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A.c. conduction through MIM sandwich samples of evaporated thin films of V_2O_5 and V_2O_5/B_2O_3

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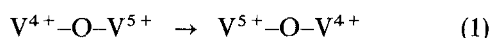
The a.c. electrical properties of evaporated V_2O_5 and co-evaporated V_2O_5/B_2O_3 films have been investigated. The conductivity in both types of film follows the theory of Elliott for single polaron hopping. The behaviour of capacitance, tangent of loss angle and dielectric loss agrees with the model proposed by Goswami and Goswami. The co-evaporated films of V_2O_5/B_2O_3 show better dielectric properties than simple V_2O_5 with increasing content of B_2O_3. Because of their hygroscopic character, the films with B_2O_3 content larger than 40% are observed to be unstable in the atmosphere.

1. Introduction

The electrical properties of V_2O_5-based glasses have been studied extensively by many authors [1–4]. In transition metal oxide glasses, the charge transport requires the presence of the transition metal in at least two of its valence states and the conduction occurs by the transfer of an electron from a reduced valency to a higher valency ion and consequently the conduction is through the d-levels of the transition metal. The electron is essentially localized and almost certainly self-trapped through the formation of a small polaron. It is suggested that the transition metal oxide glasses and ionic conducting materials such as borosilicate glass have a common feature that in both, the basic charge transport mechanism involves hopping of a polaron in the first case and ions in the second case [5]. Haemers *et al.* [6] have interpreted the a.c. conduction for V_2O_5 single crystals on the basis of a variable-range hopping mechanism between localized states situated at the Fermi level.

Nadkarni and Shirodkar [7] have suggested that the observed electrical properties (d.c. as well as a.c.) of $Al/V_2O_5/Al$ could be explained by taking into account the crystallite–crystallite interfacial Schottky-type barrier which exists because of the granular nature of these films. Dmitrieva *et al.* [8] found the electrical conductivity in V_2O_5 to be proportional to the concentration of V^{4+} ions and the transfer of charge to take place due to an exchange of valencies between V^{4+} and V^{5+} ions. Ioffe and Patrina [9] confirmed the existence of V^{4+} centres in V_2O_5 crystals through electron spin resonance (ESR) studies. Allserma *et al.* [10] proposed that for V_2O_5, an electron on a V^{4+} centre will migrate to an adjacent V^{5+} centre following an overall mechanism



$$V^{4+}\text{–O–}V^{5+} \rightarrow V^{5+}\text{–O–}V^{4+} \quad (1)$$

The localization of an electron on a V^{4+} centre will result in the formation of a polaron. The motion of such a polaron may be responsible for the conduction in V_2O_5.

Recently Shimakawa [11] has suggested that in spite of the well-accepted fact of small polaron formation in transition metal oxide glasses, no satisfactory analysis of d.c. and a.c. transport exists. According to him the a.c. conductivity, which is strongly correlated to the d.c. conductivity, can never be explained by the theories based on a pair approximation. Rather it must be interpreted in terms of a continuous-time random-walk (CTRW) approximation. Linsley *et al.* [4], while studying electrical conduction through vanadium phosphate glasses, observed a low-temperature and low-frequency region where the conductivity increased slightly less than linearly but at higher temperature they observed a frequency-squared dependence; at the same time the a.c. conductivity in this high-frequency region became temperature dependent. A similar behaviour has also been observed by Owen and Robertson [12] for chalcogenide glasses.

Timson and Hogarth [13] have reported that by the addition of B_2O_3 to SiO, the dielectric loss can be reduced. Vardhan *et al.* [14] have also reported that the addition of B_2O_3 to SiO results in an increase in the dielectric constant of SiO films. They suggested that some structural changes brought about by B_2O_3 in SiO/B_2O_3 composite films might be responsible for such a change in the dielectric constant. Mikoda *et al.* [15] have observed that the addition of B_2O_3 to glasses containing PbF_2 reduced the dielectric loss by the suppression of crystallization. Culea and Nicula [16] have suggested that the electrical conductivity of V_2O_5–B_2O_3 glasses is decreased and the activation energy is increased when the B_2O_3 content in the glass is increased. From the infrared data of V_2O_5–B_2O_3 glasses, Culea *et al.* [17] suggested that the glass former oxide breaks the bridging bonds V–O–V and consequently inhibits the electron hopping.

We have studied the mechanism governing the a.c.

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conduction through evaporated V_2O_5 and co-evaporated V_2O_5/B_2O_3 films.

2. Experimental procedure

The samples for electrical measurements were deposited on to 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 [18], and finally evaporating metal for the top electrode. The rates of evaporation and film thickness could be controlled. Six devices, each having an effective area of 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 copper base 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.

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 200 mV.

3. Results

The a.c. conductivity as a function of frequency at different temperatures for evaporated thin (200 nm) films of simple V_2O_5 is shown in Fig. 1. Fig. 2 shows the variation of capacitance with the frequency for the same sample as in Fig. 1 under similar conditions. The conductivity–temperature curves for the same sample can be seen in Fig. 3. The plot of log frequency against inverse temperature for the same sample as in Fig. 1 following the formula of Simmons *et al.* [19] is shown in Fig. 4. The variation of a.c. conductivity with frequency of applied field at different temperatures for co-evaporated V_2O_5/B_2O_3 (200 nm) thin films can be seen in Fig. 5. Capacitance, tan δ and dielectric loss as functions of frequency for the same sample as in Fig. 5 and under similar conditions, are shown in Figs 6, 7 and 8, respectively. Fig. 9 represents the variation in the conductivity for the same sample as in Fig. 5 at different frequencies. The frequency of the applied field plotted as a function of inverse temperature for constant values of capacitance according to the Simmons

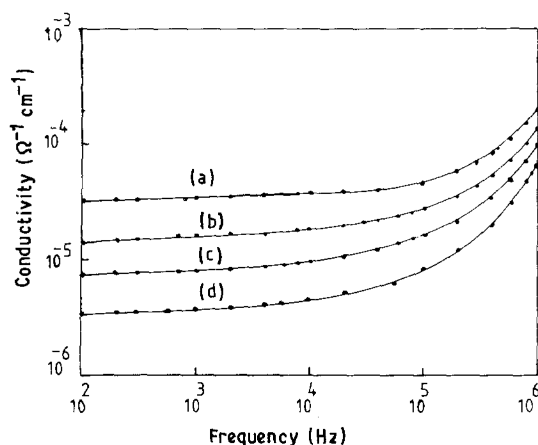

Figure 1 Conductivity plotted against frequency for evaporated V_2O_5 (200 nm) thin films at different temperatures, (a) 253 K, (b) 223 K, (c) 188 K, (d) 153 K.

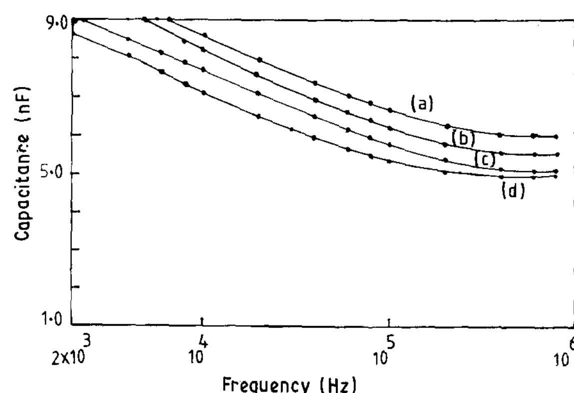

Figure 2 Capacitance plotted against frequency for the same sample as in Fig. 1 under similar conditions.

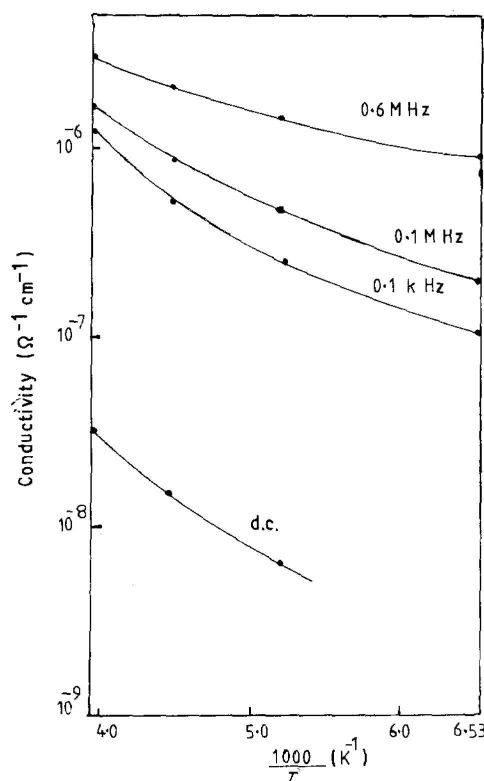

Figure 3 Conductivity plotted against inverse temperature at different frequencies for V_2O_5 (200 nm) thin films.

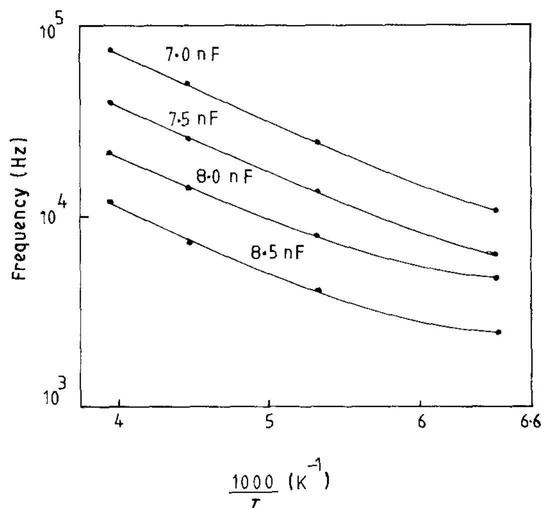

Figure 4 Frequency plotted against inverse temperature for the same sample as in Fig. 1 at different constant capacitance values following the Simmons formula.

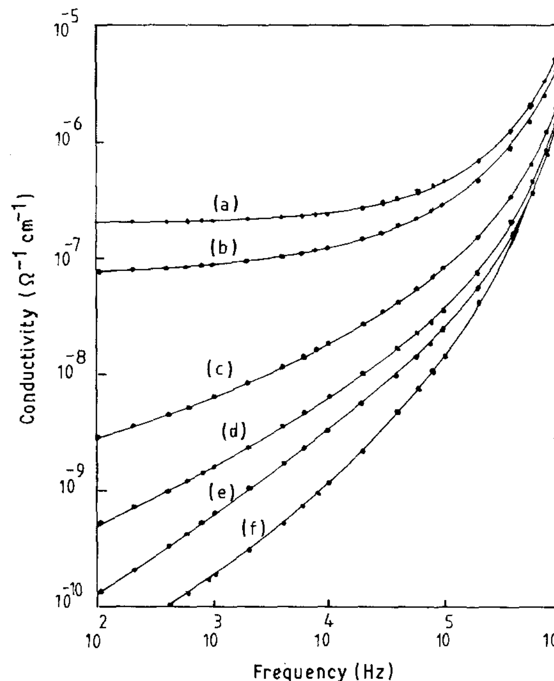

Figure 5 Conductivity plotted against frequency for co-evaporated V_2O_5/B_2O_3 (200 nm) thin films at different temperatures, (a) 327 K, (b) 293 K, (c) 253 K, (d) 223 K, (e) 183 K, (f) 153 K.

et al. [19] formula for the same sample as in Fig. 5 can be seen in Fig. 10.

4. Discussion

It has been observed that at low temperatures and frequencies the a.c. conductivity shows a sublinear frequency dependence behaviour of hopping conduction [2]. Under the application of an alternating field the conduction follows a power-law frequency dependence of the type

$$\sigma(\omega) = A\omega^s \quad (2)$$

where A and s are temperature-dependent parameters. The above type of a.c. conduction behaviour was first observed by Pollak and Geballe [20] in n-type doped silicon at low temperatures and was well described by an exponent s equal to 0.8. The power-law frequency-dependent behaviour of conductivity has been observed in many disordered materials such as amorphous semiconductors, organic solids and oxide glasses [21]. Owen [5] suggested that in amorphous solids the response of ionic, polaronic and electronic effects to the a.c. field is essentially described by Equation 2. Usually the hopping of electrons or polarons between the localized states in the mobility gap is responsible for the power-law frequency dependence [22].

Austin and Mott [23], adopting the pair approximation, suggested that the a.c. loss is mainly due to the electron jumps between the pairs of localized states. According to them the a.c. conduction process can be considered as a phonon-assisted tunnelling process through the potential barrier between the localized states. They proposed a mathematical expression for the a.c. conductivity as

$$\sigma_{a.c.}(\omega) \propto k\omega T[\ln(\nu_{ph}/\omega)]^4 \quad (3)$$

where k is the Boltzmann constant, ν_{ph} is the phonon frequency, T is absolute temperature and ω is the radial frequency of the applied field. According to Equation (3) [23] the exponent s for the frequency

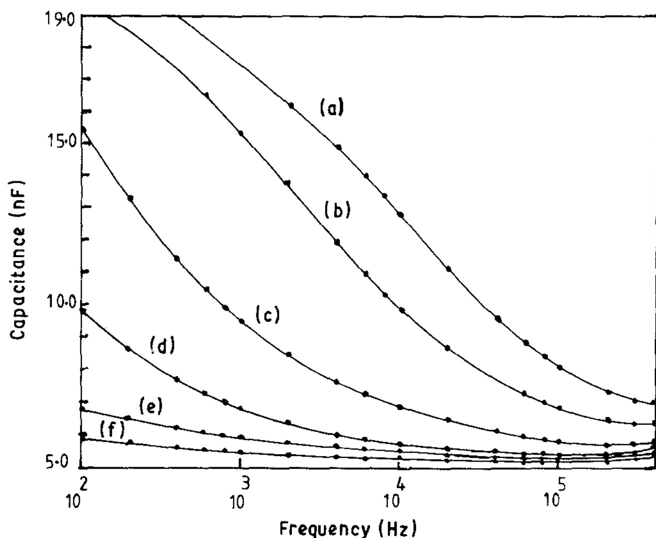

Figure 6 Capacitance plotted against frequency for the same sample as in Fig. 5 under similar conditions.

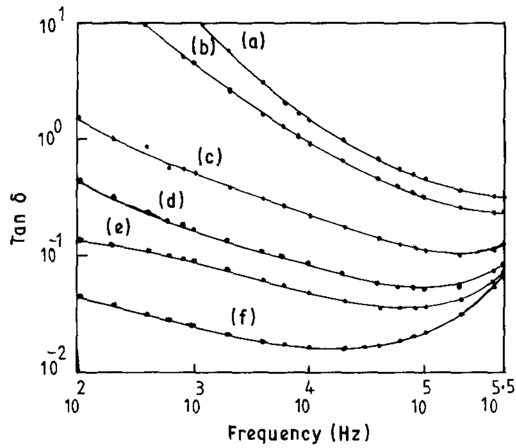

Figure 7 Tangent of loss angle plotted against frequency for the same sample as in Fig. 5 under similar conditions.

power law behaviour of the conductivity at high frequencies is given by

$$s = d\ln\sigma(\omega)/d\ln\omega = 1 + 4/\ln(\omega/\nu_{ph}) \quad (4)$$

where ν_{ph} is the phonon frequency. From Equation (4) it appears that s is a decreasing function of frequency. This has never been observed experimentally; normally the value of s increases with frequency [5]. In addition to this, for the explanation of the most commonly observed values of s which are close to unity for most of the amorphous solids at low temperatures, the value of ν_{ph} has to be assumed to have a value as high as 10^{20} Hz which is unrealistic. Also the value of s comes out to be independent of temperature which is normally not observed. The authors further suggested that in the case of polaron formation the last term, i.e. $[\ln(\nu_{ph}/\omega)]^4$ in Equation 3 should be replaced by $[\ln(\nu_{ph}/\omega) - W_H/kT]^4$, in order to consider the effect of polaron formation, where W_H is the polaron hopping energy. So in the case of polaron formation, the

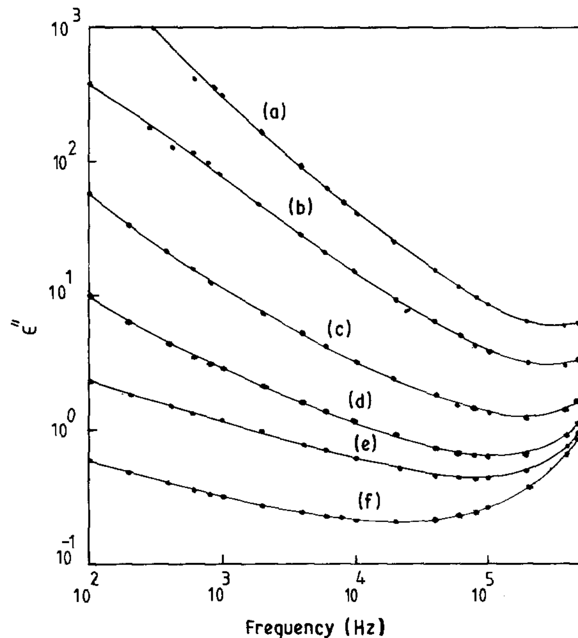

Figure 8 Dielectric loss plotted against frequency for the same sample as in Fig. 5 under similar conditions.

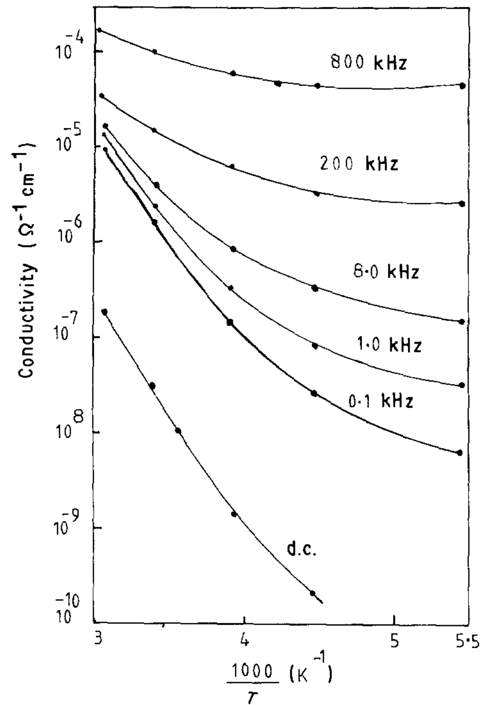

Figure 9 Conductivity plotted against inverse temperature for the same sample as in Fig. 5 at different frequencies.

expression for conductivity can be written as

$$\sigma_{a.c.}(\omega) \propto kT\omega[\ln(\nu_{ph}/\omega) - W_H/kT]^4 \quad (5)$$

In that case, the value of s according to Equation (5) becomes temperature dependent and can be written as

$$s = d[\ln\sigma_{a.c.}(\omega)]/d(\ln\omega) \approx \{1 - 4/[\ln(\nu_{ph}/\omega) - W_H/kT]\} \quad (6)$$

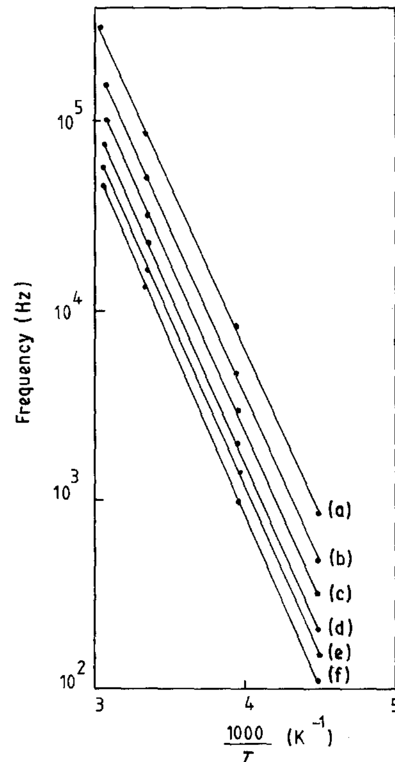

Figure 10 Frequency plotted against inverse temperature for the co-evaporated V_2O_5/B_2O_3 (200 nm) thin films following the Simmons formula at different constant values of capacitance, (a) 7.0 nF, (b) 7.5 nF, (c) 8.0 nF, (d) 8.5 nF, (e) 9.0 nF, (f) 9.5 nF.

The variation of s with temperature is given by the expression

$$ds/dT = 4W_H/\{kT^2[\ln(\nu_{ph}/\omega) - W_H/kT]^2\} \quad (7)$$

From Equation 7 it is concluded that the derivative of s with respect to T is always positive, indicating an increase in s with increasing temperature. Also according to Equation 3 the a.c. conductivity is directly proportional to the absolute temperature of the device. In our case we observe that $\sigma_{a.c.}(\omega)$ is not directly proportional to absolute temperature and also s is not independent of temperature but decreases with increase in temperature. All these observations are contrary to the predictions from the theory of Austin and Mott [23].

Elliott [24], following the Pike [25] theory, suggested that the a.c. conduction process may be visualized as the simultaneous hopping of two electrons between neighbouring defect centres over the barrier separating the centres (bipolaron hopping). He proposed an expression for $\sigma_{a.c.}(\omega)$ as

$$\sigma_{a.c.}(\omega) \propto \varepsilon(\varepsilon W_m)^{-6}(\omega^s/\tau_0^{1-s}) \quad (8)$$

where

$$s = 1 - 6kT/W_m \quad (9)$$

where W_m is the optical band gap, τ_0 is the characteristic relaxation time, and ε is 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. It should be noted that D^- and D^+ are diamagnetic centres. In this formalism D^+, D^0 and D^- are the centres with zero, one and two captured electrons, respectively. D^0 is a single polaron.

Elliott [24] further suggested that in the case of the centre having some D^0 character, which should be detectable by ESR techniques, the hopping species would be a single polaron (D^0) and the energy required to remove an electron from a D^0 centre would be approximately $W_m/4$. So in the case of single polaron hopping the value of s in Equation 8 can be written as

$$s = 1 - 24kT/W_m \quad (10)$$

The experimental value of s for V_2O_5 (200 nm) films measured from the slope of Fig. 1 in the frequency range 2×10^5 to 8×10^5 Hz at room temperature is found to be 0.76. If we calculate the theoretical values of s at room temperature using Equations 9 and 10 using the value of optical energy gap (2.40 eV) as measured by us, these values are determined as 0.94 and 0.75, respectively. As the theoretical value calculated from Equation 9 agrees with the experimental value, we conclude that the conduction mechanism in films is governed by the Elliott [24] theory of single polaron hopping. Similarly the experimental value of s for composite V_2O_5/B_2O_3 (200 nm) films as measured from the slope of Fig. 5 at room temperature in the frequency range 4×10^4 to 4×10^5 Hz is 0.77. Again the theoretical values of s according to Equations 9 and 10 at the measured optical energy gap (2.70 eV), respectively, are found to be 0.94 and 0.76, respectively. This behaviour of V_2O_5/B_2O_3 (200 nm) films is also consistent with a single polaron conduction mechanism as proposed by Elliott [24]. We have detected the presence of V^{4+} species by means of the ESR technique and these are acting as D^0 (the single polaron species).

In order to calculate the activation energy corresponding to a.c. conduction we have plotted log frequency of the applied field against inverse temperature for constant values of capacitance according to the relationship proposed by Simmons *et al.* [19] as

$$\omega \propto \exp(-\Delta E/kT) \quad (11)$$

The value of the a.c. activation energy is determined to be 0.42 eV, and that corresponding to the d.c. conductivity as calculated from the slope of the d.c. curve from Fig. 9 is found to be 0.44 eV. From the comparison of these values we conclude that the same charge centres are involved in both types of a.c. and d.c. conduction mechanism for co-evaporated V_2O_5/B_2O_3 films. This type of behaviour could not be observed for simple evaporated V_2O_5 films. All other factors, such as the variation of dielectric constant, tangent of loss angle and the capacitance with frequency can be satisfactorily explained by the model of Goswami and Goswami [26] except the fact that above room temperature the V_2O_5 films seemed to show a negative capacitance at higher frequencies which will be discussed in a later paper.

5. Conclusion

In both types of evaporated films (V_2O_5 and V_2O_5/B_2O_3), the a.c. conduction mechanism follows the single polaron hopping theory of Elliott. The same charge centres are found to take part in both a.c. and d.c. conduction processes. The dependence of tangent of loss angle, dielectric constant and capacitance on the frequency fits the model of Goswami and Goswami. Co-evaporated V_2O_5/B_2O_3 films with B_2O_3 contents higher than 40% are observed to be of a hygroscopic nature and thus difficult to use in technological applications unless hermetically sealed.

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