JOURNAL OF MATERIALS SCIENCE 21 (1986) 3829–3835

Some electrical properties of co-evaporated GeO–BaO thin films

M. Y. NADEEM, C. A. HOGARTH
Department of Physics, Brunel University, Uxbridge, Middlesex UB8 3PH, UK

The direct-current electrical conduction both before and after the electroforming process is investigated in thin layers of GeO_2 co-evaporated with BaO and sandwiched between various metallic electrodes. The mobility associated with the conduction at low temperature (hopping) is evaluated. Electroformed devices show voltage-controlled negative resistance and electron emission. The effect of the nature of the metallic electrodes and that of the dielectric thickness on these electrical properties is reported.

1. Introduction

One of the several mechanisms of d.c. conduction in thin layers sandwiched between metallic electrodes is the contact-limited Schottky emission [1]. The current density J at a high field E is found to obey the relation

$$J = AT^2 \exp\left(\frac{\beta_s E^{1/2} - \phi_0}{kT}\right) \qquad (1)$$

where $A = 120$ in conventional units, ϕ_0 is the barrier height at zero field and $\beta_s = (e^3/4\pi\varepsilon_0\varepsilon_R)^{1/2}$ is the Schottky coefficient of the barrier lowering in which e is the elecronic charge, ε_0 is the permittivity of free space and ε_R is the high-frequency relative dielectric constant. The low-temperature conduction in many amorphous evaporated thin films is believed to be due to a low-mobility hopping process [2, 3]. The mobility μ_H associated with fluctuation-activated hopping [4] is related to the current density J by the expression

$$J = e\mu_H N_t E \exp(-\Delta E/kT) \qquad (2)$$

where N_t is the trap density and ΔE is the activation energy involved. An electroforming process first reported by Kreynina *et al.* [5] in $Al/Al_2O_3/Ag$ has been observed in many other oxides [6, 7], halides [8], polymers [9] and sulphides [10]. During the electroforming process some interesting features such as voltage-controlled negative resistance (VCNR), emission currents and memory effects are established in the electrical behaviour of the M/I/M sandwich structures. In this paper we report the electrical conduction before and after the electroforming process in the co-evaporated thin layers of GeO_2–BaO sandwiched between various electrodes (copper, silver, aluminium and gold). The effects of the nature of electrodes and the dielectric thickness on these characteristics are also given.

2. Experimental work

A thermal co-evaporation technique as developed by Hogarth and Wright [11] was employed to prepare our samples in a Balzers 510 coating unit on to clean Corning 7059 glass slides. The d.c. electrical measurements were performed in a subsidiary vacuum system equipped with all the necessary facilities and using conventional circuits. The substrate temperature was lowered by firmly attaching the slides to a brass enclosure into which liquid nitrogen could be poured. Tungsten boats were used to evaporate all the materials except aluminium, for which tungsten spirals supporting the aluminium were used.

3. Results and discussion

3.1. Measurements prior to electroforming

The d.c. conduction in GeO_2–BaO before the electroforming process has been reported by the present authors [12] to be due to electrode-limited Schottky emission. A typical log I_c–$V_b^{1/2}$ curve (I_c = circulating current, V_b = applied voltage) for a 145 nm thick 50% GeO_2–50% BaO film with aluminium electrodes is given in Fig. 1. The device was fresh and unformed. A linear dependence was observed from 1.6 V. The slope of the plot ($m \approx 0.947$) yielded the values $\varepsilon_R = 3.5$, $\beta_s = 2 \times 10^{-5}\,\mathrm{eV\,m^{1/2}\,V^{-1/2}}$. For devices with gold electrodes a linear relation between log I_c and $V_b^{1/2}$ is seen from Fig. 2, which gives the typical current–voltage dependence for a 265 nm thick 70% GeO_2–30% BaO dielectric film. The linearity in these characteristics was observed between 1 V and 5 V which gives the experimental value of β_s equal to $2.5 \times 10^{-4}\,\mathrm{eV\,cm^{1/2}\,V^{1/2}}$. Similar calculations with copper and silver electrodes were made and Table I gives the dependence of β_s on the nature of the metallic electrode, confirming the electrode-limited conduction in our samples.

It is worth mentioning here that the barrier lowering coefficient was found to be almost independent of the dielectric thickness as long as the electrode material was the same.

3.2. Temperature dependence

Strong support in favour of the Schottky emission in our sample comes from the temperature dependence of the circulating current at a fixed bias. In Fig. 3 we have plotted log I_c against the absolute temperature for an Ag/GeO_2–BaO/Ag device at two fixed values of bias voltage. The current was found to be essentially

0022-2461/86 $03.00 + .12

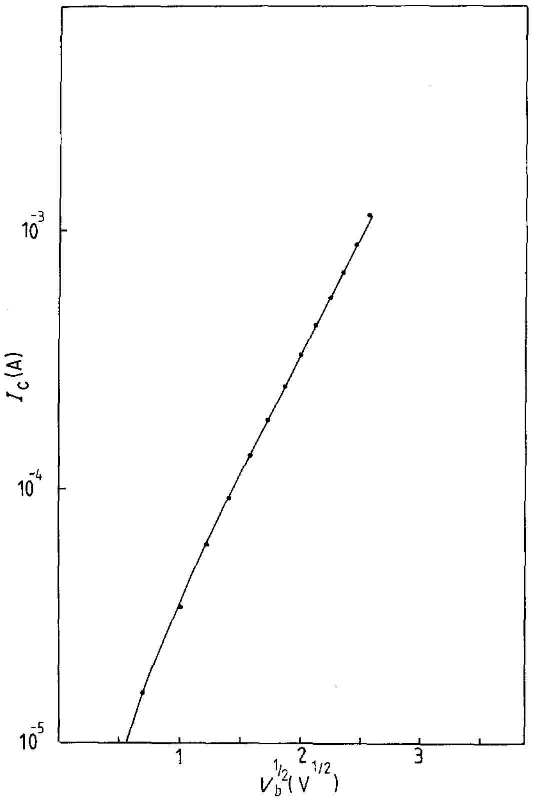

Figure 1 Log I_c as a function of $V_b^{1/2}$ for an Al/GeO_2–BaO/Al thin-film sandwich (dielectric thickness 145 nm).

temperature-independent below 215 K. Above 215 K, it rose very sharply with increase in temperature following the strong temperature dependence of the Schottky current. When the temperature-independent current $I_T = 8.75 \times 10^{-5}$ A was subtracted from the total current and a plot of log $(I_c - I_T)/T^2$ against $10^3/T$ was drawn (Fig. 4), it was found to be linear. This supported further the Schottky mechanism. The activation energy associated with this process was calculated to be 0.37 eV.

TABLE I Dependence of β_s on the nature of the metallic electrode

Supporting electrode	β_s (eV cm$^{1/2}$ V$^{-1/2}$)
Cu	1.70×10^{-4}
Ag	1.59×10^{-4}
Al	2.20×10^{-4}
Au	2.50×10^{-4}

3.3. Conduction at low temperatures

The mobility μ_H associated with the hopping conduction can be estimated from Fig. 5 which is a plot of log I_c against $10^3/T$ for the same device as that of Fig. 4. For a point on the curve with $I_c = 8.75 \times 10^{-5}$ A and $T = 10^3/6.95$, we obtain using Equation 2 $\mu_H N_t = 6.57 \times 10^{10}$ cm^{-1} V^{-1} sec^{-1}. Using the typical vaue of the trap density $N_t \approx 10^{14}$ cm^{-3} we obtain $\mu_H \approx 6.57 \times 10^{-4}$ cm^2 V^{-1} sec^{-1}.

3.4. Electroforming

Fig. 6, Curve (a) gives the current–voltage characteristic for a fully formed Cu/GeO_2–BaO/Cu diode. The device was formed at 4 V. A peak in the circulating current of value 1.93×10^{-2} A was exhibited at 4 V followed by a differential negative-resistance region which extended up to 11 V. After this the circulating current remained almost constant until the breakdown of the film. The typical dependence of the emission current I_e upon the bias voltage V_b is represented by Curve (b). This current was measured by means of a metallic plate kept at 100 V with respect to the top electrode to collect the emitted electrons. After a slight fall at 4.5 V, the emission current increased very sharply with the applied voltage and saturated to a level of 1.5×10^{-6} A at 13.5 V.

The forming of a GeO_2–BaO structure with silver electrodes was accomplished by keeping the device at 4 V for some time during which the conductivity

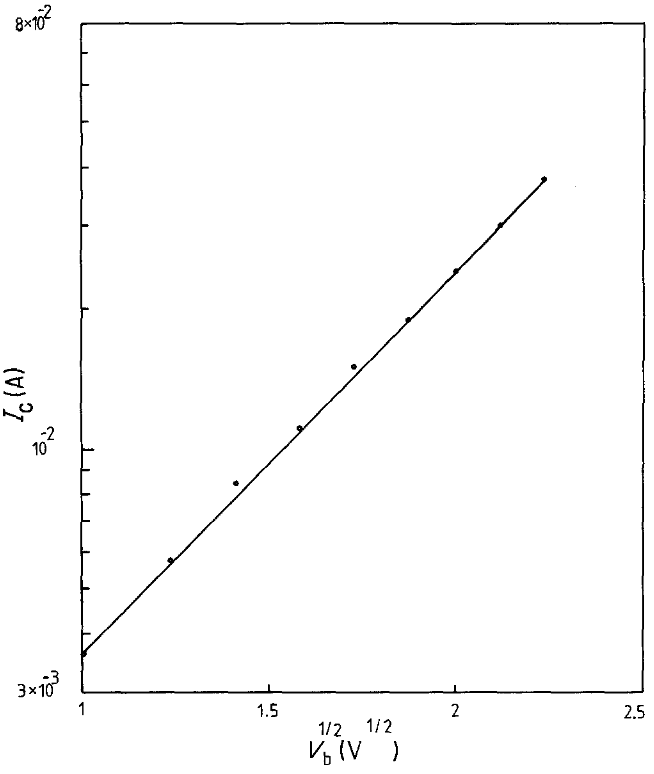

Figure 2 Log I_c as a function of $V_b^{1/2}$ for a Cu/GeO_2–BaO/Cu thin-film sandwich (dielectric thickness 265 nm).

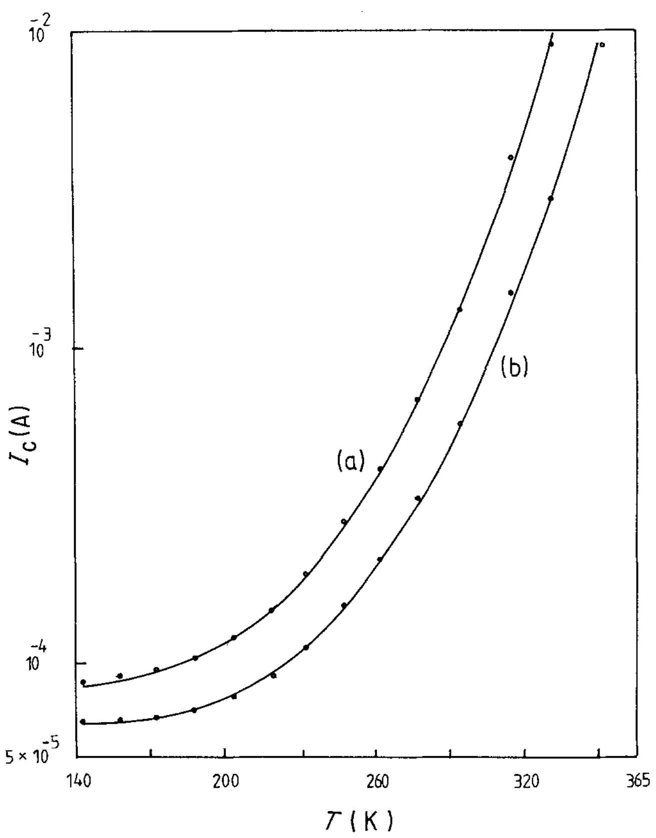

Figure 3 Log I_c as a function of temperature at two fixed bias voltages (a) 4 V, (b) 3 V, for an Ag/GeO_2–BaO/Ag sandwich sample.

increased by two orders of magnitude (Fig. 7). Variation of the emission current is shown by the second curve on the diagram.

Aluminium proved to be a passive electrode material for the forming process. Most of the Al/GeO_2–BaO/Al diodes could not be electroformed. Nevertheless, in a very few cases, a device with aluminium electrodes did show forming effects. One such typical example is given in Fig. 8. The electroforming was accomplished at 18 V.

3.5. Effect of the nature of the metallic electrode

From the above results, we gain an idea of the effect of the nature of the electrode material on the electrical properties of the formed GeO_2–BaO layers. However, to establish and analyse these observations more precisely, devices under similar conditions of evaporation were fabricated with different electrode materials. The thickness of the electrode was about 60 nm. Each device was formed to give optimum VCNR and related properties. Figs 9 and 10 give, respectively, the variation of I_c and I_e with V_b. We note that the peak voltage V_m decreases with electrode material in the order Al–Cu–Ag, and the current density increases in the same order. The emission current is higher for silver electrodes and lower for aluminium electrodes. These results fully support the models of electroforming given by Hickmott [13, 14] and Greene *et al.* [8].

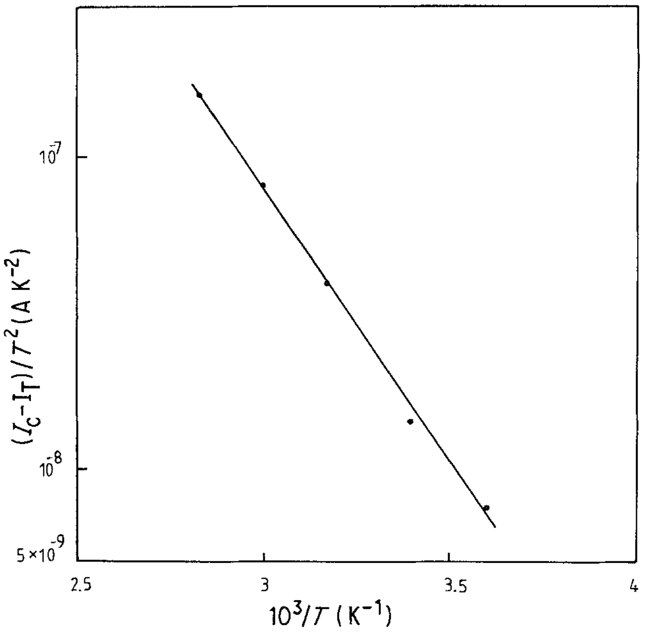

Figure 4 The function (I_c − I_T) T^2 in terms of inverse temperature, for V_b = 4 V, indicating a Schottky emission process.

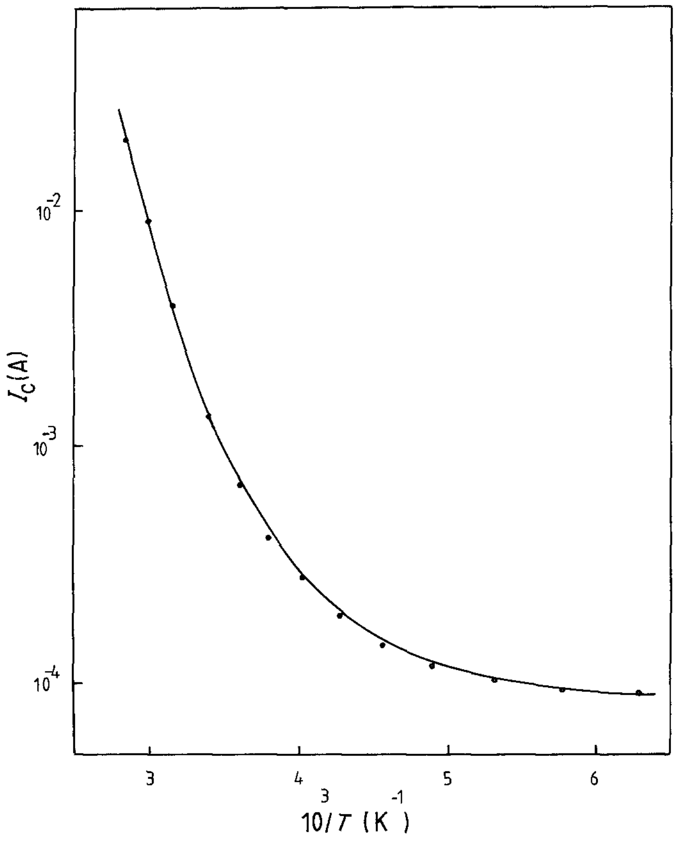

Figure 5 Circulating current as a function of inverse temperature for an Ag/70% GeO_2–30% BaO/Ag sandwich sample (4 V applied; sample thickness 300 nm).

3.6. Dielectric thickness effect

Five layers of different dielectric thickness were deposited on the same substrate during a single evaporation cycle. The supporting electrodes were 50 nm thick aluminium layers and the thicknesses of the insulating layers were 110, 195, 290 and 400 nm. These thicknesses were achieved by the movement of a special mask with which it was possible to cover the specified regions of the substrate on rotating the mask from outside the vacuum chamber. The diodes of various thicknesses were then subjected to a constant applied voltage and the circulating currents were

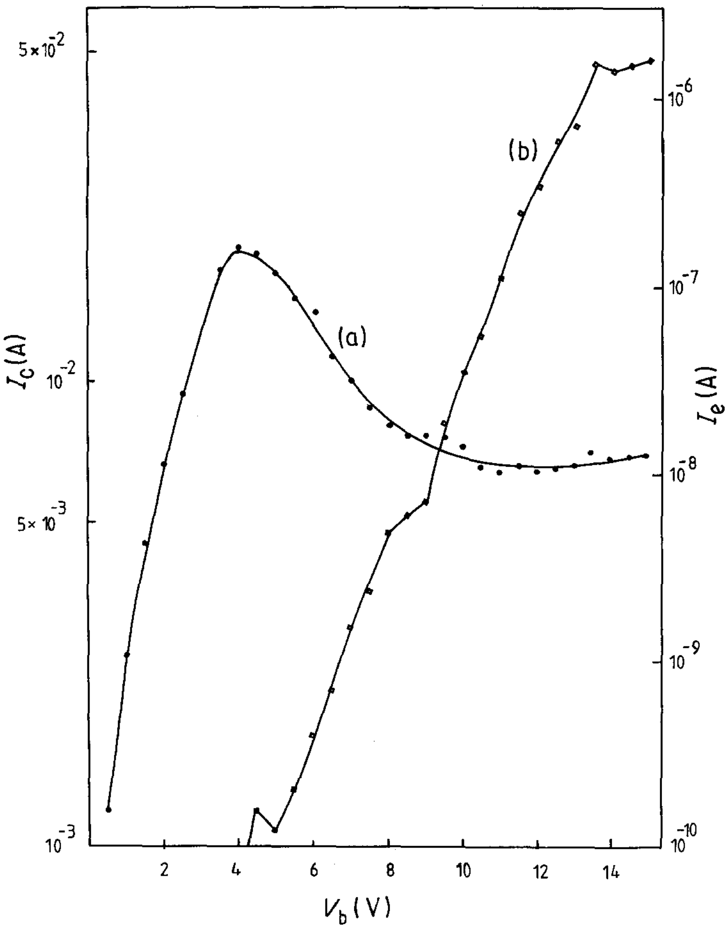

Figure 6 (a) Circulating current I_c, (b) emission current I_e, as functions of applied voltage V_b, for a Cu/80% GeO_2–20% BaO/Cu sandwich sample (thickness 150 nm).

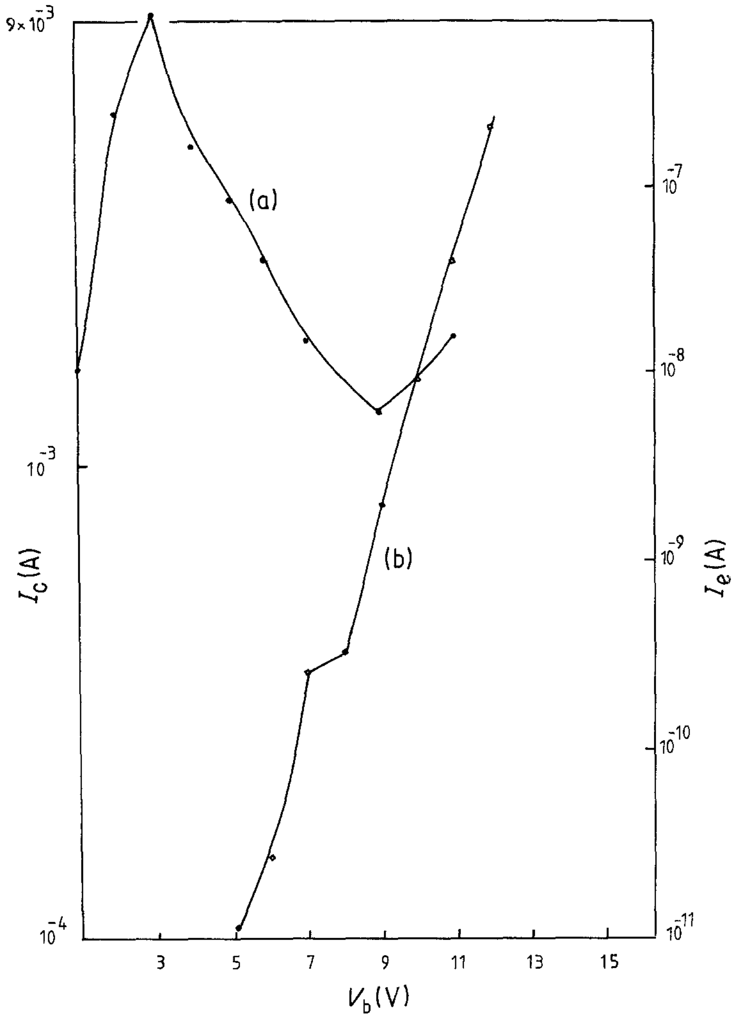

Figure 7 Variation of (a) I_c, (b) I_e with V_b for an Ag/70% GeO_2–30% BaO/Ag sandwich sample (thickness 200 nm).

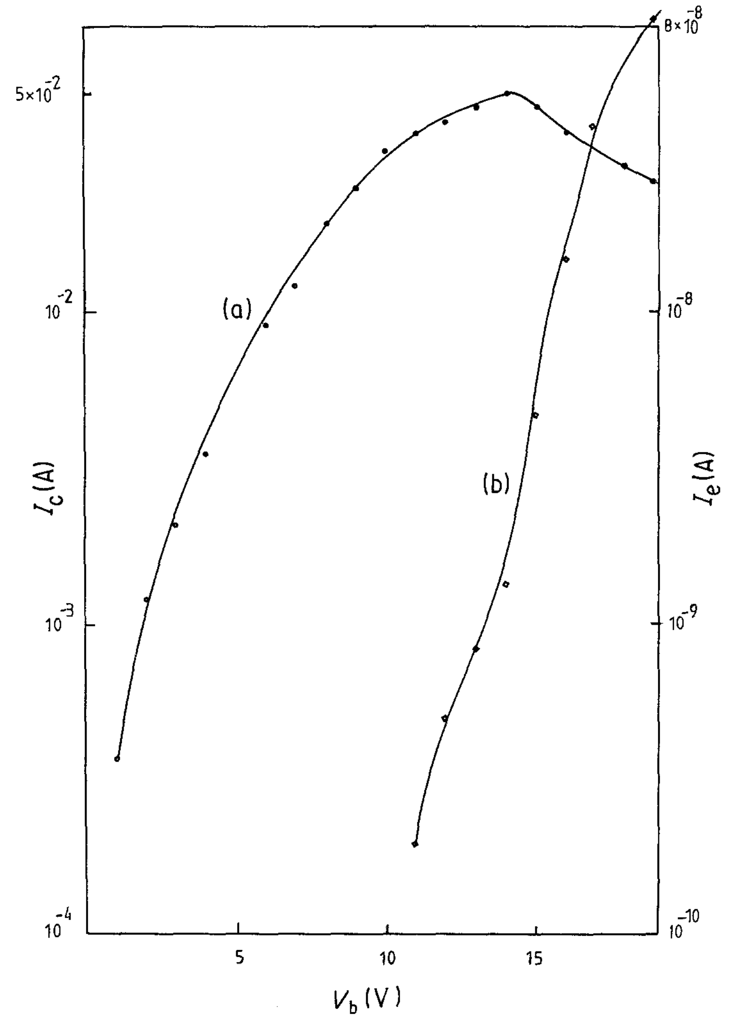

Figure 8 (a) I_c, (b) I_e as functions of V_b for an Al/50% GeO_2–50% BaO/Al sandwich sample (thickness 145 nm, formed at 18 V).

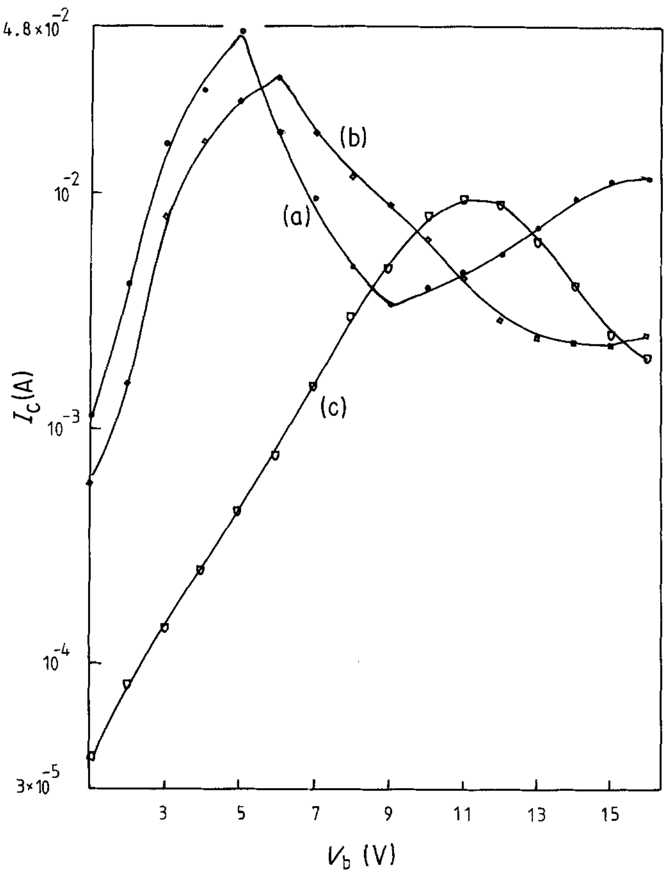

Figure 9 Variation of I_c with V_b for a 65% GeO_2–35% BaO dielectric 200 nm thick carrying 60 nm thick electrodes: (a) Ag, (b) Cu, (c) Al.

recorded to seek any information regarding the effect of the dielectric thickness.

Fig. 11 gives the log I_c dependence against $d^{-1/2}$, which is a direct consequence of the Schottky Equation 1 since $E = V_b/d$. According to Equation 1, the theoretical value of the slope of such a plot is

$$m = (\beta_s V_b^{1/2}/kT)\log e$$

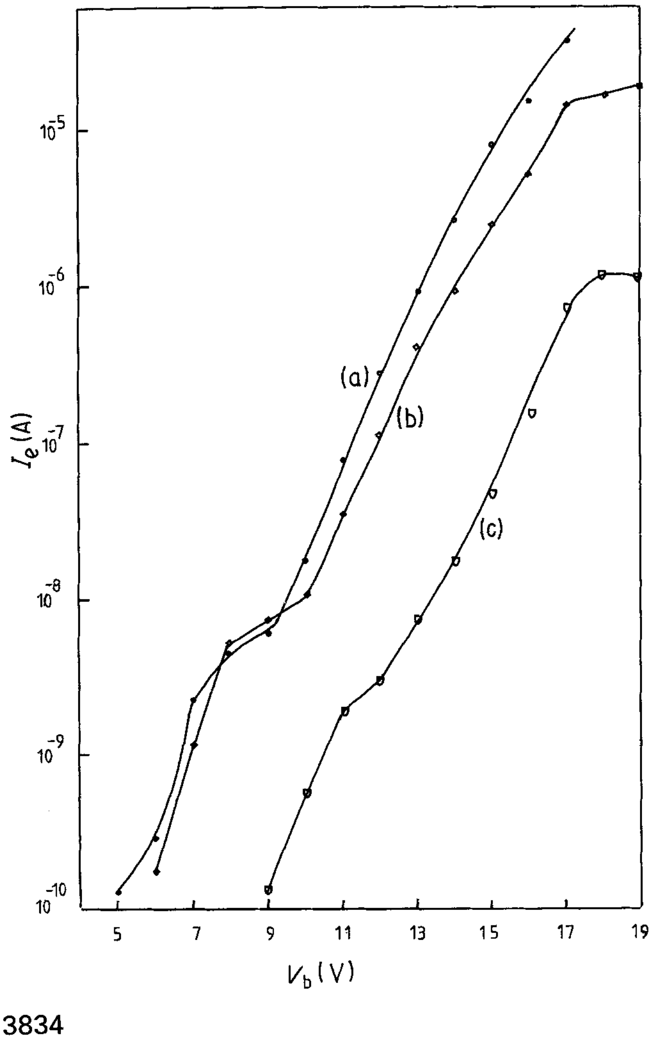

Figure 10 I_e as a function of V_b for the devices of Fig. 9, showing the influence of electrode material: (a) Ag, (b) Cu, (c) Al.

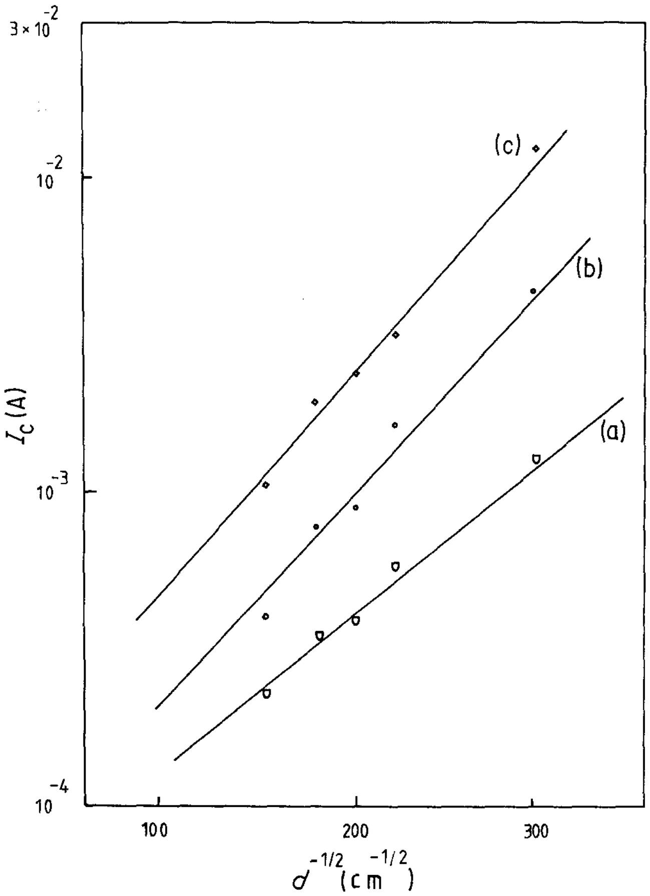

Figure 11 The circulating current as a function of insulator thickness at fixed bias voltages for an Al/70% GeO_2–BaO/Al sandwich sample: V_b = (a) 2 V, (b) 3 V, (c) 4 V.

At $V_b = 3\,V$, our experimental curve gives $m = 6.51 \times 10^{-3}\,cm^{1/2}$ which corresponds to the following values of β_s and ε_R:

$$\beta_s = \frac{mkT}{\log e\ V_b^{1/2}} \approx 2.2 \times 10^{-4}\,eV\,cm^{1/2}\,V^{-1/2}$$

$$\varepsilon_R = \frac{e^3}{4\pi\beta_s^2} \approx 2.97$$

References

1. W. SCHOTTKY, *Phys. Z.* **15** (1914) 872.
2. N. F. MOTT, *Phil. Mag* **24** (1971) 911.
3. N. F. MOTT and E. A. DAVIS, "Electronic Processes in Non-crystalline Materials" (Clarendon Press, Oxford, 1971) p. 39.
4. K. W. BÖER, *J. Non-Cryst. Solids* **4** (1970) 583.
5. G. S. KREYNINA, L. N. SELIVANOV and T. I. SHUMSKAIA, *Radio Engng. Elect.* **5** (1960) 219.
6. R. D. GOULD and C. A. HOGARTH, *Int. J. Elect.* **37** (1974) 157.
7. J. G. SIMMONS and R. R. VERDERBER, *Proc. R. Soc.* **A301** (1967) 77.
8. P. D. GREENE, E. L. BUSH and I. R. RAWLINGS, in Proceedings of Symposium on Deposited Thin Film Dielectric Materials, New York, 1968, edited by F. Vratny (The Electrochemical Society, New York, 1969) p. 167.
9. K. H. GUNDLACH and J. KADLEC, *Phys. Status Solidi (a)* **10** (1972) 371.
10. R. R. SUTHERLAND, *J. Phys. D* **4** (1971) 468.
11. C. A. HOGARTH and L. A. WRIGHT, in Proceedings of International Conference on Physics of Semiconductors, Moscow, 1968 (Academy of Sciences, Leningrad, 1968) p. 1274.
12. M. Y. NADEEM and C. A. HOGARTH, *Phys. Status Solidi (a)* **72** (1982) K 203.
13. T. W. HICKMOTT, *J. Appl. Phys.* **35** (1964) 2118.
14. *Idem, ibid.* **35** (1964) 2679.

Received 18 November 1985
and accepted 10 January 1986