JOURNAL OF MATERIALS SCIENCE 22 (1987) 3342–3348

Some electrical properties of mixed amorphous thin films of germanium and silicon monoxide before electroforming

W. D. B. S. ABEYSURIYA, C. A. HOGARTH
Department of Physics, Brunel University, Uxbridge UB8 3PH, Middlesex UK

The co-evaporated SiO_x–Ge system was studied. Thin-film MIM sandwich structures were deposited by vacuum evaporation at a pressure of $\approx 10^{-4}$ Pa and were measured at a pressure of 10^{-3} Pa. The conductivity at low temperature and under d.c. fields has been found to be governed by a combination of an electronic hopping process and free-band conduction. At fields greater than $2 \times 10^6\,V\,m^{-1}$, it is concluded that the conduction process is governed by the Poole–Frenkel effect. Comparison with earlier results on SiO_x–GeO_2 films showed small differences in activation energy for conduction for samples of broadly similar overall composition.

1. Introduction

It is well known that 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. Free-band conduction may take place in the conduction or valence band. For electrons travelling in the extended states of the conduction band, at least a few kT above the energy E_c (bottom of the conduction band), the mobility would be expected to approach that of a crystalline material with a correction for a high density of scattering centres which would reduce the mobility. If the temperature is raised, the conductivity changes because the Fermi level sweeps past the mobility edge. There will be a sharp change in conductivity 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

$$\sigma = \sigma_0 \exp(-E_a/kT) \qquad (1)$$

where E_a is the activation energy.

For the Poole–Frenkel effect, which involves field-enhanced thermal excitation of electrons from shallow traps at energy ϕ below the conduction band, we have according to Mead [1]

$$I \propto \exp\left(\frac{\beta_{PF}E^{1/2} - \phi}{kT}\right) \qquad (2)$$

where β_{PF} is the Poole–Frenkel constant given by $(e^3/\pi\varepsilon_0\varepsilon_R)^{1/2}$ in which e is the electronic charge, ε_R is the relative dielectric permittivity and ε_0 the permittivity of free space, and E is the applied electric field.

Jonscher and Ansari [2] have plotted the log I against $E^{1/2}$ characteristics for a series of M–SiO–Al devices with the metal M being aluminium, magnesium, titanium and copper for a range of samples. Irrespective of the electrode material these gave a value of $\beta = 2.2 \times 10^{-5}\,eV\,m^{1/2}\,V^{-1/2}$. Thus it is confirmed that the conduction mechanism was not due to high-field Schottky emission but to the bulk-limited Poole–Frenkel effect and was independent of the electrode material. Moreover Hirose and Wada [3] showed a similar independence of the current–voltage characteristics of the electrode material and concluded that conduction was due to the bulk-limited Poole–Frenkel mechanism. In considering a number of previous investigations Jonscher and Hill [4] have revealed that a true Poole–Frenkel effect has been confirmed for SiO and amorphous germanium separately at high fields, and it could be postulated that the high-field conduction mechanism of the co-evaporated material SiO_x–Ge could also follow the Poole–Frenkel effect.

Some optical properties of co-evaporated SiO_x–Ge have been reported [5]. In this paper we describe some electrical properties of M–(SiO_x–Ge)–M samples before electroforming.

2. Experimental details

Metal–insulator–metal (MIM) sandwich structures were obtained by depositing metal (bottom electrode), insulator (SiO_x–Ge) and metal (top electrode) on top of each other on 7059 Corning glass substrates.

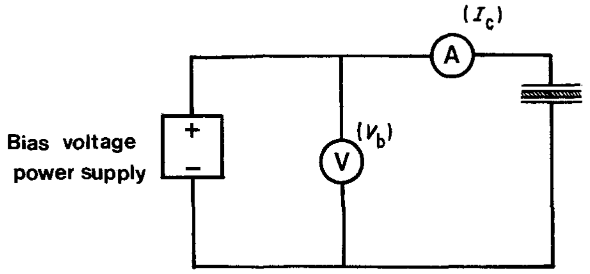

Figure 1 Diagram of circuit for measuring circulating current (I_c) for different values of applied voltage (V_b).

0022-2461/87 $03.00 + .12

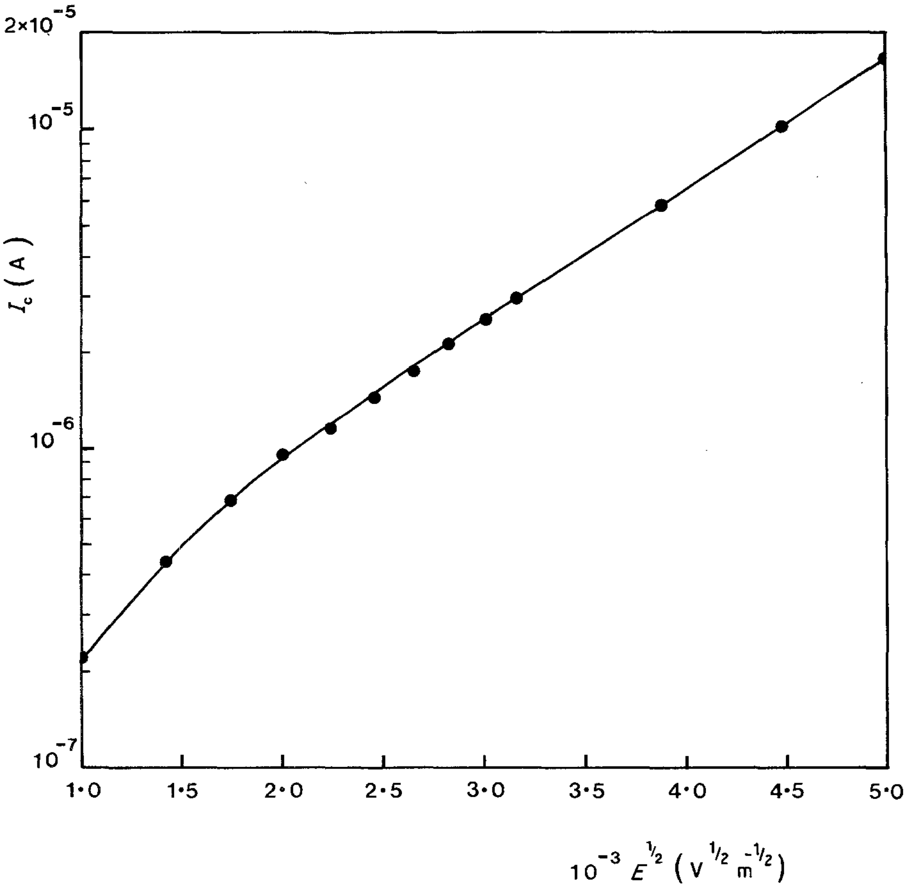

Figure 2 Circulating current as a function of square root of applied field for an Ag–(90 mol % SiO–10 mol % Ge)–Ag sample of dielectric thickness ≈ 100 nm.

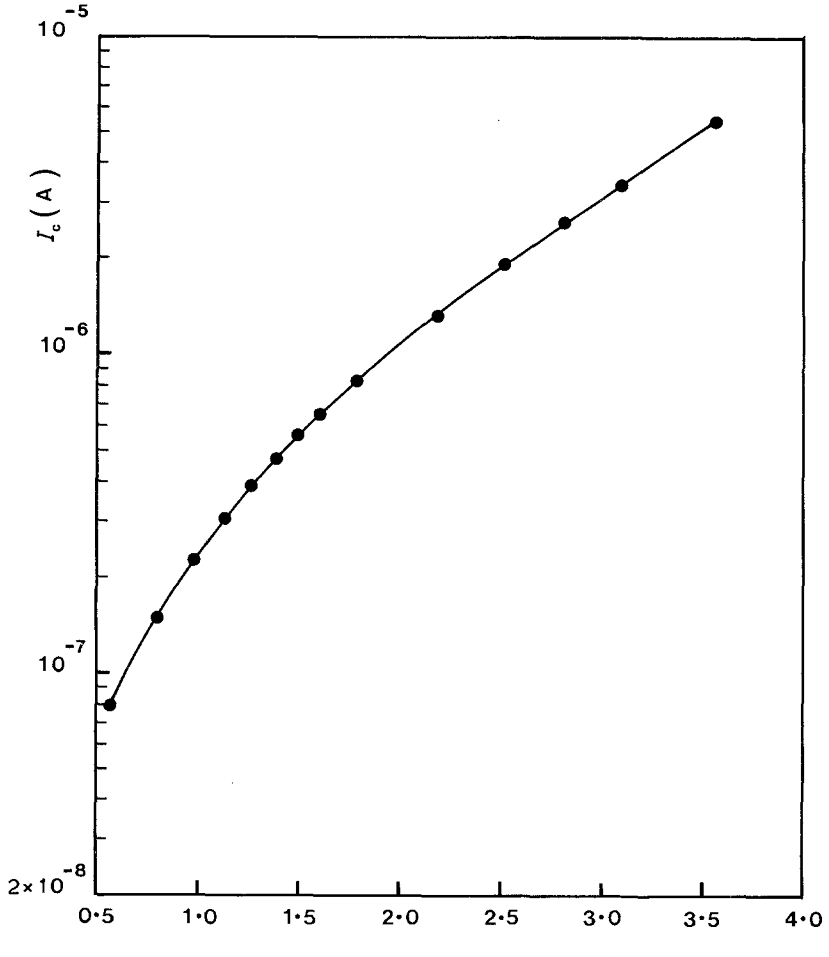

Figure 3 Circulating current as a function of square root of applied field for an Al–(92 mol % SiO–8 mol % Ge)–Al sample of dielectric thickness 314 nm.

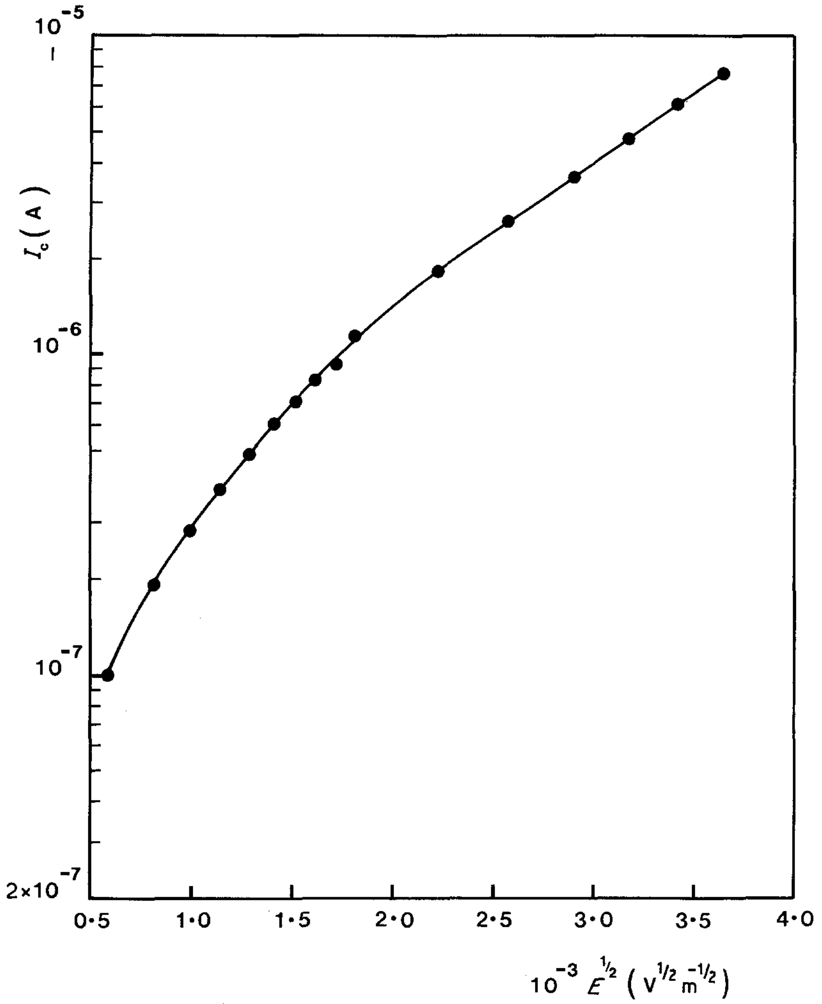

Figure 4 Current as a function of square root of applied field for an Au–(91 mol % SiO–9 mol % Ge)–Au sample of dielectric thickness ≈ 301 nm.

Germanium and aluminium were evaporated using a tungsten conical basket and spiral, respectively. Tantalum boats were used for the evaporation of SiO and copper, and molybdenum boats were used to evaporate silver and gold. Deposition of the MIM sample was carried out at a pressure in the range 1 to 7 × 10^{-4} Pa (1 to 5 × 10^{-6} torr). The electrical circuit for measuring current–voltage characteristics is shown in Fig. 1. The d.c. current–voltage characteristics were measured in a conventional manner. A d.c. bias voltage was supplied by a Coutant LB-200 power supply and the circulating current was measured using an electronic Avometer Type EA 113. The bias voltage was measured using a digital multimeter.

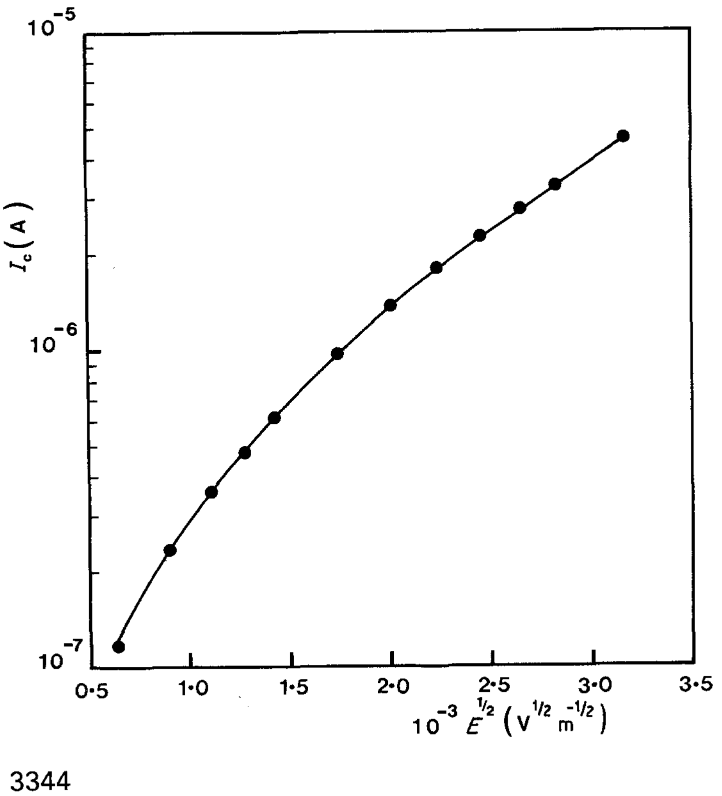

Figure 5 Current as a function of square root of applied field for a Cu–(92 mol % SiO–8 mol % Ge)–Cu sample of dielectric thickness ≈ 500 nm.

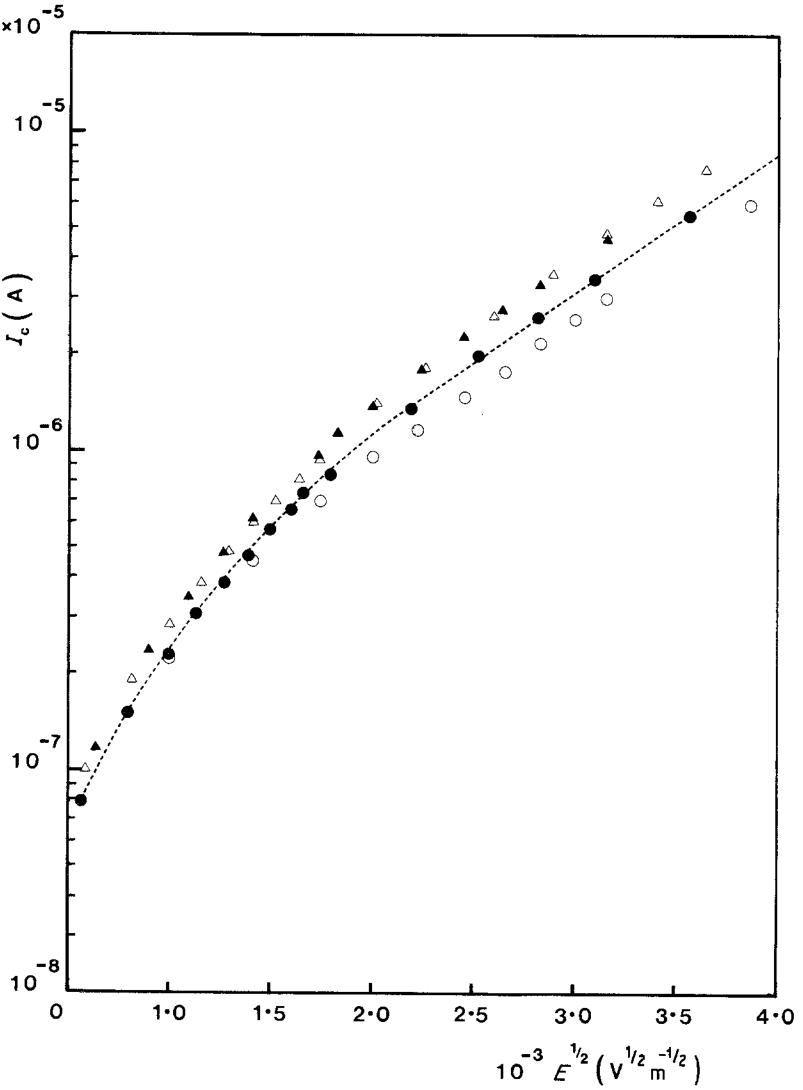

Figure 6 Combined results of Figs 2 to 5, demonstrating the slight significance of various electrode materials: (△) gold, (▲) copper, (●) aluminium, (○) silver.

3. Results and discussion

3.1. High-field conduction mechanism

Figs 2 to 5 show the log I against $E^{1/2}$ characteristics for M–(SiO$_x$–Ge)–M structures with various electrode materials. A comparison of these results is given in Fig. 6. The results shown in Fig. 6 suggest that the log I against $E^{1/2}$ characteristics are essentially independent of the electrode material. According to Figs 2 to 6, log I increases linearly with increasing $E^{1/2}$ when E is sufficiently high. The straight lines in the high-field region suggest that the conduction mechanism should be due to either the Poole–Frenkel or Schottky mechanism.

The gradient of the straight-line portion of the graph in Fig. 6 gives

$$m = 4.3 \times 10^{-4}\,\mathrm{V}^{-1/2}\mathrm{m}^{1/2}$$

Using Equation 2 the experimental value of β is

$$\beta_{\mathrm{exp}} = 2.53 \times 10^{-5}\,\mathrm{eV\,m^{1/2}V^{-1/2}}$$

The theoretical value of β for the Poole–Frenkel mechanism is given by $\beta_{\mathrm{PF}} = (e^3/\pi\varepsilon_0\varepsilon_{\mathrm{R}})^{1/2}$, i.e.

$$\beta_{\mathrm{PF}} = \frac{7.58 \times 10^{-5}}{\varepsilon_{\mathrm{R}}^{1/2}}\,\mathrm{eV\,m^{1/2}V^{-1/2}}$$

Since the theoretical value of β for the Schottky mechanism is $\beta_{\mathrm{S}} = (e^3/4\pi\varepsilon_0\varepsilon_{\mathrm{R}})^{1/2}$, then

$$\beta_{\mathrm{S}} = \frac{3.79 \times 10^{-5}}{\varepsilon_{\mathrm{R}}^{1/2}}\,\mathrm{eV\,m^{1/2}V^{-1/2}}$$

Assuming the dominant mechanism to be Poole–Frenkel, the value of dielectric constant obtained is 9. If the Schottky mechanism is to dominate, the value of dielectric constant should be 2.3. This is low for a material with substantial ionic bonding. Therefore the high-field conduction mechanism is predominantly of the Poole–Frenkel type. Furthermore the Schottky mechanism could also be discarded, as the experimental value of dielectric constant of the material SiO$_x$–Ge, obtained in terms of the Schottky mechanism, leads to a value less than the dielectric constant of the individual materials SiO and germanium.

3.2. Temperature dependence of conductivity

The current–voltage characteristics at different temperatures for a 500 nm thick, preformed Cu–91 mol % SiO$_x$–9 mol % Ge)–Cu sample are shown in Fig. 7. The results indicate that the current increases with increase in voltage at all temperatures studied. Analysis of these results further reveals that the current increases with the temperature at a given voltage.

The conductivity σ is plotted as a function of

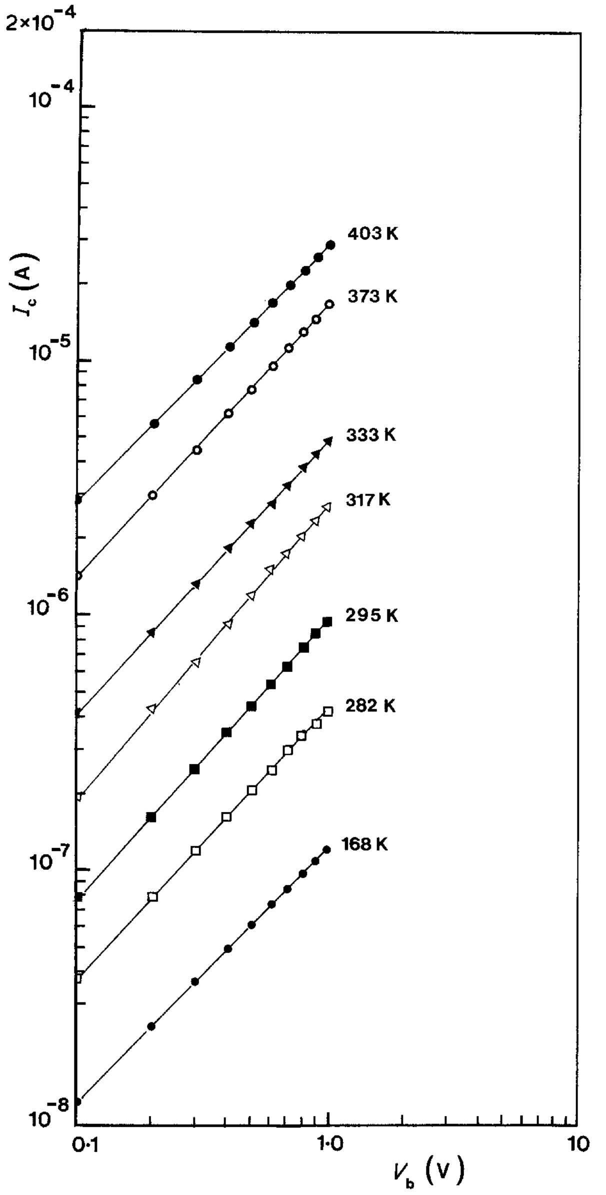

Figure 7 V_b–I_c characteristics of a Cu–(91 mol % SiO–9 mol % Ge)–Cu sample at several temperatures. Dielectric thickness ≈ 500 nm.

reciprocal temperature for the above sample in Fig. 8. According to Equation 1, the activation energy can be obtained from the gradient of the slope of the straight portion of this curve. The plot is a straight line above a given transition temperature and indicates that at high temperature the conduction takes place by transport in the extended states. At lower temperatures the slope is less steep, suggesting a change in transport mechanism which may involve hopping conduction.

3.3. Variation of activation energy with the composition

The current–voltage characteristics at different temperatures and for different compositions of the SiO_x–Ge system were obtained. The conductivity as a function of reciprocal temperature was plotted for the above films with different compositions. The combined results are shown in Fig. 8. Values of the activation energy for these films were obtained from the gradients of the curves and are given in Tables I and II. Using these data the variation of activation energy with the germanium content is shown in Fig. 9. It is evident from Fig. 9 that there is a rapid decrease in activation energy as the content of germanium in SiO increases up to 23.5 mol %. Nevertheless, there is an increase in activation energy as indicated by the slight gradient of the curve which can be explained by assuming that the appropriate energy level or band becomes degenerate when more than 23.5 mol % Ge is added to the dielectric. In such circumstances only a small change in the value of E_a could be expected for further additions.

TABLE I Variation of activation energy with composition for SiO_x–Ge

Composition (mol %)		Activation energy, E_a(eV)
Ge	SiO_x	
0	100	0.47*
5	95	0.41_8
9	91	0.35_8
14	86	0.31_8
16	84	0.26_8
25	75	0.16_3
48	52	0.15_2
58	42	0.14_0

*From Timson [6].

In Fig. 9 the equivalent activation energy obtained from the earlier results of Rahman [7] on the SiO–GeO_2 system is shown for interest. The composition point has been estimated in terms of the molecular percentage of germanium in the SiO–GeO_2 system. The values shown in the present work on the SiO_x–Ge system are consistent with the idea that very little interspecies bonding occurs in the materials.

As in Fig. 9, the value of activation energy at a given composition in the SiO–GeO_2 system is higher than the value of activation energy in the SiO_x–Ge system. This could be explained in terms of disorder, i.e. the disorder increases when adding an oxide (GeO_2) to SiO rather than adding an element (germanium) to the SiO.

4. Conclusions

The occurrence of hopping conduction between localized trapping states below room temperature is confirmed by the d.c. activation energy decrease with temperature. Band-like conduction can be assumed above room temperature since the activation energies for the conductivity above room temperature are greater than the values below room temperature. The addition of germanium to silicon oxide by co-evaporation leads to an increase in the disorder, resulting in a decrease in activation energy. Measurements made on M–(SiO_x–Ge)–M sandwiches with different metal electrodes confirm that the electrical

TABLE II Variation of activation energy with composition for SiO–GeO_2 [7]

Composition (mol %)		Ge (mol %) in SiO	Activation energy, E_a (eV)
GeO_2	SiO		
–	37	38.65	0.22_1
65	35	39.39	0.21_8

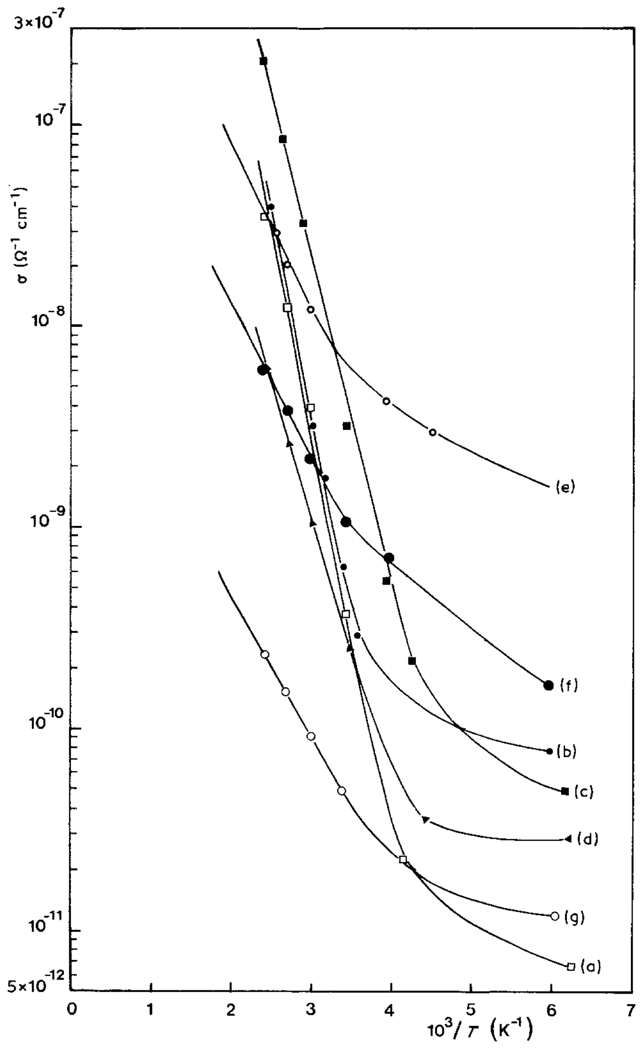

Figure 8 Conductivity σ as a function of temperature for seven Cu-(SiO-Ge)-Cu samples: germanium content (mol %) (a) 5, (b) 9, (c) 14, (d) 16, (e) 25, (f) 48, (g) 58.

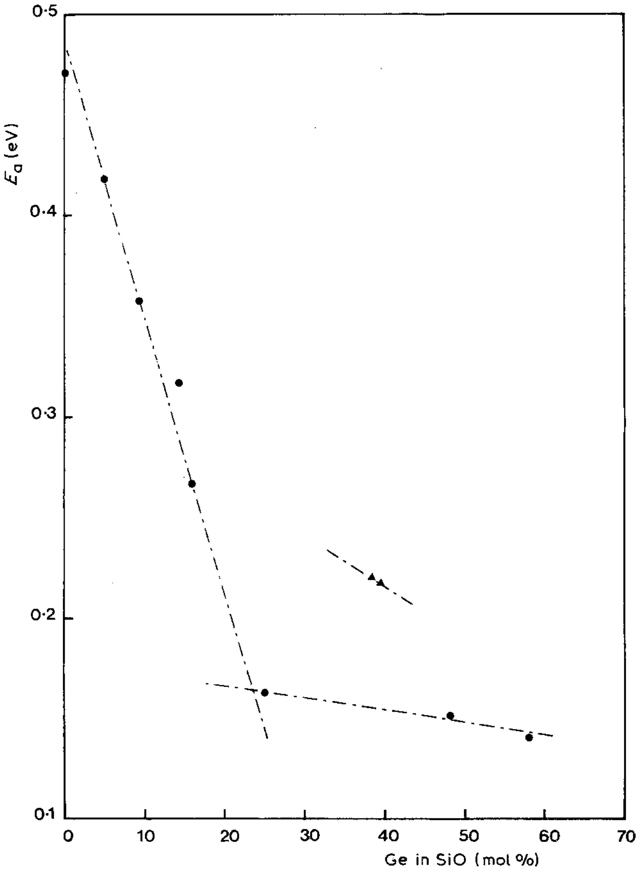

Figure 9 (●) Variation of activation energy E_a with germanium content in SiO-Ge thin films; (▲) estimated from results of Rahman [7] on SiO-GeO_2 films.

conduction mechanism at room temperature and at high fields above $10^6\,\mathrm{V\,m^{-1}}$ is a bulk process of the Poole–Frenkel type.

References

1. C. A. MEAD, *Phys. Rev.* **128** (1962) 2088.
2. A. K. JONSCHER and A. A. ANSARI, *Phil. Mag.* **23** (1971) 205.
3. H. HIROSE and Y. WADA, *Jap. J. Appl. Phys.* **4** (1965) 639.
4. A. K. JONSCHER and R. M. HILL, in "Physics of Thin Films", Vol. 8, edited by G. Hass, M. H. Francombe and R. W. Hoffman (Academic, London, 1975) p. 169.
5. S. K. J. AL-ANI, C. A. HOGARTH and S. W. D. B. ABEYSURIYA, *J. Mater. Sci.* **20** (1985) 2541.
6. P. A. TIMSON, PhD thesis, Brunel University (1971).
7. A. S. Md. S. RAHMAN, PhD thesis, Brunel University (1981).

Received 3 November 1986
and accepted 28 January 1987