Effects of temperature on the resistivity of vacuum deposited Cu-MgF_2 cermet thin films: an investigation of conduction mechanism

G. KATUMBA, L. OLUMEKOR
Physics Department, University of Zimbabwe, P.O. Box MP 167, Mt Pleasant, Harare, Zimbabwe
E-mail: katumba@compcentre.uz.ac.zw

Cermet thin films of Cu-MgF_2 were deposited onto glass substrates using a conventional resistive heating co-evaporation technique. Films of starting compositions 40, 60 and 80 vol% Cu and average thicknesses 60, 145 and 285 nm were deposited at elevated substrate temperatures between 300 and 393 K in a vacuum of 1.33×10^{-3} Pa. Room temperature D.C. resistivity measurements were performed at atmospheric pressure from which activation energies and TCRs for the cermet films were determined. It was observed that the resistivity (ρ) data fitted into the ln $\rho \propto 1/T$ relationship. The activation energies were found to decrease with increase in film thickness and increase in metallic content of the cermet films whilst the TCRs were all negative. From the trends in both activation energies and TCRs it was concluded that the predominant conduction mechanism was tunnelling of thermally activated charge carriers.

1. Introduction
Temperature dependence of the electrical properties of cermet films has been investigated by many authors [1–6]. Generally, the temperature dependence of the conductivity, σ of cermet films and amorphous semiconductors is given by Robertson [6] as:

$$\sigma = \sigma_0 \exp\left[-\left(\frac{T_0}{T}\right)^n\right] \tag{1}$$

where σ_0 is the minimum value of conductivity when metallic conductivity sets in and T_0 is a parameter dependent on the density of states at the Fermi level, $N(E_F)$, and the rate of decay, α, of a wave function for the conduction electron.

Conduction mechanisms in these films can be inferred from Equation 1. If n is unity then the conduction is predominantly by thermal activation of charge carriers to states of energy E lying kT from the Fermi energy, E_F. If $n < 1$, then conduction occurs by hopping in localised states around the Fermi energy, E_F. This occurs if the density of states, $N(E_F)$, is low so that as the temperature falls, an electron must hop to distant sites to locate a level within $\approx kT$ of its energy. The classic power law for variable range hopping (VRH) at E_F is $n = 1/4$ as observed by Mott [7]. If only the $T^{-1/4}$ regime is found it is conventional to take α^{-1}, the decay length of the localised state wave function, as $\approx$0.1 nm and estimate $N(E_F)$ from:

$$T_0 = \frac{16\alpha^3}{kN(E_F)} \tag{2}$$

The minimum conductivity, σ_0 can also be used to infer conduction mechanisms [6]. If $\sigma_0 \geq 10\ \Omega^{-1}\ \mathrm{m}^{-1}$ (or $\rho_0 \leq 0.1\ \Omega$ m) then conduction occurs by activation of charge carriers to extended states beyond the conduction band, E_c or the valence band, E_v. If $\sigma_0 < 10\ \Omega^{-1}\ \mathrm{m}^{-1}$ then conduction occurs by hopping between localised states on near-neighbour sites.

It has also been observed that thin film deposition or annealing at substrate temperatures greater than 300 K produces a decrease in resistivity, ρ and a reduction in the activation energy, ΔE determined from [6, 8]:

$$\rho = \rho_0 \exp\left[\frac{E_a}{2kT}\right] \tag{3}$$

where ρ_0 is the limiting resistivity.

The nature of the charge carriers in each of the conduction mechanisms discussed above can be investigated by performing thermopower or Hall effect measurements on the films.

In this study the conduction mechanism in Cu-MgF_2 cermet thin films is investigated through DC conductivity measurements on the films. The investigation is concerned with the determination of activation energy and TCR values for various thicknesses and various starting compositions of the cermet thin films. Trends in and magnitude of these two parameters are then used to draw conclusions about the transport mechanism in the cermets.

2. Experimental
2.1. Cermet preparation
Cu-MgF_2 cermet thin films were prepared by the conventional resistive heating co-evaporation technique

onto glass substrates. A total number of 180 samples of the cermets were used in the investigation. The starting compositions studied were 40, 60 and 80 vol % Cu and each of these three compositions contained 60 samples. Deposition was performed in a vacuum of 1.33×10^{-3} Pa at substrate temperatures 303, 318, 333, 363, 377 and 393 K.

2.2. Electrical and thickness measurements

Direct resistance measurements were made on the cermet films at room temperature and at atmospheric pressure using a Hewlett Packard digital voltmeter, model 3456A. The 4-point probe [9, 10] configuration of the voltmeter was used for all resistance measurements. The nominal accuracy of the digital voltmeter is 2%.

Film thickness measurements were performed using the Michelson interferometry technique [11]. Three sizes of average film thickness, namely 60 ± 6, 145 ± 8 and 285 ± 9 nm, were used and each size was averaged over 60 samples.

Resistivity and sheet resistance calculations were performed using the measured resistance values, the measured film thicknesses and aspect ratio of 6.89 ± 0.02.

2.3. Data processing

Graphs of ln ρ against $1/T$ were plotted and the slopes and intercepts determined. The values of the slopes and intercepts were in turn used to calculate the activation energy, E_a, and ρ_0 respectively for the cermets.

Graphs of sheet resistance, R, vs. temperature, T, which are not shown here, were plotted and used to determine the temperature coefficients of resistance (TCRs) of the cermets at 313 K.

3. Results and discussion

The variation of resistivity, ρ, with $1/T$ of the Cu-MgF_2 cermet films is shown in Figs 1–3. All the ln ρ vs. $1/T$ graphs were linear and fitted Equation 3. The $1/T$ dependence appears to suggest that $n = 1$ in Equation 1 and, therefore, conduction in this cermet system is predominantly by thermal activation of charge carriers.

The variation of E_a and ρ_0 with thickness and composition is shown in Table I from which it may be observed that E_a decreases with increase in film thickness. This table also shows that E_a increases with increase in dielectric content of the cermet films. Olumekor and Beynon [3, 12] have made similar observations in Mn-MgF_2 cermet thin films. Agarwal *et al.* [10] and Das

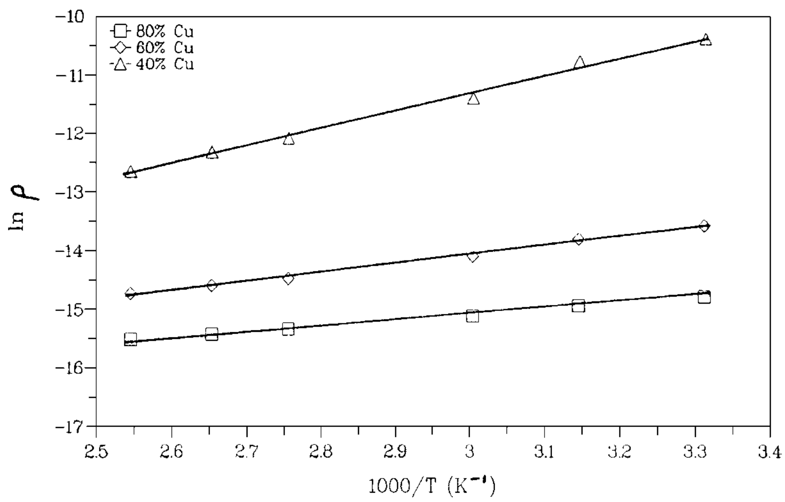

Figure 1 The variation of resistivity with inverse deposition temperature for Cu-MgF_2 cermets of thickness 60 nm.

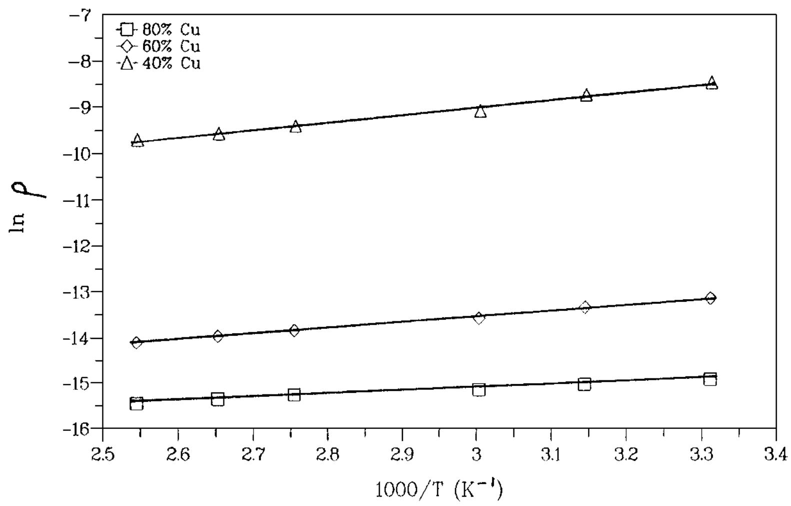

Figure 2 The variation of resistivity with inverse deposition temperature for Cu-MgF_2 cermets of thickness 145 nm.

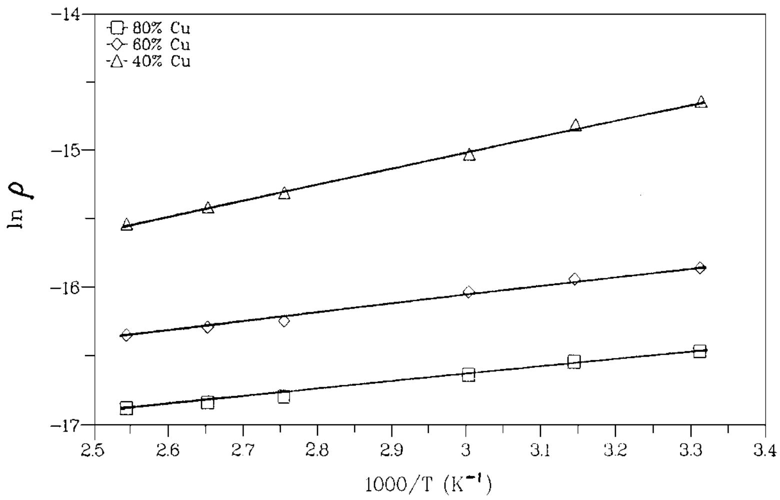

Figure 3 The variation of resistivity with inverse deposition temperature for Cu-MgF_2 cermets of thickness 285 nm.

TABLE I Variation of activation energy with composition and thickness of Cu-MgF_2 cermets

Composition (vol % Cu)	Thickness (nm)	E_a (meV)	ρ_0 (10^{-8} Ω m)
80	60 ± 6[a]	167 ± 7[a]	1.52 ± 0.03[a]
	145 ± 8	115 ± 10	3.6 ± 0.1
	285 ± 9	74 ± 3	4.81 ± 0.05
60	60 ± 6	262 ± 10	1.34 ± 0.05
	145 ± 8	215 ± 7	3.16 ± 0.06
	285 ± 9	114 ± 3	4.67 ± 0.05
40	60 ± 6	520 ± 20	0.31 ± 0.02
	145 ± 8	280 ± 20	103 ± 1
	285 ± 9	195 ± 5	3.78 ± 0.04

[a]Error estimates are standard error in the mean.

and Bahulayan [13] also observed a similar trend in SnSe and $Pb_{0.6}Sn_{0.4}Te$ thin films, respectively. A more detailed comparison of the activation energy values obtained by other authors is given in Table II.

For a particular comparison, Olumekor and Beynon [3] observed E_a to lie in the range 8 to 150 meV for Mn-MgF_2 cermets with thicknesses in the range 25 to 100 nm and in the composition range 39 to 100 vol % Mn whereas E_a for Cu-MgF_2 cermets in the present study ranged from 520 meV to about 70 meV for the thickness range 60 to 285 nm and composition range 40 to 80 vol % Cu. Olumekor and Beynon [3] associated the trend in activation energy with a combination of an activated and a metallic conduction process acting in parallel in the Mn-MgF_2 cermets. These two conduction mechanisms can initially be assumed for the Cu-MgF_2 cermets.

Mehra *et al.* [14], on the contrary, observed that the activation energy for conduction in amorphous Te_xSe_{1-x} films increased with increasing film thickness. They associated this observation with the fact that a variable range hopping (VRH) conduction mechanism predominates in thinner films. The contribution of this conduction mechanism at higher temperatures decreases with increasing film thickness, resulting in an overall increase in activation energy with increase in film thickness for given composition [14]. This phenomenon is contrary to that observed in Cu-MgF_2

TABLE II Comparison of activation energy values for various film types

Authors	Film type	Thickness (nm)	Composition (vol %)	E_a (meV)
Beynon and Olumekor [12]	Mn-MgF_2 cermets	25	60 Mn[a]	108
		25	80 Mn[a]	59
		25	100 Mn[a]	24.6
Olumekor and Beynon [3]	Mn-MgF_2 cermets	25–100	39 Mn	150–21
		25	39–100 Mn	150–31
		50	39–100 Mn	83–8
Mehra *et al.* [14]	Te_xSe_{1-x} amorphous	25–160[b]	$x = 0.90$	46–83[b]
		25–160[b]	$x = 0.85$	50–100[b]
		25–160[b]	$x = 0.80$	68–170[b]
Agarwal *et al.* [10]	SnSe[c] crystalline	—	—	7; 410[d]
Das and Bahulayan [13]	$Pb_{0.6}Sn_{0.4}Te$ polycrystalline	43–330	—	220–120
Katumba and Olumekor	Cu-MgF_2 cermets	60–285	40 Cu	520–195
		60–285	60 Cu	262–114
		60–285	80 Cu	167–74

[a]Composition in wt % Mn.
[b]Activation energy increasing with increasing film thickness.
[c]Not necessarily thin films.
[d]Temperature dependence: 303–353 and 360–443 K respectively.

TABLE III Variation of TCRs of Cu-MgF_2 cermets deposited at elevated substrate temperatures with composition and thickness of the cermets

Composition (vol % Cu)	Thickness (nm)	TCR, α (ppm $^\circ C^{-1}$)
80	60 ± 6	$-9{,}600 \pm 600$
	145 ± 8	$-7{,}200 \pm 400$
	285 ± 9	Near zero
60	60 ± 6	$-12{,}500 \pm 600$
	145 ± 8	$-11{,}100 \pm 500$
	285 ± 9	Near zero
40	60 ± 6	$-27{,}200 \pm 900$
	145 ± 8	$-21{,}700 \pm 700$
	285 ± 9	Near zero

films, probably due to the intrinsic difference between $Te_x Se_{1-x}$ which is an alloy film and Cu-MgF_2 which is a cermet. The absence of VRH conduction mechanism in the Cu-MgF_2 cermets was therefore inferred.

From Table I it may be observed that ρ_0 is of the order of 10^{-8} Ω m which is less than 0.1 Ω m. As explained in Section 1, this observation indicates that conduction is by activation of charge carriers.

The variation of TCRs with thickness and composition is shown in Table III. It was observed that Cu-MgF_2 cermets of thicknesses 60 and 145 nm and compositions 40, 60 and 80 vol % Cu had high negative TCR values of about $-27{,}000$ ppm $^\circ C^{-1}$ while cermets of same compositions but of thickness 285 nm had near zero TCR values. High negative TCR values are usually associated with a thermally activated conduction mechanism [15, 16]. Swanson and Campbell [17] linked negative TCR values in thin films to electrical discontinuities and hence to tunnelling of thermally activated charge carriers. Abeles *et al.* [8] also associated negative TCR values with tunnelling of thermally activated charge carriers and further pointed out that positive TCR values are a sign of metallic conduction. Since all the TCR values for the Cu-MgF_2 cermets were found to be equal or less than zero, it was concluded that the dominant conduction mechanism in these cermets was tunnelling of thermally activated charge carriers.

4. Conclusions and comments

Cu-MgF_2 cermet thin films of thicknesses 60 ± 6, 145 ± 8 and 285 ± 9 nm and starting compositions 40, 60 and 80 vol % Cu were successfully prepared and it was observed that the dominant conduction mechanism in these cermets was tunnelling of thermally activated charge carriers. It was further observed that cermets of thickness 285 nm and compositions 40, 60 and 80 vol % Cu had near zero TCR values which suggests that these cermets could be of practical use in the manufacture of discrete or integrated resistor components for electronic circuits.

Acknowledgements

Sincere gratitude to the Research Board of the University of Zimbabwe for funding fully this research.

References

1. O. ENTIN-WOHLMAN, Y. GEFEN and Y. SHAPIRA, *J. Phys. C: Solid State Phys.* **16** (1983) 1161.
2. PING SHENG, B. ABELES and Y. ARIE, *Phys. Rev. Letts.* **31** (1973) 44.
3. L. OLUMEKOR and J. BEYNON, *Thin Solid Films* **53** (1978) L9.
4. S. P. McALISTER, A. D. INGLIS and D. R. KROEKER, *J. Phys. C: Solid State Phys.* **17** (1984) L751.
5. T. J. COUTTS, *Thin Solid Films* **4** (1969) 429.
6. J. ROBERTSON, *Adv. Phys.* **35** (1986) 317.
7. N. F. MOTT in "Metal-Insulator Transitions" (Taylor and Francis Ltd., Oxford, 1974) p. 35.
8. B. ABELES, PING SHENG, M. D. COUTTS and Y. ARIE, *Adv. Phys.* **24** (1975) 407.
9. L. I. MAISSEL, in "Handbook of Thin Film Technology" (McGraw-Hill, New York, 1970) pp. 13-6.
10. A. AGARWAL, S. H. CHAKI, S. G. PATEL and D. LAKSHMINARAYANA, *J. Mater. Sci.*: *Mater in Electron.* **5** (1994) 287.
11. F. A. JENKINS and H. E. WHITE, in "Fundamentals of Optics" (McGraw-Hill, 1975) p. 253.
12. J. BEYNON and L. OLUMEKOR, *Thin Solid Films* **24** (1974) S30.
13. V. D. DAS and C. BAHULAYAN, *J. Appl. Phys.* **80** (1996) 1633.
14. R. M. MEHRA, S. C. AGARWAL, S. RANI, R. SHYAM, S. K. AGARWAL and P. C. MATHUR, *Thin Solid Films* **71** (1980) 71.
15. P. K. REDDY, G. K. BHAGAVAT and S. R. JAWALEKAR, *ibid.* **70** (1980) 27.
16. A. H. BOONSTRA and C. A. H. A. MUTSAERS, *ibid.* **67** (1980) 13.
17. J. G. SWANSON and D. S. CAMPBELL, *ibid.* **1** (1967) 183.

Received 20 October 1998
and accepted 5 May 1999