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A.c. conduction in evaporated MoO_3/SiO amorphous thin films

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The dielectric properties of vacuum-deposited MoO_3/SiO films of different compositions studied in the frequency range 10^2 to 10^6 Hz at various temperatures (193 to 393 K) are reported. The properties of the film capacitor are found to be temperature and frequency dependent. The decrease in a.c. conductance with increasing concentration of SiO in MoO_3 may be attributed to the increasing number of trapping centres generated in MoO_3/SiO films during the evaporation process.

1. Introduction

A.c. measurements are an important means for studying the dynamic properties (capacitance, conductance, permittivity and loss factor) of a dielectric. The advantage of a.c. measurements over the d.c. measurements is that internal time-dependent processes in the insulator can be investigated with a.c. measurements. Moreover, the a.c. voltage bias need never exceed a few hundred millivolts. Thus the maximum field within the insulator film is kept to a minimum and there is little danger of more than one conduction process being active. This measurement also helps to distinguish between localized and free-band conduction. In the case of localized conduction, the conductivity, $\alpha_{a.c.}$, increases monotonically with radial frequency, ω, whilst for the free-band conduction the conductivity decreases with frequency. A number of investigations has been carried out on the frequency dependence of electrical conductivity in many glassy and amorphous semiconductors [1–9]. It has been pointed out by Elliott [1] that a variety of conduction mechanisms can yield the ω^s behaviour for the a.c. conductivity, but in general, it is difficult to establish which of the above effects determines a given observed conduction process. A careful study of the temperature dependence of s (s is an index) can provide us with more information in order to make a choice between the different theories for explaining the law $\sigma_{a.c.}(\omega) \propto \omega^s$.

The experimental results can be interpreted in terms of a model initially proposed by Pollak and Geballe [10]. This model involves a thermally assisted hopping conduction mechanism between localized states. Pike [4] has analysed classical hopping over the barrier separating the localized states in such materials.

In this study, the a.c. electrical properties of mixed MoO_3/SiO amorphous films are reported. There is very little information available about MoO_3 because of the considerable difficulties in preparing specimens suitable for the investigation of physical properties. Nadkarni and Simmons [11, 12] reported that the existence of Schottky barriers is believed to be due to a strong donor band in the insulator established during the vacuum evaporation. SiO dielectric films are of considerable interest because of their use in the electronics industry as capacitor materials. Simmons [13] reported that both donor and trapping centres are created in SiO films due to the dissociation of SiO into SiO_2 and free silicon. Furthermore, the SiO structure contains active defects in both structure and composition. These defects are associated with oxygen deficiencies in the film giving rise to vacancy states and unstable structural defects, i.e. interstitial oxygen. Jourdain *et al.* [9] reported that their a.c. results on SiO cannot be analysed in terms of a quantum hopping conduction mechanism proposed by Pollak and Geballe [10], but the results seem to be in agreement with the theory derived by Pike [4]. The height of the barrier is lowered by the overlapping of the Coulomb potentials at the two sites. They further reported that the values of activation energy associated with the localized states and calculated from the Pike model agree with the d.c. activation energy as measured.

According to Kondo *et al.* [14], the a.c. conduction in the radio frequency range depends on frequency and temperature in amorphous chalcogenide semiconductors ($\sigma(\omega, T) = A\omega^s$ where A and s are temperature-dependent parameters). They interpreted their results in terms of a combined mechanism of correlated barrier hopping (CBH) of bipolarons (two electrons hopping between charged defects D_+, D_-) and single polarons (one electron hopping between a neutral defect D_0 and a charged defect D_-, and one hole hopping between D_0 and D_-). They further reported that intrinsic defects similar to those in amorphous SiO_2 are believed to exist and contribute to a.c. conduction in amorphous SiO films. 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 we have investigated the a.c. electrical properties of mixed MoO_3/SiO films as a function of composition. The effects of temperature on the conductance and capacitance are also reported.

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2. Experimental procedure

Thin amorphous films of the mixed oxide system MoO_3/SiO were fabricated in a Balzers BA510 coating unit by deposition on to clean Corning 7059 glass substrates in the form of metal–oxide–metal sandwich electrode structures at a pressure of about 6×10^{-6} torr using a co-evaporation technique. All other techniques used to measure the film thickness, cleaning of the substrates and d.c. measurements are similar to those described earlier [15].

3. Results

A large number of films of different compositions were measured as functions of frequency and temperature. The measurements were carried out in the frequency range 10^2 to 10^6 Hz and in the temperature range 193 to 393 K. The experimental results are usually interpreted in terms of a model initially proposed by Pollak and Geballe [10], modified by Pike [4] and subsequently modified by Elliott [1]. This model involves a hopping conduction by electrons (thermally assisted) between localized states. Pike pointed out that classical hopping over the barrier separating the localized states can sometimes occur.

It is well known that the total measured a.c. conductivity, $\sigma_{a.c.}$, may be represented in a wide variety of amorphous semiconductors and insulators by the experimental relation

$$\sigma_{a.c.} = \sigma_{total} - \sigma_{d.c.} \quad (1)$$

where $\sigma_{d.c.}$ is the d.c. conductivity and $\sigma_{a.c.}$ is the true a.c. conductivity which is frequency, f, dependent. Fig. 1 shows the frequency (f) dependence of a.c. conductivity for 300 nm thick MoO_3/SiO samples of various compositions and Fig. 2 illustrates the frequency dependence of a.c. conductivity for a typical specimen (70 mol % MoO_3/30 mol % SiO) at various temperatures. At high frequencies the curves approximate to a square law dependence on frequency and show relatively little dependence on temperature. At low frequencies the $\log \sigma$–$\log f$ graphs are good straight lines and are temperature sensitive. One can find a frequency range (depending on temperature), where the a.c. conductivity, $\sigma_{a.c.}$ obeys the law

$$\sigma_{a.c.} \propto \omega^s \quad (2)$$

where s is an index which is temperature dependent and which tends to unity [1] as the temperature is lowered. For the sample shown in Fig. 2, s decreases from 0.83 to 0.39 (as shown in Fig. 3) when the temperature increases from 193 to 393 K. Furthermore, the variation of a.c. conductivity with temperature can be expressed by the relation,

$$\sigma_{a.c.} = A(T)\omega^s(T) \quad (3)$$

where A is a complex parameter weakly temperature

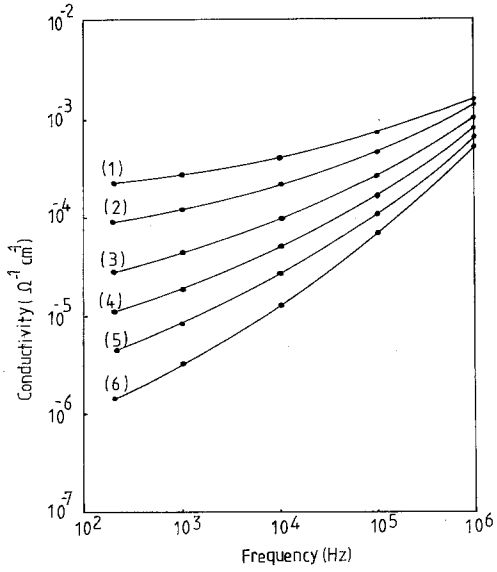

Figure 1 Variation of a.c. conductivity with frequency for 300 nm thick MoO_3/SiO samples having compositions (1) 100% MoO_3, (2) 90 mol % MoO_3/10 mol % SiO, (3) 80 mol % MoO_3/20 mol % SiO, (4) 70 mol % MoO_3/30 mol % SiO, (5) 60 mol % MoO_3/40 mol % SiO, (6) 50 mol % MoO_3/50 mol % SiO.

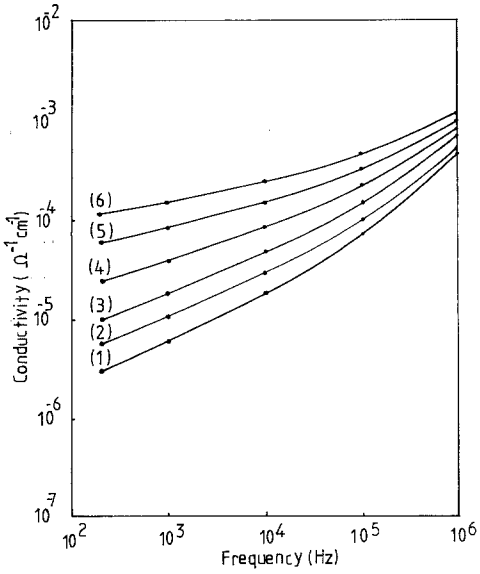

Figure 2 Variation of a.c. conductivity with frequency at different temperatures for a 300 nm thick sample of 70 mol % MoO_3/30 mol % SiO, (1) 193 K, (2) 233 K, (3) 273 K, (4) 313 K, (5) 353 K, (6) 393 K.

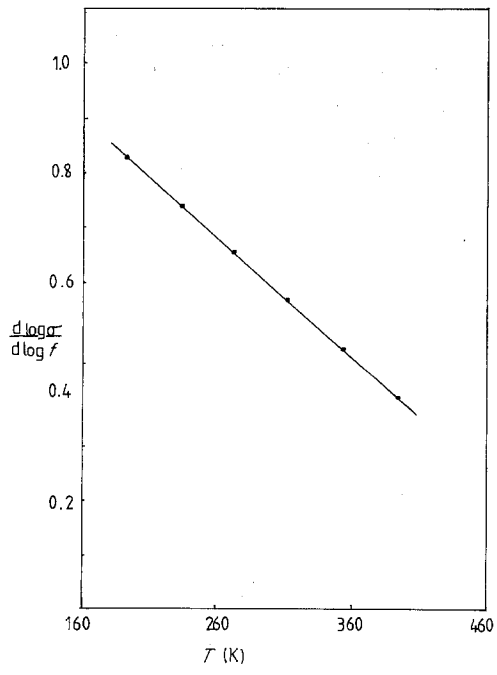

Figure 3 Temperature dependence of the slope of conductivity–frequency characteristics of sample shown in Fig. 2.

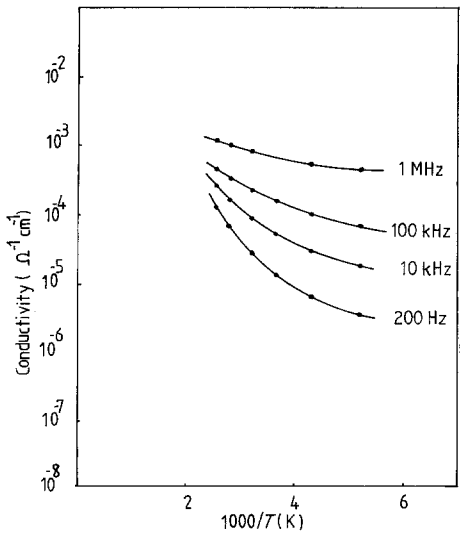

Figure 4 Conductivity plotted as a function of $1000/T$ at fixed frequencies for a 300 nm thick sample of Fig. 2.

dependent. From Fig. 3 it can be seen that

$$s = \frac{\mathrm{d} \log \sigma}{\mathrm{d} \log f} = -AT + B \qquad (4)$$

where A and B are constants, f is the frequency $(\omega/2\pi)$ and T is the absolute temperature. Hence $\sigma_{\mathrm{a.c.}}(\omega) \propto f^{-(AT-B)}$.

Fig. 4 shows the a.c. conductivity at different frequencies as a function of reciprocal temperature. Table I shows the activation energy, both d.c. and a.c. at 0.2 V and at various applied frequencies. It is seen from Table I that the a.c. conductivity seems to approach the d.c. conductivity asymptotically with increasing temperature. At low temperature the d.c. conductivity has an activation energy different from that corresponding to high temperature, and it is probable that hopping conduction at the Fermi level prevails at low temperatures [9].

Fig. 5 shows a typical variation of capacitance with frequency at various temperatures for a 300 nm thick sample at fixed composition 70 mol % MoO_3/30 mol % SiO. A decrease of capacitance with increasing frequency is noted and this is probably associated with an increasing current leakage with increasing frequency, a phenomenon which is normally associated with a capacitance reduction. The change in capacitance with frequency becomes less marked as the temperature is decreased. The variation of capacitance, C, with frequency (below 10^4 Hz) for the temperature range 193 to 393 K (as shown in Fig. 5) is of the form

$$C \propto f^{-1/x} \qquad (5)$$

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

Frequency (kHz)	Activation energy (eV)	
	193 to 210 K	350 to 393 K
d.c. (at 0.2 V)	0.032	0.18
0.2	0.018	0.10
10	0.010	0.06
100	0.008	0.04
1000	0.005	0.02

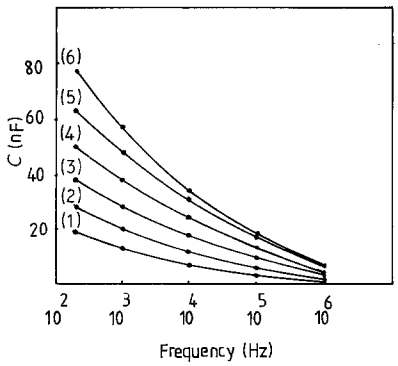

Figure 5 Variation of capacitance with frequency at various temperatures for a 300 nm thick sample of 70 mol % MoO_3/30 mol % SiO, (1) 193 K, (2) 233 K, (3) 273 K, (4) 313 K, (5) 353 K, (6) 393 K.

where x is approximately equal to 6. The value of x changes with change in composition.

4. Discussion

It has been noted that the conductivity shows a strong frequency dependence leading to a square law at high frequencies. This also coupled with low activation energies at low temperature (Table I). All these are indicative of electronic hopping conduction. Different theories have been put forward to explain the a.c. conduction mechanism. A theory in which the exponent varies with temperature and increases when T decreases was initially proposed by Pike [4] to explain his results for the a.c. conduction in scandium oxide. In this model, the transport of the carriers between localized states is mainly due to hopping over the barrier separating two nearest neighbour sites, rather than tunnelling through the potential barrier. Because of the barrier height this process in general involves many polarons. The localized site potentials are taken to be of coulombic form; the barrier height and the distance separating these two sites are respectively W and R, and W_m is the maximum barrier height (the energy difference between the ground states and extended states). The equation relating these parameters is given by

$$W_m - W = e^2/(\pi\varepsilon_0\varepsilon_r R) \qquad (6)$$

where ε_0 is the permittivity of free space and ε_r is the effective dielectric constant. Elliott [1] extended the Pike theory to the a.c. conduction of amorphous chalcogenides. Assuming a Coulombic interaction, the barrier height over which a carrier hops is given by

$$W = W_m - 4ne^2/(\varepsilon_r R) \qquad (7)$$

where n is the number of carriers that hop (e.g. $n = 2$ for bipolarons, $n = 1$ for single polarons). The a.c. conductivity according to Elliott's model is given by

$$\sigma(\omega) = \frac{\pi^2 N^2 \varepsilon}{24}\left(\frac{8e^2}{\varepsilon W_s}\right)^6 \frac{\omega^s}{\tau_0 \beta} \qquad (8)$$

where N is the concentration of localized sites, τ_0 is the effective relaxation time ($\approx 10^{-13}$ sec), $s = 1 - \beta$ at low temperature, $\beta = 6kT/W_m$ and W_m is the barrier separating distant pairs. The pair relaxation time is assumed to be

$$\tau = \tau_0 \exp(W/kT) \qquad (9)$$

The exponent s is related to W_m by

$$1 - s = 6kT/W_m \quad (10)$$

where k is the Boltzmann constant and T is the absolute temperature. The parameter W_m is approximately equal to the band gap of the material, measured optically. In order to test the validity of the Elliott theory for other amorphous material such as thin insulating films, we substitute the measured value of optical band gap (1.68 eV) of 70 mol % MoO_3/30 mol % SiO in Equation 10. The value of s is found to be 0.90 at room temperature which is consistent with the values of some chalcogenide materials [1]. The experimentally measured value of s from Fig. 3 for room temperature at approximately 10^5 Hz $\approx$ 0.65 whereas at 10^3 Hz the value of s is 0.85 which is much closer to the value calculated theoretically. The low values of activation energy at low temperature (Table I) are indicative of electronic hopping conduction at high frequencies. At low temperatures the d.c. conductivity has an activation energy different from the high temperature value and it is probable that hopping conduction at the Fermi level prevails at the lower temperatures [9]. Simmons [13] pointed out that an evaporated SiO 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. When SiO is mixed in MoO_3 the conductivity of the films is decreased. During co-evaporation the silicon ions are incorporated in the MoO_3 lattice and increase the overall disorder in the system. When the content of SiO is increased in MoO_3 the concentration of trapping centres is increased in the mixed MoO_3/SiO films due to the imperfect structure of evaporated SiO, as a result of which the conductivity of the mixed MoO_3/SiO films is decreased. Donor centres are created in SiO films due to the dissociation of SiO into SiO_2 and free silicon [13]. The increase in conductivity due to increase in temperature of the 70 mol % MoO_3/30 mol % SiO arises from an increasing concentration of donors. The mobility of the donors in the highly disordered material is increased with increase in temperature which also helps to enhance the conductivity at the higher temperatures.

The variation of capacitance with both frequency and temperature in MoO_3/SiO films can be explained by using the model proposed by Goswami and Goswami [8] of a circuit containing a single capacitance element together with a discrete resistance, R, in parallel with the capacitor and a series lead resistance, r. The effect of temperature on capacitance can then be considered from the following equation.

$$C_s = 1/\omega^2 R^2 C + C = (1 + D^2)C \quad (11)$$

where $D = 1/\omega RC$ and C_s is the equivalent series capacitance of the circuit; if, however, $1/\omega^2 R^2 C$ is much smaller than C, then $C_s = C$. This condition can be obtained in a capacitor system either by increasing R, i.e. by lowering the temperature or by raising ω. A suitable combination of these parameters along with an appropriate value of C will lead to the frequency independent capacitance.

The capacitance generally decreases not only with the rise of frequency but also with the lowering of temperature and in our results never attains a constant value even at the highest frequency (10^6 Hz). The major contribution to capacitance arises from the atomic and more probably from ionic polarization. However, with the increase of temperature the contribution from dipolar orientation would increase considerably and hence the capacitance would also increase. The increase in capacitance with the decrease in frequency may be attributed to interfacial polarization in that region. The charge carriers existing in the dielectric film can migrate from some distance under the influence of electric field. When they are blocked at electrodes a space charge region is developed, which in turn leads to a substantial increase in a capacitance at the lower frequency.

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