_3/40 mol % SiO, (6) 50 mol % MoO_3/50 mol % SiO.

constant for both the Poole–Frenkel and Schottky effects are shown in Tables I and II for a 300 nm thick 70 mol % MoO_3/30 mol % SiO sample at various temperatures during measurements and for a variety of compositions respectively.

The variation of current I_c with inverse temperature for a 300 nm thick 70 mol % MoO_3/30 mol % SiO sample at various biasing voltages in the range 0.1–1.0 V is shown in Fig. 3 for the temperature range 193–393 K. The values of activation energy both at low and high temperatures are shown in Table III.

4. Discussion

In amorphous materials both free band and hopping conduction may take place as in crystalline materials. These conduction mechanisms may be separated experimentally by operating in the appropriate temperature ranges. Voltage–current characteristics are examined to elicit any correlation with the conduction mechanisms most often observed in thin film work. The Schottky effect is the conduction of electrons by the thermal excitation over the potential barrier between electrons at the Fermi level of the injecting electrode and the insulator conduction band. The Poole–Frenkel effect is bulk-limited and conduction occurs by field-assisted emission of electrons from localized centres located at an energy ϕ below the insulator conduction band. One can sometimes differentiate between the two types of conduction mechanisms by comparing the derived values of their dielectric constants with the values of the high frequency dielectric constant obtained from capacitance measurements. For the Schottky type of conduction the values of ε_r lie in the range 0.25–1.43 and for Poole–Frenkel type of conduction the values of ε_r lie in the range 1.01–5.7. The value of the high frequency dielectric constant through capacitance measurements lies in the range 3.4–7.0 which is consistent with earlier work [12, 17], suggesting that the high field conduction mechanism is predominantly of the Poole–Frenkel type, but current thinking suggests that the demarcation between the Schottky and Poole–Frenkel effects is less clear than previously thought and there are doubts about the precise interpretation of the voltage–current characteristics at high fields. Some effect of the barrier conditions at the metal/oxide contact might be

TABLE I Experimental values of some parameters of a 300 nm thick Al–70 mol % MoO_3/30 mol % SiO–Al sample measured at various temperatures

Temperature (K)	β_{exp} (10^{-4} eV $V^{-1/2}$ $cm^{1/2}$)	Relative permittivity (n = 4, Schottky) estimated	Relative permittivity (n = 1, Poole–Frenkel) estimated
193	3.17	1.43	5.72
233	4.05	0.87	3.28
273	4.87	0.60	2.40
313	5.62	0.45	1.80
353	6.30	0.35	1.40
393	7.50	0.25	1.01

TABLE II Experimental values of some parameters of 300 nm thick Al-MoO_3/SiO-Al samples measured at 273 K at various compositions

Composition (mol %)		β_{exp} (10^{-4} eV $V^{-1/2}$ $cm^{1/2}$)	Relative permittivity (n = 4, Schottky) estimated	Relative permittivity (n = 1, Poole–Frenkel) estimated
MoO_3	SiO			
100	0	3.56	1.13	4.52
90	10	3.66	1.07	4.28
80	20	3.80	0.98	3.92
70	30	4.87	0.58	2.32
60	40	5.20	0.52	2.08
50	50	5.60	0.45	1.80

expected at high fields even though the main barrier-lowering effect is associated with localized (Poole–Frenkel) centres.

If the temperature is raised, the current changes because the Fermi level sweeps past the mobility edge. There will be sharp changes in current only if the free-band mobility is much greater than the hopping mobility. The general form of this process can be expressed by the equation

$$I = I_0 \exp(-E/kT) \qquad (3)$$

where E is the activation energy for donors or traps, and

$$I_0 = e\mu N_d VA/d \qquad (4)$$

where μ is the mobility, N_d is the impurity density or trap density and A is the active area of the film capacitor. According to Equation 3, the activation energy can be obtained from the gradient of the slope of the straight portion of the curves in Fig. 3. In our results such a transition takes place within the temperature range 270 to 290 K (Fig. 3). This suggests that more than one conduction mechanism is involved. The low temperature values of the activation energy lie in the range 0.024–0.033 eV suggesting that at low temperature the conduction takes place by hopping. The higher temperature values of activation energy lie in the range 0.14–0.20 eV suggesting that the conduction takes place by transport in the extended states (free-band conduction). This gradual transition from hopping conduction to free band conduction may be due to overlapping of localized levels and free band [18]. If the slope for the higher temperature region in Fig. 3 is extrapolated to $1/T = 0$, then

$$\mu N_d = I_0 d/eVA = 3 \times 10^{15}\,\text{cm}^{-1}\,\text{V}^{-1}\,\text{sec}^{-1}$$

where d = 300 nm, V = 1 V, $A = 0.1\,\text{cm}^2$ and μ is the free band mobility. Both Cohen [19] and Mott [20] agree on a lower limit for the free band mobility $\mu = 100\,\text{cm}^2\,\text{V}^{-1}\,\text{sec}^{-1}$ which leads to an estimated value of the trap density $N_d = 3 \times 10^{13}\,\text{cm}^{-3}$. If the slope for lower temperature region in Fig. 3 is extrapolated to $1/T = 0$ and using the same value of trap density (N_d) as above, $\mu_H N_d = 9.38 \times 10^{11}\,\text{cm}^{-1}\,\text{V}^{-1}\,\text{sec}^{-1}$, where μ_H is the value of mobility in the lower temperature region, i.e. the hopping mobility. Thus $\mu_H = 3.1 \times 10^{-2}\,\text{cm}^2\,\text{V}^{-1}\,\text{sec}^{-1}$. This low value of mobility associated with an ohmic V_b–I_c characteristic is consistent with the localized state conduction (hopping) at low field and low temperature which is also consistent with the work of De Mey [21]. According to Thomas *et al.* [22] the hopping mechanism in silicon involves two dangling bonds:

$$D_0 + D_0 = D_+ + D_- \qquad (5)$$

where D_0 are neutral paramagnetic dangling bonds and D_+ and D_- are the charged states of the same bonds.

Simmons [23, 24] has pointed out that the conductivity of a wide band gap insulator such as silicon oxide must be explained by the presence of donors. The low activation energy observed for silicon supports this view. It is suggested that the donors are associated with free silicon which certainly occurs in evaporated silicon oxide [25]. Furthermore an evaporated insulating film is an imperfect structure and must contain a high trap density, the effect of which is to reduce the conductivity of the films [23, 24]. SiO is a better insulator than MoO_3 due to its wider band gap. When the content of SiO is increased in MoO_3, the conductivity is decreased. This result can be explained in the following manner. During co-evaporation silicon ions

TABLE III Activation energy for two ranges of temperature of a 300 nm thick sample of 70 mol % MoO_3/30 mol % SiO at various applied voltages

Applied voltage (V)	Activation energy (eV)	
	193–210 K	350–393 K
0.1	0.033	0.20
0.2	0.032	0.18
0.6	0.026	0.16
1.0	0.024	0.15

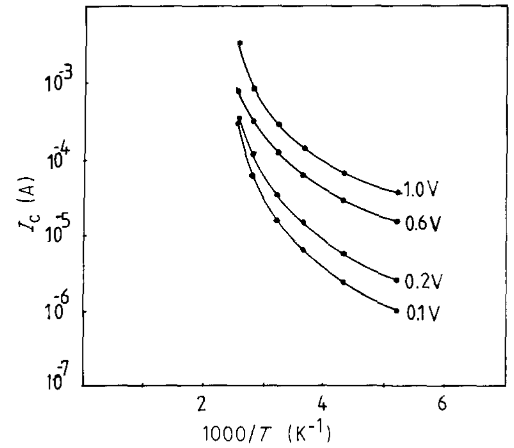

Figure 3 Circulating current as a function of inverse temperature at five applied voltages for a 300 nm thick Al–70 mol % MoO_3/30 mol % SiO–Al assembly.

incorporated in the MoO_3 lattice increase the overall disorder in the system. When the content of SiO is increased in the mixed MoO_3/SiO films the concentration of trapping centres is increased, as a result of which the conductivity of the mixed MoO_3/SiO films is decreased.

Nelson and Weeks [25] have reported that vacuum evaporation may lead to the incorporation of defect centres consisting of an oxygen ion vacancy with trapping centres in SiO films. The behaviour of these defect centres appears to be analogous to that of F and F' centres in alkali halides. They also reported that thermal release of the trapped electrons was possible. Another centre, i.e. an interstitial non-bridging oxygen ion was a very common defect in silicate glasses and these may also be present in the films described here. According to Simmons [23, 24] donor centres are created in SiO films due to the dissociation of SiO into SiO_2 and free silicon. According to Stahelin and Busch [27], an MoO_3 film contains a number of oxygen vacancies capable of capturing one or two electrons. Oxygen vacancies capable of capturing one or two electrons are analogous to F and F' centres in alkali halide crystals and act as donors in which one electron of a doubly charged centre may be ionized thermally and the other only optically. Normal ionization gives rise to two charge carriers namely an electron and a singly-charged oxygen vacancy. Thus the increase in conductivity due to increase in temperature of the 70 mol % MoO_3/30 mol % SiO sample is ascribed to the increasing concentration and higher mobility of these types of charge carriers.

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