JOURNAL OF MATERIALS SCIENCE **39** (2004) 319– 321

Film thickness and deposition rate dependence of thermoelectric power of Cu-GeO$_2$ thin cermet films

I. LUCY
Department of Physics, Rajshahi University, Rajshahi 6205, Bangladesh
E-mail: irine@librabd.net

Thermoelectric power (TEP) measurements provide the most reliable information about the nature of charge carriers. Combined with dc conductivity, thermoelectric power measurements allow the conduction operative in the films to be systematically investigated. According to Mott and Davis [1] the sign of TEP is a more reliable indicator than the Hall co-efficient for determining whether the material is *n*-type or *p*-type. TEP measurement is particularly useful for small mobility materials in which Hall effect measurements are extremely difficult to make. In this study the variation of TEP with thickness and deposition rate has been studied.

Cu-GeO$_2$ cermet thin films of various thickness (100, 200 and 400 nm) and deposition rates (1, 2 and 3 nm/s) were deposited on corning 7059 alkali free aluminosilicate glass substrate *in vacuo* (about 1 mPa) from two molybdenum boats by co-evaporation [2] using 99.3% pure Cu power (Koch-Light Laboratories Ltd.) and 99.999% pure GeO$_2$ powder (Aldrich Chemical Company, Inc.). The co-evaporation for the fabrication of thin films for mixing metal and ceramic is preferred over single boat evaporation as the deposition parameters can be closely controlled with this technique and as a result, the film properties are more reproducible. A type-K chromel-alumel thermocouple (RS Components Ltd.), connected to a Comark microprocessor thermometer (Model 6400), was used to monitor the temperature of the substrate. To obtain 100 nm thick 20 vol% Cu–80 vol% GeO$_2$ film, 20 nm of Cu was mixed with 80 nm of GeO$_2$ by controlling the deposition rates of the sources. The deposition rates and film thicknesses 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).

The thermoelectric power, S, was measured using integral technique [3] *in vacuo* in the temperature range 290 K to 600 K on planar samples of 50 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 TEP 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 n VK^{-1} [4], which is negligibly small compared to S_{film}. Hence

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

The TEP 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 dependence of TEP with temperature for 50 vol% Cu film of thicknesses 100, 200 and 400 nm, deposited at a rate of 0.8 nm/s. Fig. 2 obtained from Fig. 1 is a graph of TEP vs. thickness for selected temperatures. As can be seen, TEP increases with increasing thicknesses.

The transport properties of a material in thin film state will be different when compared with the properties of the same material in the bulk state. In thin film state in addition to the normal bulk scattering processes, scattering of carriers may also occur at external and internal (grain boundary) surfaces. As the external surface-to-volume ratio is an inverse function of the thickness of a film and the grain size is also small (less than the thickness of the film), it is expected that as the thickness of the film changes, the extent of the carrier scattering by internal and external grain boundary will also change. Consequently, transport properties of thin films will be functions of thickness. This dependence of the properties of a film on thickness is termed the classical size effect. Tellier [5] proposed the effective mean free path model to explain the thickness dependence of the resistivity of polycrystalline films. It was modified further by Pichard *et al.* [6] to include a discussion of the Seebeck coefficient S_{f} of a polycrystalline film. The relation is

$$S_{\text{f}} = S_{\text{g}}\left\{1 - \frac{3}{8}\frac{(1-p)l_{\text{g}}}{t}\frac{U_{\text{g}}}{1+U_{\text{g}}}\right\} \tag{1}$$

where subscripts f and g are related to the thin film and infinitely thick film, respectively, $U_{\text{g}} = (\partial \ln l_{\text{g}}/\partial \ln E)_{\text{E}_{\text{F}}}$ is the energy dependence of the mean free path l_{g} of the charge carriers, t is the thickness of the thin film and p is a specularity parameter which gives the fraction of the charge carriers that are specularly scattered from the surface. This model predicts

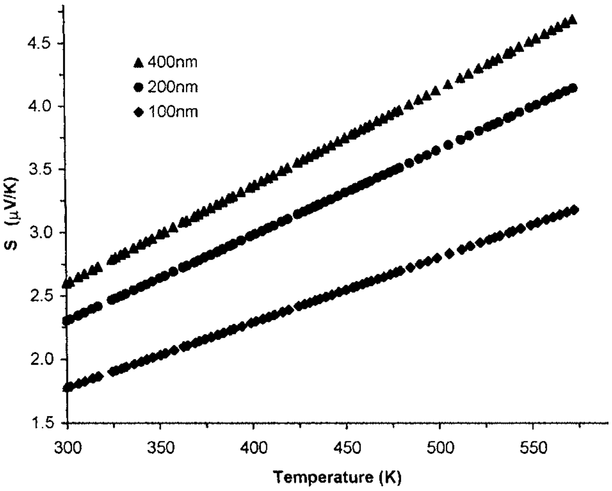

Figure 1 Thermoelectric power vs. temperature plot for 50 vol% Cu films of various thicknesses.

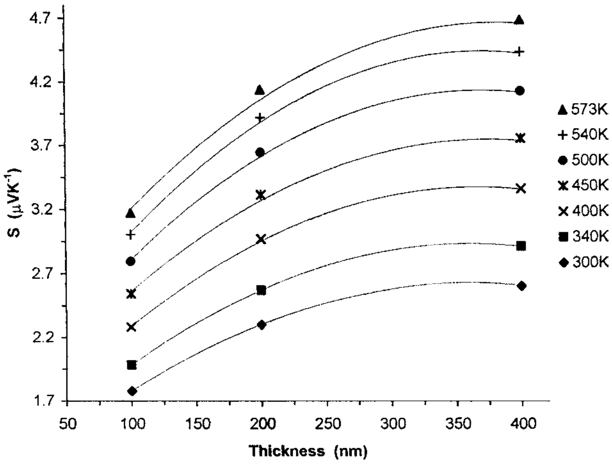

Figure 2 Variation of thermoelectric power vs. thickness of 50 vol% Cu films at selected temperatures.

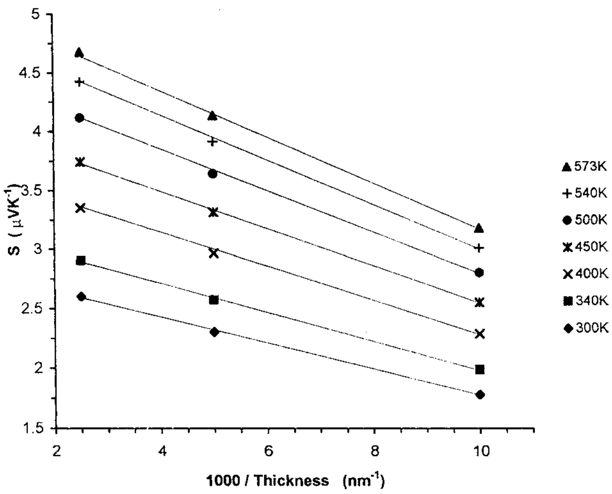

Figure 3 Variation of thermoelectric power vs. inverse thickness of 50 vol% Cu films at selected temperatures.

that the TEP of a thin film should decrease with decreasing thickness.

Fig. 3 shows TEP vs. reciprocal thickness plot. The experimental TEP values at different selected temperatures exhibit a linear dependence on reciprocal thickness, as expected from the effective mean free path model. It was also found from electron diffraction shown in Fig. 4 that 50 vol% Cu films have a few bright spots on the diffraction ring and hence are polycrystalline. Hence, these samples may be expected to obey relation 1. S_g obtained from the intercepts of Fig. 3 is tabulated in Table I. Das and Lakshmi [7] and Das *et al.* [8, 9] have also observed the increase of TEP with thickness for $Se_{20}Te_{80}$ alloy, Sb and $Se_{10}Sb_{10}Te_{80}$ thin films.

TABLE I Values of S_g-calculated using Equation 1 at different temperatures

T (K)	S_g (μVK^{-1})
573	5.2
540	4.9
500	4.5
450	4.1
400	3.7
340	3.2
300	2.9

Fig. 5 shows the variation of TEP with temperature for 20 vol% Cu samples 200 nm thick, deposited at

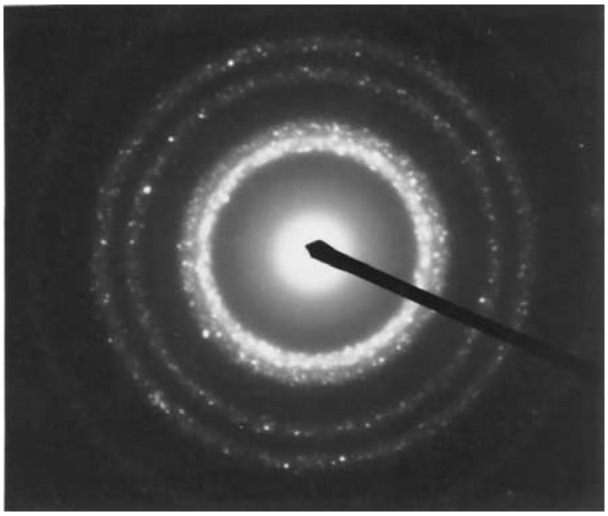

Figure 4 Electron diffraction pattern for 50 vol% Cu film, 100 nm thick, deposited at a rate of 0.8 nm/s, at a substrate temperature 600 K.

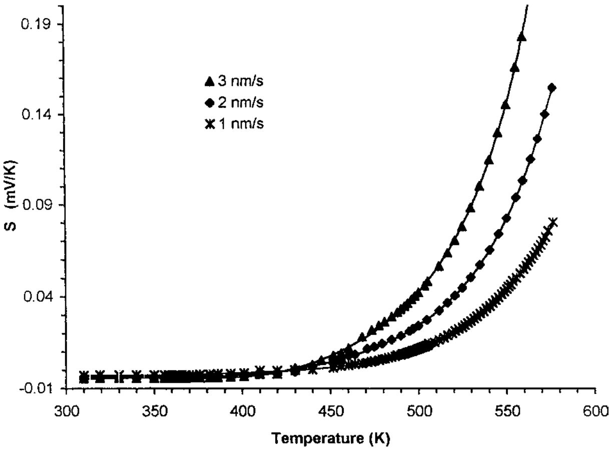

Figure 5 Variation of thermoelectric power vs. temperature of 20 vol% Cu samples deposited at various rates.

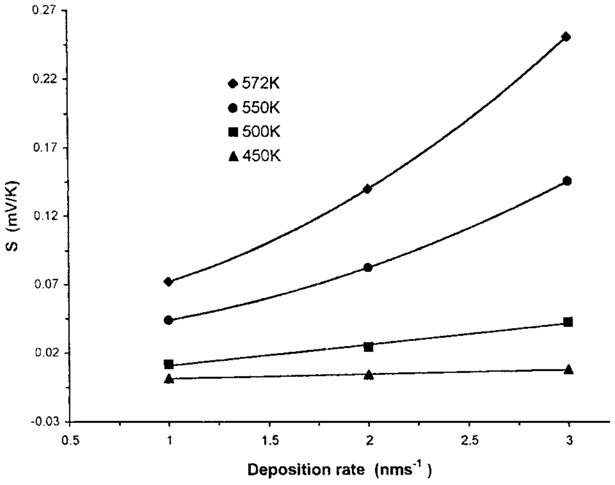

Figure 6 Variation of thermoelectric power vs. deposition rate of 20 vol% Cu films at selected temperatures.

600 K at various deposition rates. For a fixed temperature TEP increases with increasing deposition rate as shown in Fig. 6. A low deposition rate leads to a higher gaseous content in the films but a lower number of defects. Since the samples were prepared at elevated substrate temperatures (600 K) the gas content is expected to diminish because of the decreasing sticking coefficient. Thus samples prepared at the higher deposition rate are expected to have relatively higher thermoelectric power and conductivity values. Optical measurements [9] confirm that the number of defects increases with increasing deposition rate whereas DC measurements on the same sample [10] reveal that the conductivity increases with increasing deposition rate.

Acknowledgments

I am grateful to Dr. John Beynon of Brunel University, UK for his enthusiastic guidance throughout this work and to Prof. C. A. Hogarth of the same university for many useful discussions.

References

1. N. F. MOTT and E. A. DAVIS, "Electronic Processes in Non-Crystalline Materials" (Clarendon Press, Oxford, 1979) p. 235.
2. C. A. HOGARTH and L. A. WRIGHT, in Proc. Int. Conf. Phys. Semiconductors (Moscow, Nauka, Leningrad, 1968) p. 1274.
3. H. HEIKES and R. W. URE, "Thermoelectricity: Science and Engineering" (Interscience, New York, 1961) p. 311.
4. R. M. ROSE, L. A. SHEPARD and J. WULFF, "The Structure and Properties of Materials," Vol. 4, Electronic Properties (John Wiley & Sons Inc., New York, 1966) p. 179.
5. C. R. TELLIER, *Thin Solid Films* **51** (1978) 311.
6. C. R. PICHARD, C. R. TELLIER and A. J. TOSSER, *J. Phys. F* **10** (1980) 2009.
7. V. D. DAS and J. LAKSHMI, *Thin Solid Films* **172** (1989) 167.
8. V. D. DAS and N. SOUNDARARAJAN, *J. Mater. Sci.* **24** (1989) 4315.
9. V. D. DAS, K. S. RAJU and S. ARUNA, *J. Appl. Phys.* **78**(3) (1995) 1751.
10. I. B. LUCY, J. BEYNON and D. N. WATERS, *J. Mater. Sci. Lett.* **15**(6) (1996) 515.
11. I. B. LUCY, *Ind J. Pure Appl. Phy.* **37** (1999) 836.

Received 10 July
and accepted 29 July 2003