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D.C. conduction in thin films of SiO_x/V_2O_5 co-evaporated assemblies prior to electroforming

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D.C. conduction in MIM sandwich structures based on SiO_x/V_2O_5 as a dielectric has been investigated before electroforming. The electrodes make a blocking contact to the dielectric with a barrier height, ϕ_0, dependent on the type of electrode material used. The voltage–current characteristic is studied between 165 and 413 K. Below room temperature and at low fields hopping conduction is dominant; at intermediate temperatures a transition to free band conduction is observed. At higher temperatures and fields the conduction is enhanced by Schottky barrier lowering associated with an activation energy $\Delta E \simeq 0.15$ eV. Hopping conduction has also been found to be dominant above room temperature in thin films having a high density of trapping states.

1. Introduction

D.C. conduction before electroforming has been investigated for many mixed oxide MIM structures [1, 2]. It is established that conduction in SiO at high fields is due to the Poole–Frenkel effect [3, 4], while conduction in V_2O_5 has been attributed to intergranular Schottky-type barriers [5]. The present work deals with the mixed oxides of both SiO and V_2O_5. One of the effects of mixing V_2O_5 with SiO is to change the high-field conduction before electroforming from bulk-limited to contact-limited. The voltage–current characteristic before electroforming is studied between 165 and 413 K. Non-linear behaviour of the circulating current, I_c, as a function of bias voltage, V_b, is observed and explained in terms of Schottky emission at a blocking contact as the dominant process, hopping conduction also taking place, particularly at low temperatures. At higher temperatures and at lower fields in highly doped thin films the contribution from hopping conduction becomes significant.

2. Experimental work

Films were evaporated by a technique of thermal co-evaporation in a Balzers BA 510 coating unit on to clean Corning 7059 glass substrates as previously described [6]. D.C. electrical measurements were made by conventional methods in a subsidiary vacuum system at a pressure of 10^{-6} to 10^{-5} Torr. The d.c. bias voltage was provided by a Coutant LA 100.2 power supply and the current was recorded by an electronic Avometer. The voltage across the sample was monitored by a digital voltmeter. Lowering of the sample temperature was achieved by firmly attaching it to the brass base of a stainless steel tank containing liquid nitrogen. Heating the sample above room temperature was initiated by using a resistive heater inserted in holes made through the brass base. Sample temperatures were monitored with a fine copper–constantan thermocouple attached to the substrate. The form of the samples was described in an earlier publication [7].

3. Results

At low fields an ohmic behaviour was always observed in our sample followed by a non-linear dependence of current on voltage as shown in Figs. 1a, b and c for different electrode

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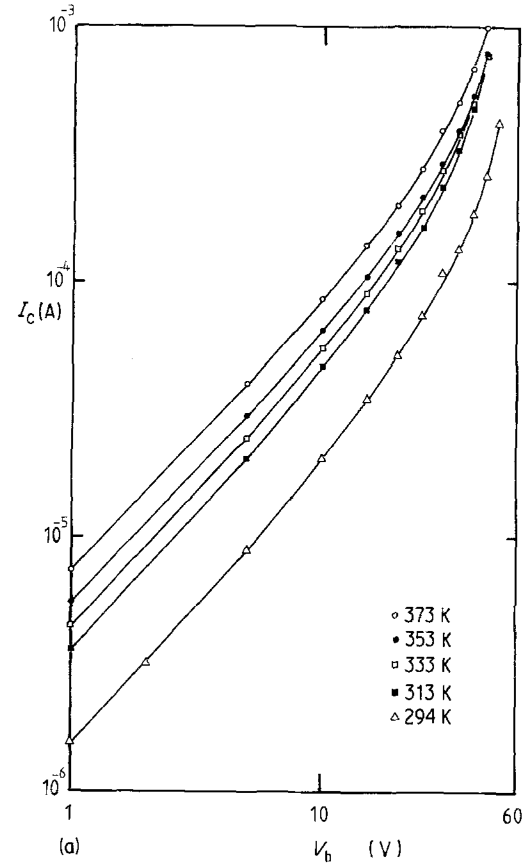
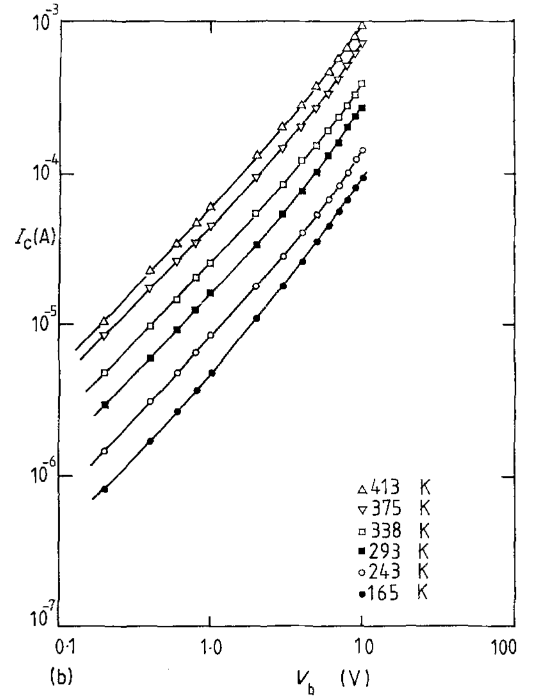




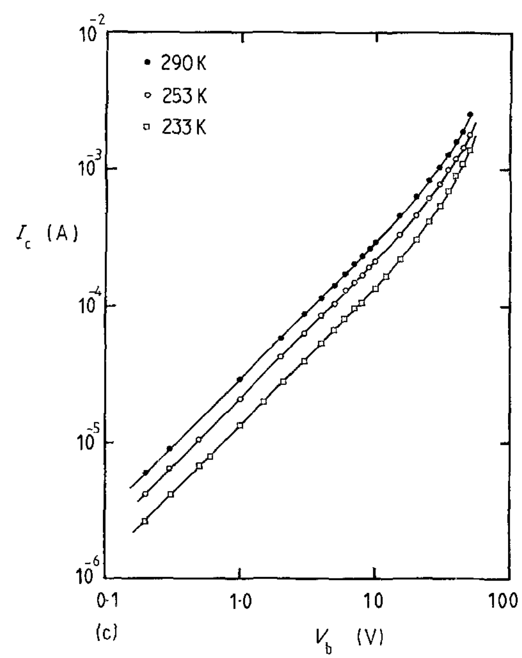


Figure 1 Voltage–current characteristics: (a) of an Al–65 mol % SiO/35 mol % V_2O_5–Al thin film assembly at four temperatures (insulator thickness 115 nm): (b) of a Cu–57 mol % SiO/43 mol % V_2O_5–Cu thin film assembly at six temperatures (insulator thickness 620 nm); (c) showing non-linear dependence at high fields for an Ag–45 mol % SiO/55 mol % V_2O_5–Ag thin film sandwich (insulator thickness 96 nm).

materials. The interpretation of these curves based on the assumption of a simple Poole–Frenkel or Schottky effect which requires the logarithm of the circulating current to be proportional to $V_b^{1/2}$, leads to values of parameters incompatible with the theory and to unreasonably low values of dielectric constant. Good theoretical agreement with the results is obtained on the assumption that a blocking contact exists, leading to a modified form of Schottky emission. At such contacts a space charge will be created in a depletion region due to the difference in the work functions of the metal and of the insulator and if there is an adequate density of donors N_d (positive when empty) in the insulator, then electrons will be emitted from these states into the metal until thermochemical equilibrium is achieved. This depletion region will extend to a distance, λ, and will give rise to an electric field in the region much higher than in the bulk. The depletion region is more resistive than the rest of the bulk due to the absence of mobile carriers and the applied potential difference will drop almost entirely across this region. The electric field, E, and subsequently the field-lowering contact barrier, $\Delta\phi$, are determined by the width λ, which in turn is determined by the density, N_d, of ionizable impurities according to the relation [8, 9]

$$\lambda = \left(\frac{2\varepsilon_0\varepsilon_r V_c}{qN_d}\right)^{\frac{1}{2}} \simeq 1052\left(\frac{\varepsilon_r V_c}{N_d}\right)^{\frac{1}{2}} \quad (1)$$

where V_c is the effective potential across the contact, $q = 1.6 \times 10^{-19}$ C, $\varepsilon_0 = 8.854 \times 10^{-14}$ F cm^{-1} and ε_r is the relative dielectric constant. The electric field at this contact is given by

$$E_c = \left(\frac{2qN_d V_c}{\varepsilon_0\varepsilon_r}\right)^{\frac{1}{2}} = 1.9 \times 10^{-3}\left(\frac{V_c N_d}{\varepsilon_r}\right)^{\frac{1}{2}} \quad (2)$$

The interaction of this field with the image force lowers the contact barrier by an amount $\Delta\phi$ and is given by

$$\Delta\phi = q\left[\frac{q^3 N_d V_c}{2(8\pi)^2\varepsilon_0^3\varepsilon_r^3}\right]^{\frac{1}{4}}$$

$$\simeq 8.26 \times 10^{-6} q\left(\frac{N_d V_c}{\varepsilon_r^3}\right)^{\frac{1}{4}} \quad (3)$$

Since the potential drop across λ is V_c then the relation governing the emission current, which is independent of the insulator thickness, is of the form [7]

$$I_c = AA^*T^2 \times \exp\left[-\frac{\phi - 8.26 \times 10^{-6} q(N_d V_b/\varepsilon_r^3)^{\frac{1}{4}}}{kT}\right] \quad (4)$$

where A is the effective area, A^* is the effective Richardson–Dushman constant, T is the absolute temperature, k is the Boltzmann constant (8.62×10^{-5} eV K^{-1}) and ϕ is the contact barrier height. V_b is the applied voltage (assumed approximately equal to V_c).

The surface density of charge N_s per unit area, which is required to screen the internal field E_c is given by [9]

$$N_s = \lambda N_d \quad (5)$$

3.1. Voltage–current dependence at low and high temperatures

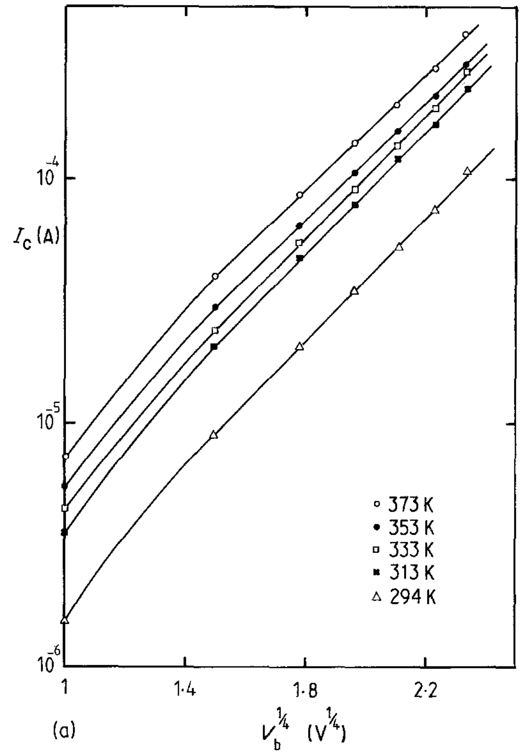
Figs. 1a to c shows three non-linear curves for MIM samples of SiO/V_2O_5 having different electrode materials. Using Equation 4, plots of $\log I_c$ against $V_b^{1/4}$ would give a value of N_d. These plots are shown in Figs. 2a to c. Using Equations 1 to 5, the average values of the parameters are $N_d \simeq 1$ to 6×10^{17} cm^{-3}, $\lambda \simeq 1 \times 10^{-5}$ to 4.8×10^{-6} cm, $E_c \simeq 1 \times 10^6$ V cm^{-1} and $N_s \simeq 1.6$ to 5.4×10^{12} cm^{-2}. The contact-barrier heights are found to be 0.65, 0.71 and 1.0 eV for silver, copper and aluminium contacts, respectively. The latter result indicates the dependence of contact-barrier height values on the contact material used and gives further evidence for the observed contact-limited conduction. The d.c. electrical resistivities of all the three thin films measured in the ohmic region were found to be in the range 1×10^8 to 6×10^9 Ω cm characteristic of typical amorphous semiconductors. Table I lists some parameters which affect the current level at room temperature for the three samples having different anode materials.

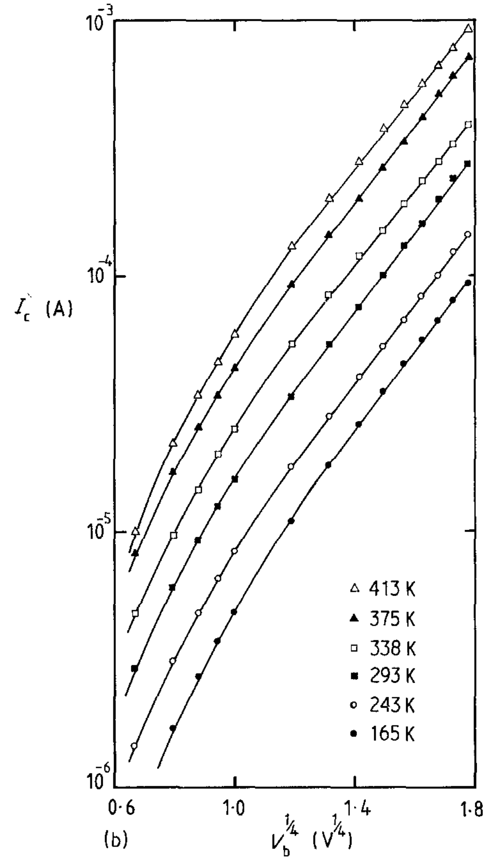
TABLE I Some parameters calculated at room temperature for the three samples which have different anode materials

Parameter	Ag sample	Cu sample	Al sample
ϕ_0 (eV)	0.65	0.71	1.0
N_d (cm^{-3})	6×10^{17}	4.7×10^{17}	1.6×10^{17}
N_s (cm^{-2})	5.4×10^{12}	2.25×10^{12}	1.6×10^{12}
λ (cm)	9×10^{-6}	4.8×10^{-6}	1×10^{-5}

3.2. Temperature dependence of current through the blocking contact

To study the effects of temperature on such a contact, measurements were carried out from 165 to 413 K over a wide range of voltages. According to Equation 4 a plot of $\log(I_c/T^2)$ against $1/T$ would yield a straight line satisfying the equation. If the initial room temperature current I_0 is subtracted from the total current, then the remaining component of current should be due to the contact-barrier lowering. This plot is shown in Fig. 3 for an $Al–SiO/V_2O_5–Al$ thin film, where the gradients of the straight lines yield activation energies between 0.10 and 0.12 eV according to the bias voltage. In Fig. 4 a plot of I_c against $1/T$ is shown for a $Cu–SiO/V_2O_5–Cu$ thin film assembly and a transition takes place within the temperature range −35 to 21° C. This suggests that more than one conduction mechanism is involved, namely hopping conduction with activation energy $\Delta E = 0.01$ eV and free band conduction with $\Delta E = 0.15$ eV controlled by the contact. It is well known [10] from studies of crystalline semiconductors that free band and impurity hopping conduction mechanisms may exist side by side and this seems to be true of some amorphous





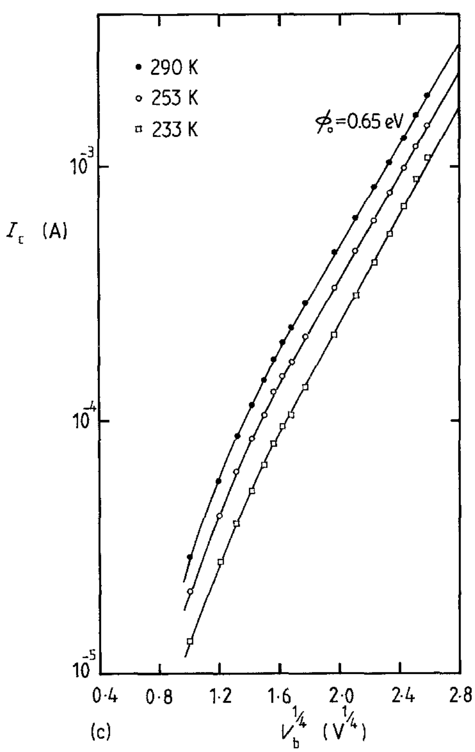


Figure 2 (a) Derived plot for an Al–SiO/V_2O_5–Al thin film to demonstrate Schottky emission. (b) Current plotted against V_b assuming Schottky emission at a blocking contact for a Cu–SiO/V_2O_5–Cu thin film assembly measured at six temperatures. (c) Plots of circulating current against $V_b^{1/4}$ assuming Schottky emission at a blocking contact for an Ag–45 mol % SiO/55 mol % V_2O_5–Ag thin film assembly.

materials, depending on the density and distribution in energy of various localized levels. The gradual transition may be due to overlapping of localized level and free band conduction, as would be the case if the Fermi level fell in the vicinity of the transition from free band to the localized tail. The current at low field varies with the temperature in accordance with the equation

$$I_c = I_0 \exp(-\Delta E/kT) \qquad (6)$$

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

$$I_0 = q\mu N_t \frac{V_b}{d} A \qquad (7)$$

where q is the electronic charge, μ is the mobility, N_t is the trap density, V_b is the bias voltage, d is the dielectric thickness and A is the active area. Using Equation 7 and assuming $N_t \simeq 1.65 \times 10^{11}$ cm^{-3} (derived from the curve of Fig. 4), the mobility was estimated to be 2.4×10^{-2} cm^2 V^{-1} sec^{-1}. This low value of mobility

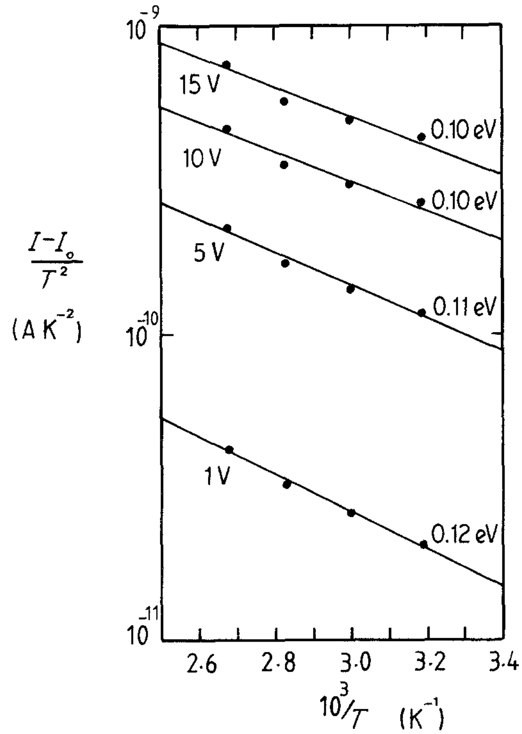


Figure 3 Total current less room temperature current as a function of inverse temperature for an Al–SiO/V_2O_5–Al thin film assembly. Insulator thickness 115 nm. (Bias voltages and derived activation energies are indicated.)

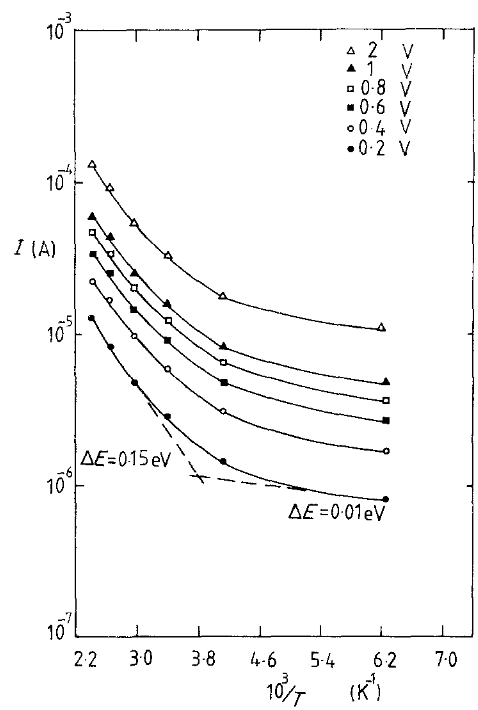


Figure 4 Circulating current as a function of inverse temperature at six applied voltages for a Cu–57 mol % SiO/ 43 mol % V_2O_5–Cu thin film assembly. (Bias voltages shown.)

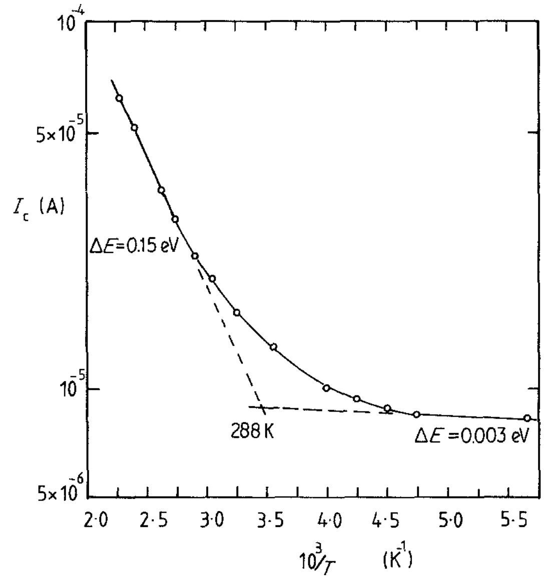


Figure 5 Dependence of circulating current on reciprocal temperature for a Cu–94 mol % SiO/6 mol % V_2O_5–Cu thin film assembly showing a transition from hopping to free-band conduction at 288 K. (Insulator thickness 910 nm, V_b = 5 V.)

and activation energy associated with an ohmic I_c–V_b characteristic is attributed to a localized state conduction (hopping) at low fields and low temperature. Further evidence of such a transition is presented in a 910 nm thin film of Cu–SiO/V_2O_5–Cu. Fig. 5 shows the dependence of circulating current on inverse temperature. A gradual transition from hopping conduction to free band conduction occurs at about 15° C with a hopping activation energy ΔE = 0.003 eV and a free band activation energy of 0.15 eV. Other parameters were determined and N_t is assumed to be equal to 3×10^{11} cm^{-3}. The estimated mobility 3.6×10^{-2} cm^2 V^{-1} sec^{-1} indicates that the hopping conduction is a dominant conduction process at low temperatures. Fig. 6 shows the hopping current subtracted from total current as a function of inverse temperature. The derived activation energy ΔE = 0.13 eV is indicative of the Schottky emission at a blocking contact at higher temperatures.

Hopping has also been observed at temperatures above room temperature. Fig. 7 shows a plot of I_c against $V^{1/2}$ for a 132 nm thick Cu–78%SiO/22%V_2O_5–Cu thin film. The curve in the high field region is not linear so that the Schottky-contact limited conduction is excluded. Fig. 8a shows a plot of I_c/T^2 against

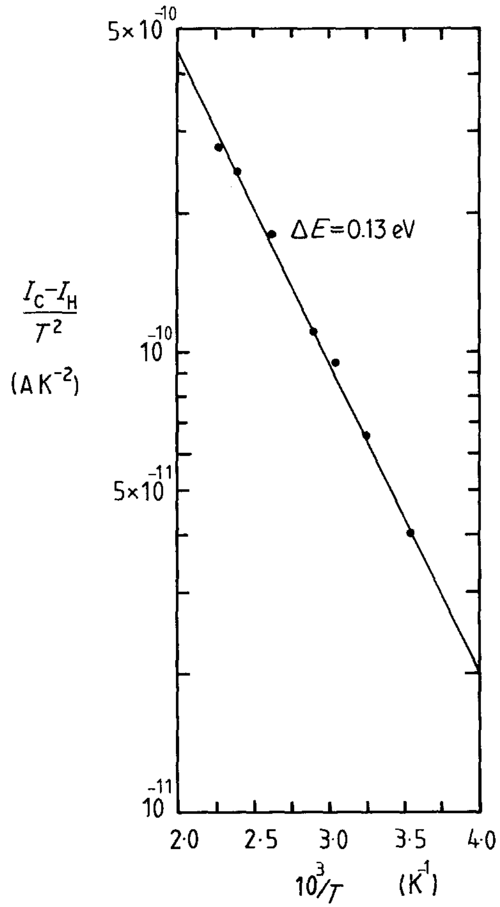


Figure 6 Circulating current less hopping current as a function of inverse temperature for a Cu–SiO/V_2O_5–Cu thin film assembly. (Insulator thickness 910 nm.)

$1/T$, whose slope yields a negative activation energy which is not allowed on the assumption of Schottky emission of a blocking contact. Therefore, I_c was plotted against $1/T$ as shown in Fig. 8b. This yields an activation energy equal to 0.036 eV typical of electronic hopping between impurity sites. Thus a bulk-limited process of the above type is taking place even at temperatures above room temperature. The curve at 1 V if extrapolated to $1/T = 0$ gives $I_0 = 8.2 \times 10^{-4}$ A. From the relation governing the currents in hopping systems (Equation 7) we obtain:

$$\mu_H N_t = 6.765 \times 10^{11}\ \mathrm{cm^{-1}\ V^{-1}\ sec^{-1}}$$

and if we assume $\mu_H = 1 \times 10^{-4}\ \mathrm{cm^2\ V^{-1}\ sec^{-1}}$ then $N_t = 6.7 \times 10^{15}\ \mathrm{cm^{-3}}$. This result indicates that the trap density in this particular thin film is higher than that of preceding examples where a transition to a higher mode of conduction has occurred because of the high donor densities and lower trap densities in the two previous thin films. This sample has a higher trap density and probably a lower donor density and therefore no transition to a higher mode of conduction has been observed.

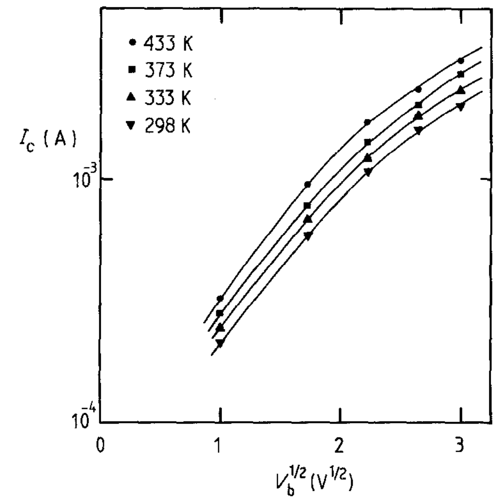


Figure 7 Curve of current against bias voltage plotted in accordance with assumption of a simple Schottky regime does not show a linear region at high applied fields. (Sample Cu–78 mol % SiO/22 mol % V_2O_5–Cu, insulator thickness 132 nm.)

Finally, Fig. 9 shows the temperature dependence of the relative dielectric constant of a 620 nm thick Cu–57%SiO/43%V_2O_5–Cu thin film.

4. Discussion

If donors lies entirely above traps in an energy band system and have a larger total density, the Fermi level falls in the donor levels. Thus a strongly activated conduction is indicative of a very low density of localized states at the Fermi level; therefore, the most likely mechanism of conduction is by free carriers in the conduction band, and the provision of carriers implies their thermal excitation over the barrier ϕ. This may eventually become enhanced by Schottky lowering of the barrier in high electric fields. This is consistent with samples showing a transition from hopping conduction to free band conduction enhanced by Schottky lowering of the barrier. Secondly if the density of donors is less than the traps, the Fermi level falls within the trap distribution and moreover if the Fermi level falls in a region of localized states, conduction with a

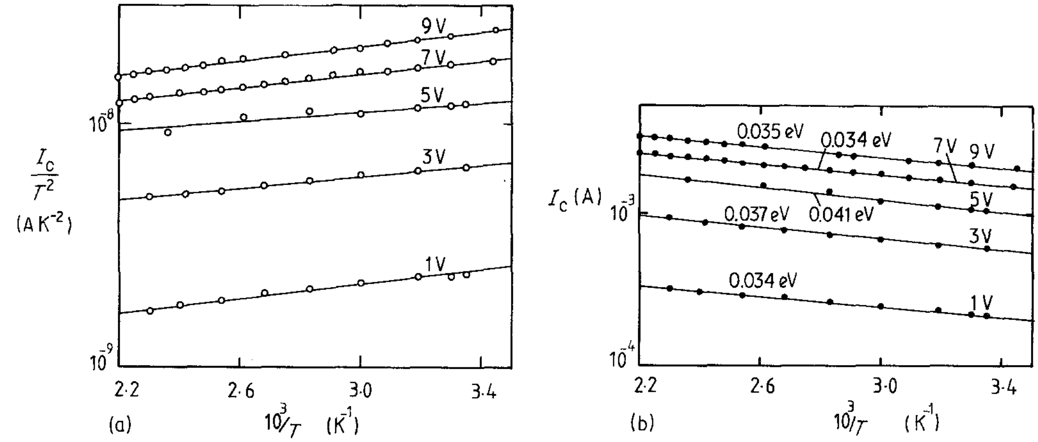


Figure 8 Assumption (a) of contact-limited conduction leads to negative activtion energy, (b) of bulk-limited conduction leads to an activation energy typical of a hopping process above room temperature. (Bias voltage and activation energy shown.)

small activation energy is possible. This conduction is especially favoured in shallow traps of high density and may be the dominant mechanism of conduction at low fields and moderately high temperatures [9].

When the density of ionizable centres is high, the height of any barrier present is likely to be small and its thickness insignificant. Accordingly the values of barrier height for the three different anode thin films are 0.65, 0.71 and 1.0 eV for silver, copper and aluminium respectively and their N_d values are estimated to be $N_{d(Ag)} = 6 \times 10^{17}\,cm^{-3} > N_{d(Cu)} = 4.7 \times 10^{17}\,cm^{-3} > N_{d(Al)} = 1.6 \times 10^{17}\,cm^{-3}$, a result consistent with the barrier height values. Moreover these estimated values of N_d have been confirmed approximately by spin density data of SiO/V_2O_5 structures published earlier by Al-Ramadhan *et al.* [11]. According to their thicknesses and relative molecular percentages and bearing in mind that their molecular compositions cannot be treated critically as precise, and cannot lead to a good measure of the donor or trap densities because of the various impurities that might have been incorporated into the film structure during the evaporation, the derived values seem reasonable. The strong dependence [12] of N_d on R/p where the donor density decreases with decreasing R/p, R being the rate of evaporation and p the pressure in the vacuum chamber, suggests that this is the main reason for the relatively low donor density measured in the SiO/V_2O_5 thin films studied here. The sharp transition from hopping conduction to free band conduction which has been demonstrated by Al-Ismail and Hogarth [13] on SiO thin films of planar geometry may be understood in terms of high spin density (effectively the donor density) of SiO equal to $6 \times 10^{18}\,cm^{-3}$ as reported by them, which is actually less than the usual value of around $10^{20}\,cm^{-3}$ taking into account the R/p parameter. The gradual transition in our SiO/V_2O_5 thin films may be attributed to the relatively low donor density of the mixed system.

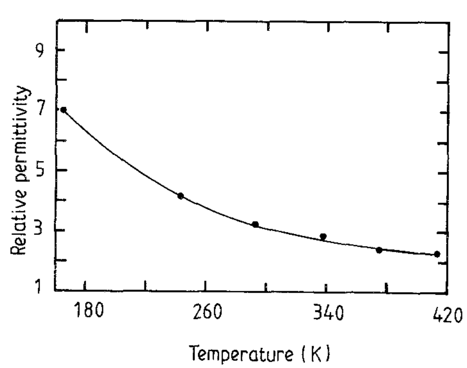


Figure 9 Temperature dependence of relative permittivity for a Cu–57 mol % SiO/43 mol % V_2O_5–Cu thin assembly.

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