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The behaviour of SiO_x/SnO thin dielectric films in an alternating electric field

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The a.c. electrical conduction through SiO_x/SnO thin films prepared by the co-evaporation technique has been investigated. The conductivity shows ω^s-type behaviour. The values of s lie between 0.75 and 0.41 depending upon the temperature. The conduction may be explained by a single polaron hopping process as proposed by Elliott. The dependences of capacitance, $\tan\delta$ and loss factor on the frequency of applied field and the temperature are also discussed. It is suggested that the centres taking part in both d.c. and a.c. conduction processes are the same. Under similar conditions, the co-evaporated SiO_x/SnO films are found to be more disordered than those of SiO_x/SnO_2.

1. Introduction

Dielectric oxides are extensively used as capacitors in microelectronic circuits and also in many other electronic and optical devices. Studies of the electronic nature of a material give information about its electrical behaviour and this may be related to structural properties. The disorder in atomic configuration and/or composition is responsible for the existence of localized electronic states or groups of states within the material. Because the charge carriers are localized, a.c. techniques are often employed to probe their behaviour [1, 2]. The a.c. conductivity, $\sigma_{a.c.}$, in many amorphous solids has been found experimentally to obey an equation of the type

$$\sigma_{a.c.}(\omega, T) = A\omega^s \qquad (1)$$

where ω is the angular frequency of the applied field and A and $s < 1$ are temperature-dependent parameters. Different conduction mechanisms can lead to ω^s type of behaviour for a.c. conductivity, but it is not easy to decide which of the those mechanisms is responsible for the observed conduction properties. However, the behaviour of the exponent s with temperature can help elucidate various theories regarding Equation 1 [3].

Many authors have investigated the a.c. conduction mechanisms through thin insulating films and have explained their results in terms of different theoretical approaches [2, 4–7]. Shimakawa [8] proposed single polaron hopping (one electron hopping between a neutral defect, D^0, and a charged defect, D^+, and one hole between D^0 and D^-) as well as bipolaron hopping (two electrons hopping between D^- and D^+ centres) to account for all the features observed in chalcogenide glass semiconductors. The a.c. conductivity in SiO_x thin films has been studied by some authors [9–11] and observed to be proportional to ω^s. Kondo *et al.* [12] interpreted the a.c. conductivity in evaporated SiO thin films in terms of correlated barrier hopping (CBH) by a single polaron (i.e. effectively one hole hopping between neutral and negatively charged defects).

Some years ago, Hogarth and Wright [13] thought of improving thin-film dielectrics for capacitors by using dielectric films in the form of mixed oxides. They found an improvement in the dielectric properties of composite SiO_x/B_2O_3 with increase in the B_2O_3 content compared with the simple SiO_x. Rahman *et al.* [14] measured the a.c. electrical properties of SiO/SnO_2 thin films and suggested that the films tend to be dielectric in character, even though SnO_2 is a fairly good conductor.

In the present paper the a.c. dielectric properties of SiO_x/SnO co-evaporated thin films are reported with a view to investigating any differences between their properties and those of the SiO_x/SnO_2 films investigated earlier [14].

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 [13], and finally metal was evaporated for the top electrode. The rates of evaporation and film thickness could be controlled. Six samples, each having an effective area of 0.1 cm^2, were made on each substrate. (All compositions are given in mol %.)

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 with the devices by means of copper strips joined with silver paste. A stainless steel tank incorporated into the top plate was used for low-

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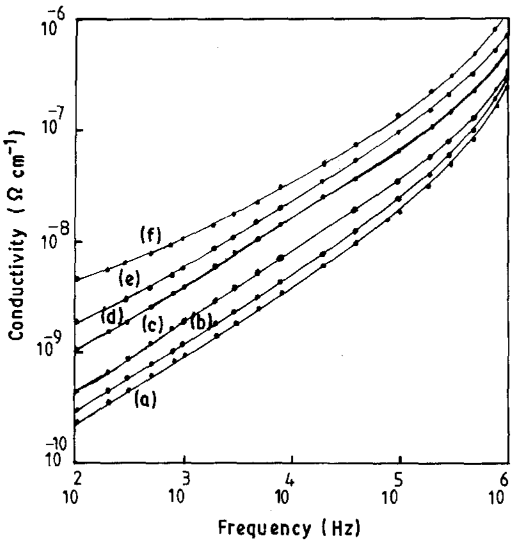

Figure 1 Electrical conductivity as a function of frequency for 80% SiO_x/20% SnO (300 nm) thin films at different temperatures: (a) 183 K, (b) 228 K, (c) 263 K, (d) 299 K, (e) 318 K and (f) 343 K.

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 using a Keithley 610C solid state electrometer.

The capacitance of the sample was measured by a Hewlett–Packard impedance analyser (5 Hz to 13 MHz) type 4192 ALF using an a.c. signal of 500 mV.

3. Results and discussion

The variation of a.c. conductivity for 80% SiO_x/20% SnO (300 nm) thin films as a function of frequency is shown in Fig. 1. The a.c. conduction process follows an ω^s-type law with s decreasing with increase in temperature. The values of s at different temperatures in the frequency range 0.1 to 100 kHz lie between 0.75 and 0.41. For higher frequencies the conductivity approaches a quadratic power law. Fig. 2 shows the variation of total conductivity (a.c. + d.c.) with the inverse of temperature at different frequencies for the same sample as in Fig. 1. The values of activation energy estimated from the slopes of these plots are given in Table I. It is observed that at higher temperatures, the d.c. part of the conductivity approaches the a.c. conductivity value. It is also worth noting that at higher frequencies the activation energy has much smaller values, indicating a different conduction process at higher frequencies.

TABLE I Values of activation energy for 80% SiO_x/20% SnO (300 nm) thin films at different frequencies of applied field

	Frequency (kHz)				
	0	0.3	3.0	8.0	300
ΔE(eV)	0.43	0.15	0.16	0.17	0.19

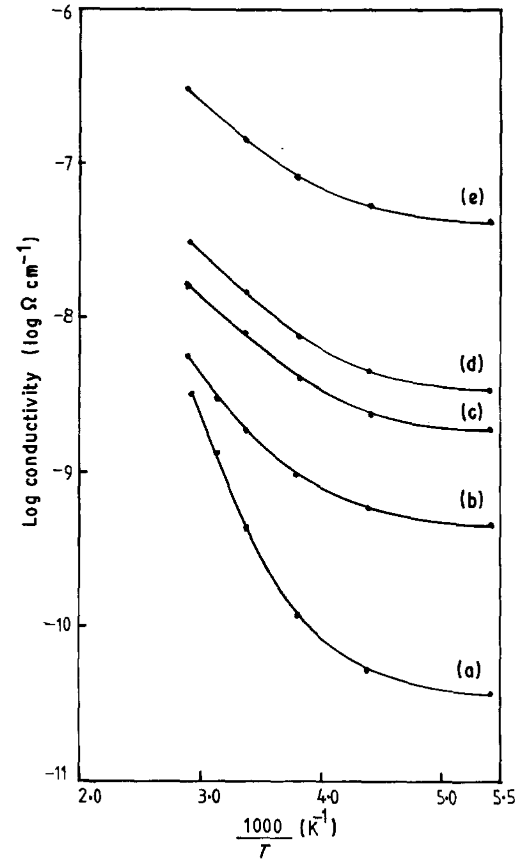

Figure 2 Log conductivity plotted against inverse temperature for the same sample as in Fig. 1 at frequencies: (a) d.c., (b) 0.3 kHz, (c) 3.0 kHz, (d) 8.0 kHz, (e) 0.3 MHz.

In order to estimate the activation energy corresponding to the true a.c. contribution to total conductivity of sample, we have plotted log frequency against inverse absolute temperature (Fig. 3) for constant values of capacitance according to the relation proposed by Simmons *et al.* [15]

$$\omega \propto \exp(-\Delta E/kT) \qquad (2)$$

The above relation is suggested to be valid for constant capacitance, whether measured in series or in parallel [15]. The activation energy calculated from the slopes of the curves in Fig. 3 using Equation 2 at room temperature is found to be 0.43 eV.

Theoretically, the total conductivity $\sigma(\omega)$ measured in a.c. fields for semiconductors or insulators can be written as

$$\sigma(\omega) = \sigma(0) + \sigma_{\text{a.c.}}(\omega) \qquad (3)$$

where $\sigma(0)$ is the d.c. conductivity and $\sigma_{\text{a.c.}}(\omega)$ is the component of conductivity depending upon the frequency of the applied field.

In order to analyse the results, different existing theories for the a.c. conductivity related to ω^s behaviour must be considered. Austin and Mott [4] improved the theory of Pollak and Geballe [16] and assumed the a.c. conduction process to be the hopping of electrons between pairs of localized states at the Fermi level. This process can be visualized as a phonon-assisted tunnelling process through the

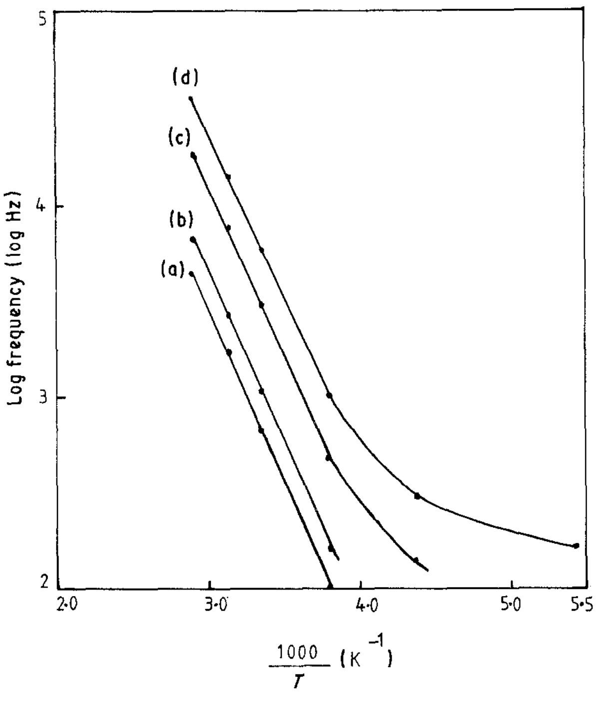

Figure 3 Log frequency plotted against inverse temperature for the same sample as in Fig. 1 and for given capacitances: (a) 5.5 nF, (b) 5.0 nF, (c) 4.0 nF, (d) 3.5 nF. (Plotted to test the Simmons formula, Equation 2.)

potential barrier between the localized states. The mathematical expression for the conductivity as proposed by them can be written as

$$\sigma_{\text{a.c.}}(\omega) \propto k\omega T[\ln(\nu_{\text{ph}}/\omega)]^4 \qquad (4)$$

where k is the Boltzmann constant, ν_{ph} is the phonon frequency, T the absolute temperature and ω the frequency of the applied field. They further suggested that in the case of polaron formation the last term in Equation 4 must be replaced by $[\ln(\nu_{\text{ph}}/\omega) - W_{\text{H}}/kT]^4$, where W_{H} is the polaron hopping energy. So in the case of polaron formation the exponent s becomes temperature dependent and the mathematical expression for conductivity takes the form

$$\sigma_{\text{a.c.}}(\omega) \propto kT\omega[\ln(\nu_{\text{ph}}/\omega) - W_{\text{H}}/kT]^4 \qquad (5)$$

Using Equation 5 the value of s can be calculated as

$$s = \text{d}[\ln\sigma_{\text{a.c.}}(\omega)]/\text{d}(\ln\omega) \approx \{1 - 4/[\ln(\nu_{\text{ph}}/\omega) - W_{\text{H}}/kT]\}$$

and the variation of s with temperature is given by expression

$$\text{d}s/\text{d}T = 4W_{\text{H}}/\{kT^2[\ln(\nu_{\text{ph}}/\omega) - W_{\text{H}}/kT]^2\} \qquad (6)$$

Equation 6 shows that the value of ds/dT is always positive which indicates that s should increase with the increase in temperature. Also Equation 4 shows that $\sigma_{\text{a.c.}}(\omega)$ is directly proportional to the absolute temperature of the device. If the present samples are considered, however, it can be observed that in this case:

(i) $\sigma_{\text{a.c.}}(\omega)$ is not proportional to absolute temperature;

(ii) s decreases with the increase in temperature.

So the theory of Austin and Mott [4] is unable to explain the behaviour of the present samples.

Elliott [6] extended the earlier Pike [2] theory to the case of the chalcogenide glasses. He suggested a process of conduction whereby the simultaneous hopping of two electrons occurs between neighbouring defect centres over the barrier separating the centres (bipolaron hopping). The expression for $\sigma_{\text{a.c.}}(\omega)$ as proposed by Elliott [6] can be written as

$$\sigma_{\text{a.c.}}(\omega) = (\pi^2 N^2 \varepsilon/24)(8e^2/\varepsilon W_{\text{m}})^6(\omega^s/\tau_0^{1-s}) \qquad (7)$$

where

$$s = 1 - 6kT/W_{\text{m}} \qquad (8)$$

W_{m} is the optical band gap, τ_0 the characteristic relaxation time, N the density of defect states per unit volume and ε the dielectric constant of the material. According to this model in the case of bipolaron hopping, the two electrons of a D^- state take an energy W_{m} to reach the conduction band in the absence of a neighbouring D^+ centre.

Elliott [6] further suggested that in the case of a very high concentration of intimate-valence alternation pairs (IVAP, the states whose separation is comparable with the radius of their wave-functions), in very close proximity to D^+ and D^- centres, ensures at least some overlap of the wave-functions, giving rise to the centre having some D^0 character, which should be detectable by electron spin resonance techniques. The hopping species in this situation would be a single polaron (D^0) and the energy required to remove an electron from a D^0 centre would be approximately $W_{\text{m}}/4$. In other words in the case of bipolaron hopping the quantity W_{m} in Equation 6 is the optical band gap of the material and for a single polaron hopping species, D^0, the value of W_{m} would be reduced by a factor of 4 as compared to the optical band gap, i.e. for single polaron hopping the quantity W_{m} would be related to the optical band gap by the relation W_{m} = (optical band gap)/4.

The optical band gap in the present case for 80% SiO_x/20% SnO (300 nm) thin films at room temperature is 1.72 eV (already reported elsewhere). The value of a.c. activation energy estimated previously for the same sample from the slope of the curves in Fig. 3 is 0.43 eV and this value is exactly one-fourth of the optical band gap. Furthermore, a value of W_{m} = 0.43 eV is put into Equation 8 in order to calculate a theoretical value of the exponent s for the same sample at room temperature, a value for s of 0.64 is found, which is in very good agreement with the experimental value found for s (0.64) at room temperature (Fig. 1).

Therefore, it is suggested that the a.c. conduction mechanism in our samples is in excellent agreement with Elliott's [6] model for single polaron hopping. Elliott [6] justified the experimental results of Street and Yoffe [17] using a similar type of argument. The existence of single polaron species, D^0 (paramagnetic centres), in the present samples has already been observed using the e.s.r. technique and reported elsewhere. It is interesting to note that in the present samples the a.c. activation energy (0.43 eV, Fig. 3) is

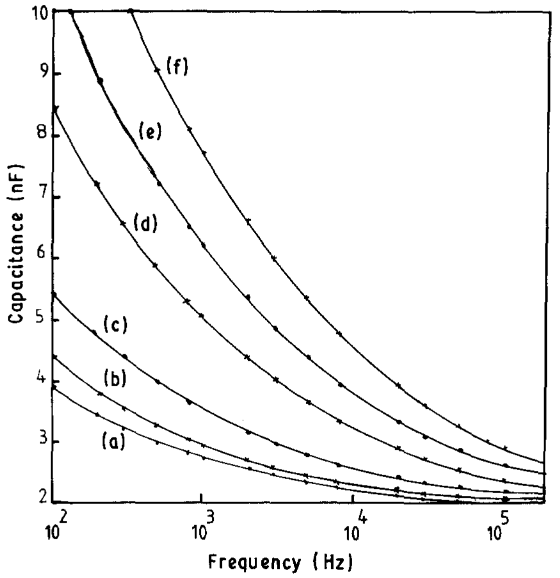

Figure 4 Capacitance plotted against frequency for the same sample as in Fig. 1 under similar conditions.

equal to the d.c. activation energy (0.43 eV, Fig. 2). This indicates that the same defect sites are responsible for both the a.c. and d.c. conductivity. A similar behaviour has also been observed by Jourdain and Despujols [16] in evaporated silicon monoxide thin films. The high-frequency region conductivity behaviour of our samples may be attributed to two-centre hopping between similar pairs of centres as proposed by Jonscher [19].

Fig. 4 shows the variation of capacitance with the variation of frequency at different temperatures for 80% SiO_x/20% SnO (300 nm) thin films. The capacitance is observed to decrease with the frequency and this decrease in the capacitance becomes less prominent for lower temperatures. It is also observed that the change in the capacitance with frequency in the low-frequency region is very much temperature dependent (it increases with the temperature) whereas it is less temperature dependent for the higher frequency region as shown in Fig. 5. The variations of the tangent of the loss angle and the loss factor with frequency are given in Fig. 6 and 7, respectively. It is observed that $\tan\delta$ has a minimum which shifts to higher frequency for higher temperatures. Such behaviour shown by our samples may be explained following the model proposed by Goswami and Goswami [20]. According to them a capacitor can be considered to consist of (i) an inherent capacity C, which is independent of temperature and frequency, (ii) a resistance R due to the dielectric film in parallel with C, and (iii) a series resistance, r, related to the leads. From these two resistances, the component R (given by the expression $R = R_0 \exp(-\Delta E/kT)$ where ΔE is an activation energy) will decrease with increasing temperature and r can be considered as temperature independent.

The expression for $\tan\delta$ can be written as

$$\tan\delta = 1/\omega RC + \omega rC \tag{9}$$

In the low-frequency region, $1/\omega Rc \gg \omega rC$ so we can write

$$\tan\delta = 1/\omega RC \tag{10}$$

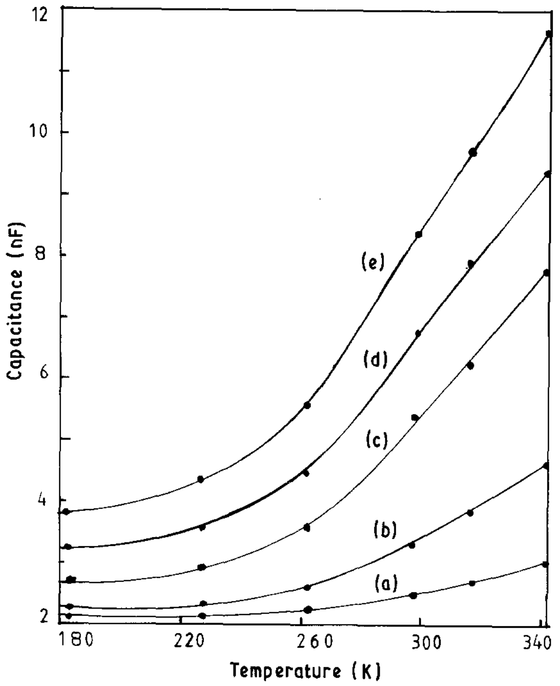

Figure 5 Capacitance plotted against temperature for the same sample as in Fig. 1 at frequencies: (a) 10.5 kHz, (b) 10.0 kHz, (c) 1.0 kHz, (d) 0.3 kHz, (e) 0.2 kHz.

Similarly, in the high-frequency region $1/\omega RC \ll \omega rC$, so in this case

$$\tan\delta = \omega rC \tag{11}$$

According to Equation 10 $\tan\delta$ decreases with increase in frequency (in the low-frequency region) whereas Equation 11 shows that $\tan\delta$ increases with the frequency (in the high-frequency region).

The shift in the minimum of $\tan\delta$ with the increase in temperature can be explained using the relation

$$\omega_{\min} = (rRC^2)^{1/2} \tag{12}$$

As the temperature is increased R will decrease, so

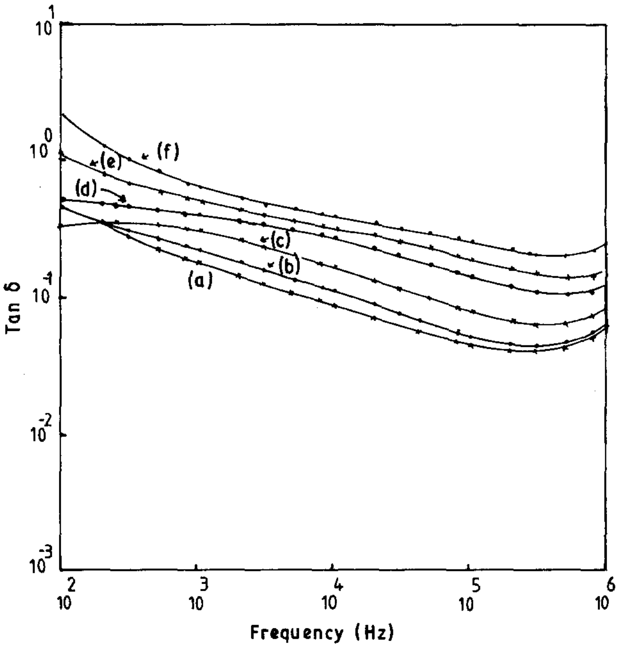

Figure 6 Tan δ plotted against frequency for the same sample as in Fig. 1 under similar conditions.

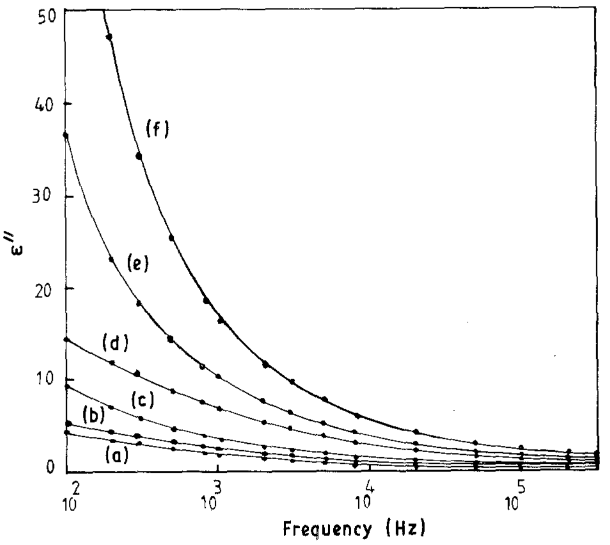

Figure 7 Loss factor plotted against frequency for the same sample as in Fig. 1 under similar conditions.

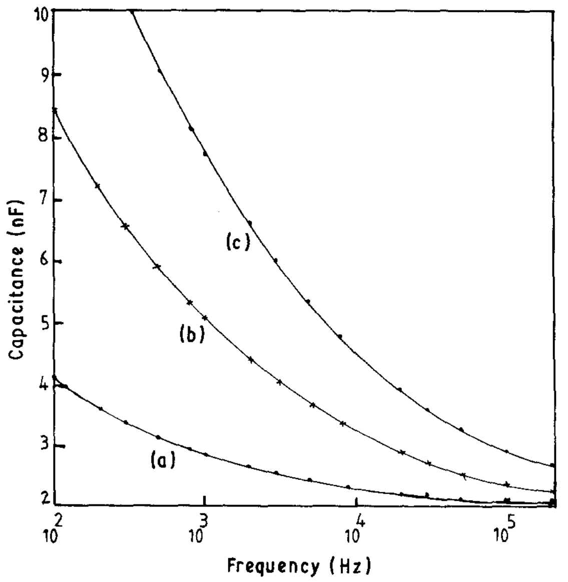

Figure 9 Capacitance plotted against frequency for the same sample as in Fig. 8 under similar conditions.

$\omega_{\min}$ (the frequency corresponding to the minimum value of $\tan\delta$) will increase.

Similarly, the dependence of capacitance on the temperature can be represented by the equation

$$C_s = (1/\omega^2R^2C) + C \tag{13}$$

where C_s is equivalent capacitance. As the temperature is increased, R in Equation 13 will decrease resulting in an increase in C_s. Also as ω is decreased, C_s will increase.

The behaviour of the present samples with change in composition as shown in Figs 8 and 9 may be explained in a similar manner.

An approximate comparison can be made of our results for 90% SiO_x/10% SnO (300 nm) thin films with those of 89% SiO_x/11% SnO_2 (330 nm) thin films given by Rahman *et al.* [14]. The conductivity of these compositions as a function of frequency at room temperature can be seen in Fig. 10. From the composition and thickness it can be assumed that the ratio of silicon to tin contents in both films is approximately the same, whereas SiO_x/SnO films will be deficient in oxygen compared to the SiO_x/SnO_2 films. The experimental value of the exponent s measured at room temperature is ≈ 0.64 whereas that reported by Rahman *et al.* [14] is 0.9. The present results were found to be in excellent agreement with Elliott's theory of single polaron hopping [6], whereas Rahman *et al.* [14] interpreted their results according to the general model of Elliott [6], i.e. bipolaron hopping. A comparison of these results leads to a very interesting conclusion.

The bipolaron hopping occurs in the case of non-intimate valence alternation pairs (NVAP), i.e. the states with the distance separating them greater than the radius of the localized wavefunction on each site. On the other hand, intimate valence alternation pairs (IVAP) are responsible for the single polaron hopping process. Elliott [6] suggested that in the case of very close proximity of D^+ and D^- centres, at least some

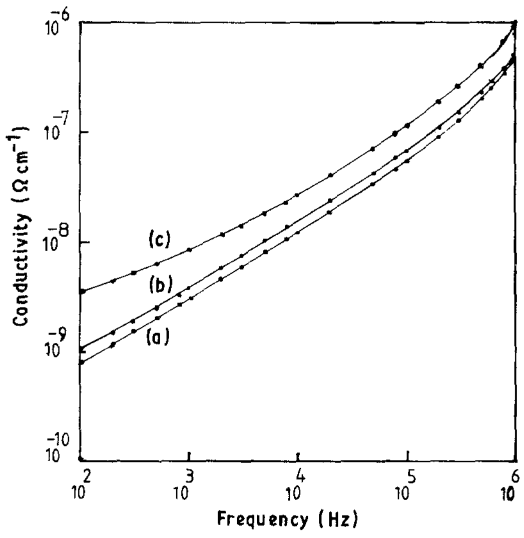

Figure 8 Conductivity plotted against frequency at room temperature for SiO_x/SnO (300 nm) thin films of different compositions: (a) 90% SiO_x, (b) 80% SiO_x, (c) 30% SiO_x.

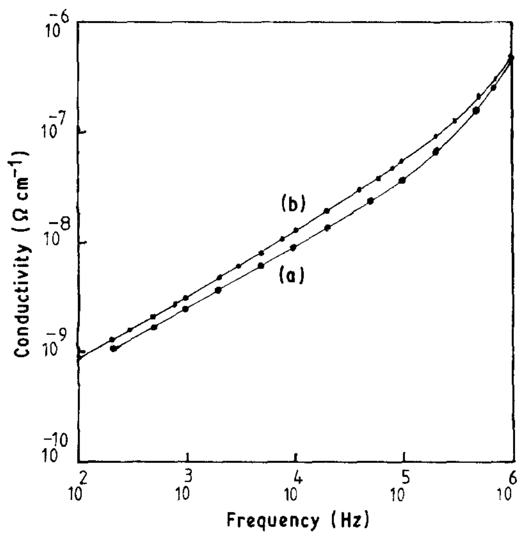

Figure 10 Conductivity plotted against frequency for (a) 89% SiO_x/11% SnO_2 (330 nm) thin films after Rahman *et al.* [14] and (b) 90% SiO_x/10% SnO (300 nm) thin films (present studies).

TABLE II The values of the exponent s, after Rahman *et al.* [14]

Frequency range (Hz)	s at			
	163 K	210 K	293 K	338 K
3×10^3–6×10^3	0.63	0.58	0.51	0.45
4×10^4–6×10^4	0.74	0.65	0.63	0.59

overlap of wavefunctions occurs and in that case D^+ and D^- centres can act as IVAPs, otherwise they will act as NVAPs. This suggests that in the case of a higher degree of disorder, the D^+ and D^- centres will act as IVAPs and for lower level of disorder these centres will act as NVAPs.

Rahman *et al.* [14] considered W_H equal to the measured optical energy gap (1.92 eV) for their samples and obtained a theoretical value of the exponent s equal to 0.92 at room temperature using Equation 8. They compared the theoretical value of s with their experimental value 0.90 calculated in the frequency range above 10^5 Hz. Their interpretation can be justified in terms of NVAPs because of less disorder in their samples (SiO_x/SnO_2) as compared to our samples (SiO_x/SnO). But according to Table II after Rahman *et al.* [14], the value of s for 89% SiO_x/11% SnO_2 (330 nm) films at room temperature in the frequency range 4×10^4 to 6×10^4 Hz (a more suitable frequency range) is 0.63. Now if the value of W_H in their case is taken as one-quarter of the measured optical energy gap (1.92 eV) then the theoretical value of s according to Equation 8 is found to be 0.68, which is more comparable to the experimental value 0.63. So it is proposed that the results of Rahman *et al.* [14] could better be explained on the basis of the Elliott [6] theory of single polaron hopping. It may be concluded that in both cases of co-evaporated (SiO_x/SnO and SiO_x/SnO_2) thin films the a.c. conduction mechanism follows the Elliott [6] model of single polaron hopping.

The conductivity for our 90% SiO_x/10% SnO (300 nm) thin films compared to 89% SiO_x/SnO_2 (330 nm) films reported by Rahman *et al.* [14] can be explained in the following way. For comparable molar content and thickness, the co-evaporated thin films of SiO_x/SnO will be deficient in oxygen content compared to those of SiO_x/SnO_2. Because of the deficiency of oxygen, the co-evaporated thin films of SiO_x/SnO will be more disordered and the band edges will penetrate further into the forbidden band gap. In this way the effective band gap of SiO_x/SnO films will be less, compared to those of SiO_x/SnO_2, so SiO_x/SnO films will be more conductive. From these observations it is concluded that under similar conditions, the co-evaporated thin films of SiO_x/SnO will be more disordered compared to those of co-evaporated films of SiO_x/SnO_2. A similar argument has already been given by us while comparing the optical band gap of co-evaporated thin films of SiO_x/SnO and SiO_x/SnO_2 [21].

4. Conclusion

The conductivity in the present samples under an alternating electric field is observed to be proportional to ω^s where the exponent s decreases with the increase in temperature. This behaviour is found to be consistent with the Elliott [6] model of single polaron hopping. The same sites in the sample structure are found to be involved in the a.c. as well as the d.c. conduction mechanisms. The dependences of capacitance, $\tan\delta$ and loss factor on frequency and temperature agree with the model of Goswami and Goswami [20]. By comparison of our results with those of Rahman *et al.* [14], we conclude that under similar conditions, the co-evaporated SiO_x/SnO thin films will be more disordered as compared to those of SiO_x/SnO_2.

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