Thermoelectric power measurements of co-evaporated Cu/GeO$_2$ thin cermet films

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Extensive studies of ceramic–metal (cermet) thin films have been carried out for many years because of their potential applications in integrated circuits [1–7]. These films are primarily insulator with metal incorporated. Electrical characterisations of cermet films were studied with various metal and dielectric compositions such as Cu/GeO$_2$ [2], Mn/SiO [4], Cu/SiO$_x$ [6], Au/SiO$_2$ [7], which were prepared by various deposition techniques. But no work has been carried out on thermoelectric power measurements of Cu/GeO$_2$. Thermoelectric power measurements provide the most reliable information about the nature of charge carriers and together with the direct current (dc) conductivity allow the conduction mechanisms operative in the films to be investigated. According to Mott and Davis [8], the sign of the thermoelectric power is a more reliable indicator than the Hall coefficient for determining whether the material is *n*-type or *p*-type. Thermoelectric power measurement is particularly useful for small mobility materials, in which Hall effect measurements are extremely difficult to make.

There are two basic techniques for measuring the relative thermoelectric power S_{AB} of the film B and reference material A: the differential and the integral method [9]. In the differential method a small thermal gradient, $\Delta T (= T_1 - T_2)$, is applied across a short sample, which gives rise to Seebeck voltage V_{AB}. In this method ΔT is kept constant while T_1 and T_2 are varied. The thermoelectric power is obtained from the slope of a Seebeck voltage V_{AB} vs. mean temperature $T (= (T_1 + T_2)/2)$ graph. To avoid assuming that the graph passes through the origin, it is necessary to measure V_{AB} at several values of ΔT and reverse the direction of temperature gradient by interchanging the source and sink. The differential method requires a smaller temperature gradient across the sample (1–10 K), which indicates that the sample can be quite small. It may be difficult to control two heater supplies manually to vary the average temperature while the temperature difference remains constant. As ΔT is small, this technique is sensitive to spurious voltage offsets. Noise from the heaters may also cause the voltage fluctuations. The V_{AB} vs. ΔT graph rarely passes through the origin indicating that spurious voltages are nearly always present. In integral method, one junction of the sample is held at a fixed temperature T_c while the temperature T_h of the other junction is varied. By convention, the Seebeck voltage is measured with respect to the hotter junction.

The value of the thermoelectric power at a substrate temperature T can be obtained from the slope of a Seebeck voltage V_{AB} vs. T_h graph. The integral technique was chosen in the present investigation because of its advantages over the differential technique, viz. the generation of negligible spurious e.m.f.s and less heater noise (as only one heater is involved instead of two in the differential technique). In this paper, the results of thermoelectric power measurements on co-evaporated Cu/GeO$_2$ films containing a higher concentration of Cu is presented.

Cu/GeO$_2$ cermet thin films were deposited on Corning 7059 alkali free alumino-silicate glass substrate *in vacuo* (about 1 mPa) from two molybdenum boats by co-evaporation in a Speedivac vacuum coating unit (model 19A/122) with some modification to allow double boat evaporation of 99.3% pure Cu powder (Koch-Light Laboratories Ltd.) and 99.999% pure GeO$_2$ powder (Aldrich Chemical Company, Inc.). The film thickness and deposition rates were controlled using two calibrated quartz crystal oscillators (Maxtec, Inc.) for the Cu and GeO$_2$ sources. The film thickness was measured by multiple beam interferometry with an Angstrometer (Solan Instruments, Model M-100).

All the samples for thermoelectric power study were prepared at 600 K at a rate of 0.8 nm/s and were 200 nm thick. The basic dimension of the sample was 3 cm×0.7 cm. To obtain 200 nm thick and 60 vol.% Cu films, 120 nm of Cu was mixed with 80 nm of GeO$_2$ by controlling the deposition rates of the sources. The deposition rate was determined by dividing the final film thickness by the time taken to deposit the film. Type-K chromel–alumel thermocouples (RS Components Ltd.), connected to Comark microprocessor thermometers (Model 6400), were used to monitor the temperature of both the hot and cold end of the film. The measuring leads and the thermocouples were insulated by PTFE sleeving and routed through two copper tubes. The Cu tubes were mounted to the inner wall of the top plate of the mea-

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suring chamber to provide mechanical stability and extra shielding to minimize electrical noise. The loading error of the voltmeter was overcome using Keithley 617 programmable digital electrometer whose input impedance $\approx$200 TΩ, about 10^3 times higher than the highest sample resistance investigated. Spurious voltages can also arise when additional junctions of dissimilar materials, such as junctions with aluminum contact pads and silver conducting paint and/or electrometer lead, are held at different temperatures. To avoid this error a U-shaped planar structure was used in this investigation and all connections to the sample were held at the sink temperature. The effect of heater noise was investigated by switching off the variac before taking the data. No noise was recorded on switching the heater on or off. It is worth noting that Rahim [10] observed heater noise on measuring the Seebeck voltage of Mn/SiO_x using the integral method.

The thermoelectric power, S, was measured *in vacuo* in the temperature range 300–600 K on planar samples of 60–100 vol.% Cu. The Seebeck voltage was measured with respect to aluminum by connecting the positive terminal of the electrometer to the cold end of the sample. The absolute thermoelectric power of the film $S_{\text{film}}(T)$ at hot junction temperature T was calculated using the relation

$$S_{\text{exp}}(T) = S_{\text{film}}(T) - S_{\text{Al}}(T)$$

where $S_{\text{exp}}(T)$ is the derivative of the measured Seebeck voltage with respect to hot junction temperature T produced by Cu/GeO_2 and Al contact films. S_{Al} is -40 nVK^{-1} [11], which is negligibly small compared to S_{film}. Hence

$$S_{\text{exp}}(T) \approx S_{\text{film}}$$

The thermoelectric power of the samples were calculated by fitting polynomials to the measured Seebeck voltage data points and then taking slopes at various hot junction temperatures.

Fig. 1 shows the variation of Seebeck voltage vs. temperature for 60 and 100 vol.% Cu films. It can be seen that the Seebeck voltage is positive and increases with temperature. The variation of thermoelectric power with temperature is plotted in Fig. 2. The thermoelectric power lies in the range of 1.7–3.6 μV/K^{-1} over the whole temperature range investigated and increases almost linearly with temperature, having a metallic-like behavior. As can be seen in Fig. 2 the thermoelectric power became more positive as the Cu content decreased for 100–60 vol.% Cu. Fig. 2 also shows the variation of thermoelectric power of a 100% Cu film and bulk Cu [12]. The graph also shows that the Cu film has a lower value of thermoelectric power than the bulk, but they exhibit the same linear increase of thermoelectric power. Chopra *et al.* [13] reported that the thermoelectric power of a Cu film behaves like bulk Cu for thickness above 120 nm. The positive value of thermoelectric power normally indicates that the majority carriers are holes. The temperature dependence and the sign of the thermoelectric power for 200 nm Cu film are similar, with values lying within 8% of bulk values [13]. It has also been observed that thermoelectric power increases with increasing thickness [14]. Hence, the thermoelectric power of a thin Cu film is expected to be lower than the thermoelectric power of bulk Cu. The thermoelectric power in this compositional region obeys the linear relation

$$S = A_1 + B_1 T \tag{1}$$

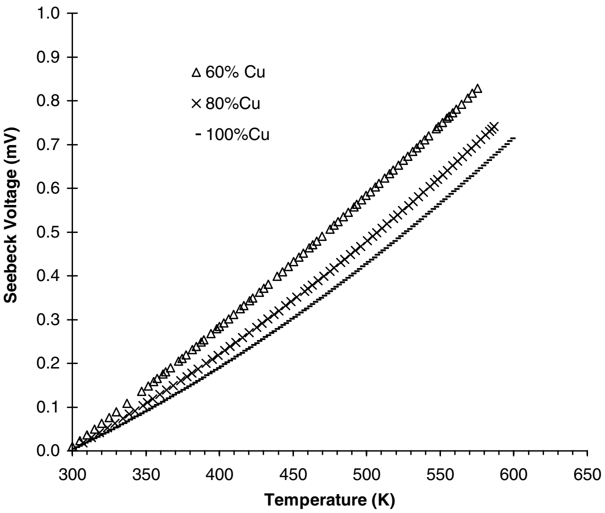

Figure 1 Variation of Seebeck voltages with temperature for 60–100 vol.% Cu films.

The values of A and B are given in Table I. Mott and Davis [15] suggested that in the metallic range of concentration S should be proportional to T and in the hopping range it should be of the form $A + BT$. Cutler and Mott [16] suggested that the thermoelectric power for hopping

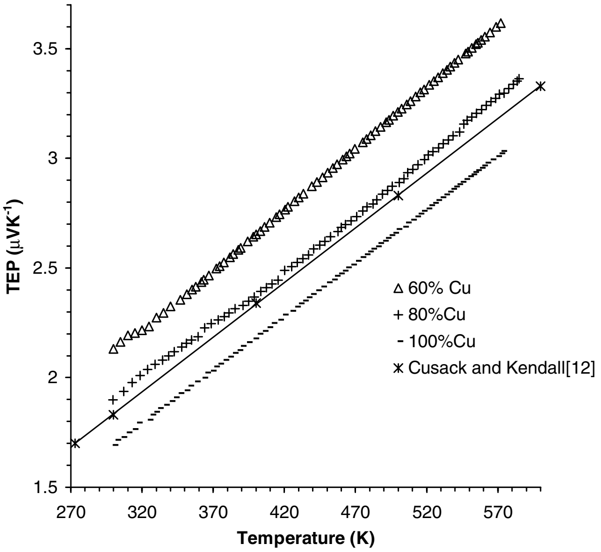

Figure 2 Variation of thermoelectric power with temperature for 60–100 vol.% Cu films.

TABLE I Values of A_1, B_1 and E_F according to equations 1 and 2

Vol.% Cu	A_1 (μVK^{-1})	B_1 (10^{-3} μVK^{-2})	E_F (eV)
60	0.44	5.6	4.36
80	0.35	5.1	4.79
100	0.24	4.9	4.99

conduction near the Fermi level might be expressed by the relation

$$S = \frac{\pi^2 k^2 T}{3e}\left[\frac{d\ln\sigma(E)}{dE}\right]_{E=E_F}$$

This relation predicts that S will increase as T increases. As the sign of the thermoelectric power is positive in this region, it implies that the major contribution to the current occurs below the Fermi level.

According to Donovan [17] and Jain and Berry [18], the thermoelectric power of a metal or degenerate semiconductor can be expressed by the relation

$$S = \frac{\pi^2 k^2 T}{eE_\mathrm{F}} \qquad (2)$$

where k is the Boltzmann's constant. Jain and Berry [18] found that the value of the Fermi energy E_F in Equation 2 is smaller in degenerate semiconductors than in metals and as a result S is larger for semiconductors than metals. This is the case with Cu/GeO$_2$ films, for which higher metallic content samples display a smaller thermoelectric power than the lower metallic samples. The values of E_F calculated from the slope (B_1) of the graphs in Fig. 3 and using Equation 2, has been tabulated in Table I.

A small value of thermoelectric power (+1.7–+3.6 μV) and a linear variation with temperature (Fig. 2) are consistent with a typical metallic behavior. A positive temperature coefficient of resistance (TCR) observed for compositions $\geq$60% Cu in Cu/GeO$_2$ films [19] also supports this. The positive sign of the thermoelectric power implies that the major contribution to the current lies below the Fermi-level in the valence band extended states.

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