JOURNAL OF MATERIALS SCIENCE **35** (2000) 4567 – 4571

Effect of composition on DC conductivity of co-evaporated Cu-GeO$_2$ thin cermet films

I. B. LUCY
Department of Physics, Rajshahi University, Rajshahi 6205, Bangladesh
E-mail: badrul@universalmail.com

Thin films containing 0 to 100 vol%Cu was prepared by thermal co-evaporation. The samples were 200 nm thick, deposited at 600 K at a rate of 0.8 nm/s. DC conductivity measurements were carried out using the van der Pauw four probe technique for 0 to 100 vol%Cu films in the temperature range 150 to 600 K. Samples containing $\geq$60 vol%Cu exhibited a 'metallic-like' behaviour with positive TCR whereas lower concentrations exhibited an activated conduction mechanism with negative TCR. © *2000 Kluwer Academic Publishers*

1. Introduction

The conduction mechanism in thin cermet films has been the subject of much interest over the past few decades [1–3]. It is widely believed that the cermet films consist of discrete metal islands dispersed in a continuous insulating matrix. Depending on the metal volume, it is possible to characterise a mixed metal-insulator film by three structural regions [4]:

Metallic: In this regime the metallic fraction is large and the metallic islands form a connected metallic network with the result that carriers can percolate directly through the connected metal islands. The micro-geometry of the metallic channels plays an important role in understanding the conduction mechanism in this regime. Typical resistivity of these films lies between 10^{-8}–10^{-3} Ω m.

Insulating: In this regime the metal grains form islands in the insulating matrix. These films have similar structures to those of discontinuous metal films and possess a negative TCR. Typical resistivity of these films lies between 10^{-4}–10^{7} Ω m.

Transitional: This is an intermediate regime between metallic and insulating regimes. Here structural inversion takes place between metallic and insulating regime. The transition between the metallic and insulating regime is characterised by a percolation threshold characterising the point at which the metallic network first becomes disconnected. This regime covers a relatively small compositional range and the resistivity does not cover more than approximately two orders of magnitude. In co-evaporated Cu-GeO$_2$ cermet films, such a transition occurs when the Cu volume fraction is in between 50%–60%.

A cermet film can have widely varying resistivity, temperature coefficient of resistivity (TCR) and high stability when exposed to normal atmospheric conditions. The resistivity of a cermet film can be adjusted by varying the composition, deposition rate, thickness, deposition temperature, etc. and it is also possible to balance the TCRs of the individual components. Consequently this material has found varied applications in the micro-electronics industry. Since a large number of properties of these films undergo rapid changes with temperature, the material can be used in a variety of thermal devices such as thermal detectors, thermometers and thermocouples.

2. Experimental procedure

Cu-GeO$_2$ cermet thin films were deposited on corning 7059 alkalifree alumino-silicate glass substrate from two molybdenum boats by co-evaporation [5] in a Speedivac vacuum coating unit (model 19A/122) with some modification to allow double boat evaporation. Film preparation arrangements follow that described by Lucy *et al*. [6]. DC electrical conductivity was measured using van der Pauw [7] four-probe technique. The samples were circular of diameter 10 mm and were contacted by four symmetrically placed 100 nm thick evaporated aluminium electrodes of diameter 2 mm. The measurements were performed in a vacuum chamber at a pressure $\approx 10^{-6}$ Torr at temperatures in the range 150 to 600 K. An auto-ranging Keithley 617 programmable digital electrometer having input impedance of 200 T ohms was used for all voltage measurements. A power supply unit (Farnell stabilised power supply E350) produced a current and a Keithley 485 auto-ranging pico-ammeter (for films <50 vol%Cu) and Black Star 3225 multimeter (for films >50 vol%Cu) were used for current measurement. A type-K chromel-alumel thermocouple was usd to monitor the temperature of the substrate in the range 300–600 K, whilst a T-type (copper/copper-nickel) thermocouple was used below room temperature up to 150 K. Both types of thermocouple (RS Components Ltd) were connected to a Comark microprocessor thermometer (Model 6400) to display the temperature. The deposition rate and film thickness were controlled using two calibrated quartz crystal oscillators (Maxtec, Inc) for the Cu and GeO_2 sources. To obtain 20 vol%Cu film of 200 nm thickness, 40 nm of Cu was mixed with 160 nm of GeO_2 film by controlling the deposition rates of the sources. The film thickness was measured by multiple beam interferometry with an Angstrometer (Solan Instruments, model M-100). Measurements of the variation of DC conductivity with temperature were carried out on samples of all compositions (0 to 100 vol%Cu) in the temperature range 150 to 600 K. The samples were 200 nm thick deposited at 600 K at a rate of 0.8 nm/s and at a total residual pressure $\approx 10^{-6}$ Torr.

3. Results and discussions

3.1. Effect of microstructure and composition

Fig. 1 compares the conductivity of a 100% Cu film with the conductivity of bulk Cu [8] as a function of temperature. The experimental values for the 200 nm Cu film are about 5 to 8% lower than those for bulk Cu. The result may explain the effect of porosity or columnar structure of Cu thin film.

The conductivity versus temperature evaluation as a function of the constant Cu volume fraction is given on Fig. 2. The conductivity increases with temperature between 150 K and 600 K for film compositions up to 50 vol%Cu. For samples in the range 60 to 100 vol%Cu the conductivity decreases with increasing temperature. The overall change in conductivity with composition is some 14 orders of magnitude at 200 K and 10 order of magnitude at 580 K.

These results indicate that films containing up to 50 vol%Cu exhibit a typical semiconductor-like behaviour with temperature whereas the higher metallic content films have a characteristic metallic behavior i.e. a negative temperature coefficient of conductivity. It is suggested that films containing more than 50 vol%Cu have a continuous chain-like metallic structure [9].

The variation of conductivity with composition at different selected temperatures is shown in Fig. 3. The graph shows that the conductivity increases strongly as the metallic content increases to 50 vol%Cu but then tends to level out, displaying a much lower rate of conductivity change. According to Neugebauer [4] a complex metal/oxide film exhibits three compositional regimes: metallic, transitional and insulating. Fig. 3 tends to verify Neugebauer's conclusion. The transitional regime occurs when the conductivity changes sharply with temperature and TCR changes sign. In Cu-GeO_2 films, a composition of around 60 vol%Cu (68 wt%Cu or 54 at%Cu) [10] was found to be the critical composition at which the film structure begins to change from a continuous metallic matrix to a continuous insulating matrix.

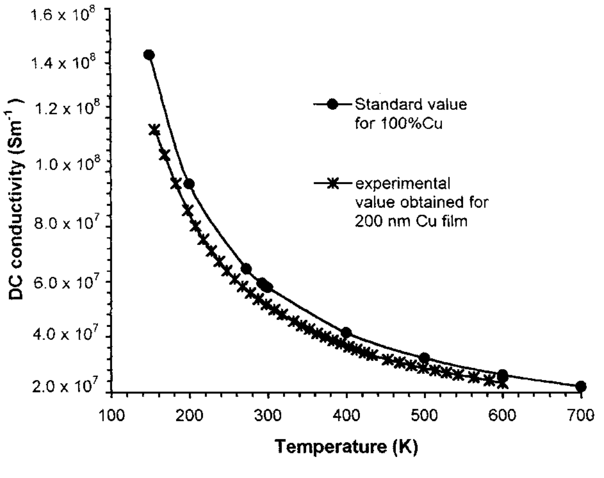

Figure 1 Comparison of the results obtained from 200 nm Cu film with the standard values for bulk Cu.

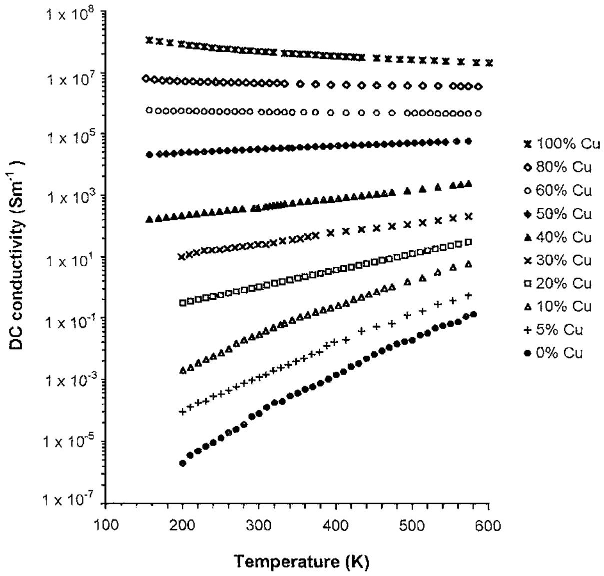

Figure 2 Variation of DC conductivity with temperature for various compositions of Cu-GeO_2 films, 200 nm, deposited at the rate of 0.8 nm/s.

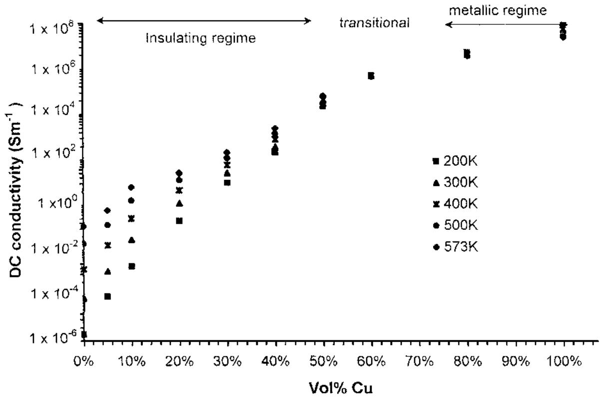

Figure 3 Variation of DC conductivity with vol%Cu at different selected temperatures.

The critical composition indicating the onset of the transitional regime has been reported by many research workers. Ostrander and Lewis [11] and Milgram and Lu [12] reported values for the critical composition of 45 and 40 vol%Cr, respectively, in co-evaporated Cr-SiO films. Abeles *et al.* [13] found a value of 60 vol%Au in Au-Al_2O_3 and Devenyi *et al.* [14] approximately 71–85 wt%Nb in Nb-Al_2O_3 films. Rahim [15] determined a critical composition of 53 vol%Mn in Mn-SiOx films prepared by single boat evaporation and Zaidi [16] determined 60 at%Mn, Cr and Cu in co-evaporated Mn-SiO_x, Cr-SiO_x and Cu-SiO_x films.

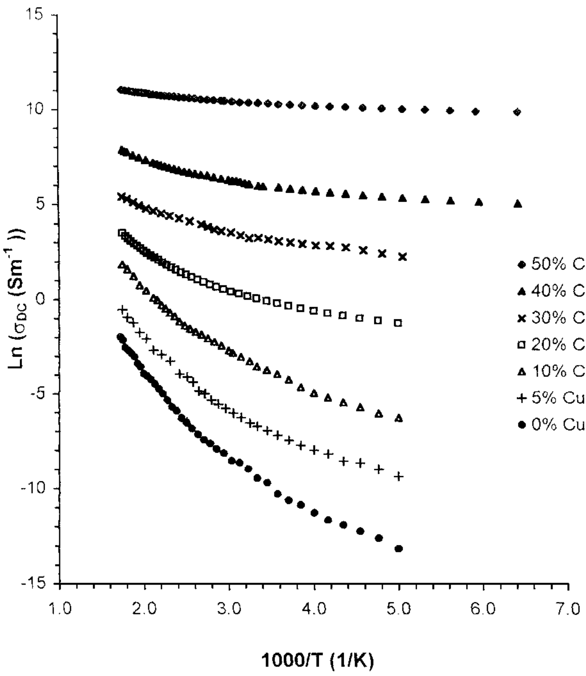

Figure 4 Variation of ln σ with inverse temperature for various compositions.

3.2. DC conductivity activation energy

The temperature-dependent activation energy E_σ is defined as

$$E_\sigma(T) = -k\left[\frac{\mathrm{d}\ln\sigma}{\left\{\mathrm{d}\left(\frac{1}{T}\right)\right\}}\right] \tag{1}$$

and can be calculated from the local gradients of ln σ vs. $1/T$ graphs. To calculate the activation energy, the conductivity of samples with $\leq$50 vol%Cu have been plotted as a function of inverse temperature in Fig. 4. It can be seen that the conductivity decreases with increasing inverse temperature and no linear dependence is observed; the increasing slope implies that the DC conductivity activation energy increases monotonically with temperature, and suggests that a thermally-activated mechanism is responsible for the conductivity. These graphs indicate that the conductivity of the samples cannot be represented by an expression with a single activation energy E_σ such as

$$\sigma = \sigma_o \exp\left(-\frac{E_\sigma}{kT}\right) \tag{2}$$

since the slope of ln σ_{DC} vs. $1/T$ graphs are changing gradually with changing temperature.

Steele and Beynon [17] suggested an empirical formula for the conductivity of Au-SiO$_x$ of the form

$$\sigma(T) = \sigma_o \exp\left(-\frac{A}{kT} + \frac{B}{kT^2}\right) \tag{3}$$

This gives an activation energy

$$E_\sigma(T) = A - \frac{2B}{T} \tag{4}$$

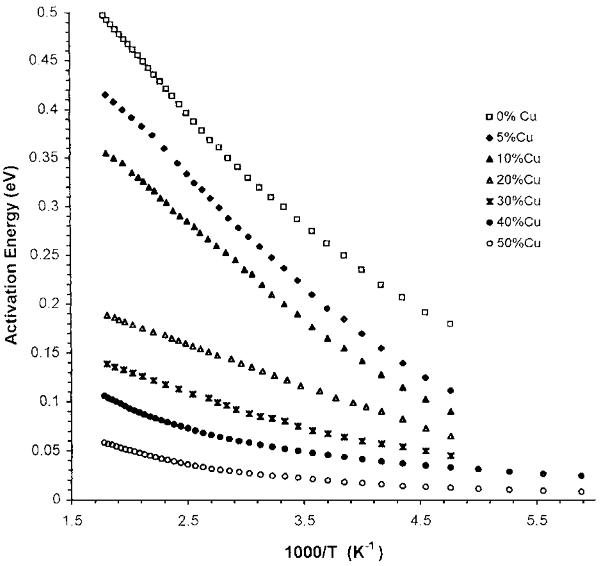

Figure 5 Variation of E_σ with inverse temperature for various compositions.

Rahman *et al.* [18] explained their results for 5, 20 and 30 wt%Cu films using Equation 5 for electron-beam evaporated Cu-GeO$_2$ films. All the graphs in Fig. 5 fit second order polynomials such as

$$E_\sigma = \frac{3A_1}{T^2} + \frac{2B_1}{T} + C_1 \tag{5}$$

Thus DC conductivity fits the expression

$$\sigma(T) = \sigma_o \exp\left\{-\left(\frac{A_1}{kT^3} + \frac{B_1}{kT^2} + \frac{C_1}{kT}\right)\right\} \tag{6}$$

The values of A_1, B_1 and C_1 are given in Table I. Table II lists values of activation energies at selected temperatures for various compositions. It can be observed that the activation energy decreases as the metallic content of the film increases. Similar types of results were obtained by other workers for Mn-SiO$_x$, Cr-SiO$_x$ and Cu-SiO$_x$ films prepared by single-boat evaporation and by co-evaporation [17, 18]. Fig. 6 shows the variation of activation energy with vol%GeO$_2$ at selected temperatures. The curves are exponential, obeying the following relation

$$E_\sigma(T) = P\,e^{QV} \tag{7}$$

where V stands for vol%GeO$_2$ in the film. Values of P and Q for five temperatures are listed in Table III. It can be observed from Table III that Q decrease but P increases with increasing temperature. Decreasing values

TABLE I Values of A_1, B_1 and C_1 in accordance with Equation (5)

Vol%Cu	A_1 (eV.K^2)	B_1 (eV.K^1)	C_1 (eV)
00	5180	−105	0.823
05	3428	−87	0.702
10	2490	−72	0.595
20	228	−23	0.271
30	1851	−34	0.246
40	1873	−30	0.192
50	1314	−20	0.116

TABLE II Values of activation energy at selected temperatures for various composition of Cu-GeO_2 thin films

	Activation Energy (eV)							
Vol%Cu	210 K	260 K	310 K	360 K	410 K	460 K	510 K	560 K
00	0.180	0.250	0.310	0.361	0.406	0.443	0.473	0.493
05	0.112	0.185	0.248	0.299	0.345	0.374	0.400	0.415
10	0.090	0.155	0.210	0.260	0.291	0.318	0.334	0.340
20	0.065	0.099	0.127	0.147	0.163	0.172	0.182	0.189
30	0.045	0.064	0.083	0.099	0.113	0.122	0.133	0.139
40	0.033	0.044	0.054	0.064	0.075	0.085	0.096	0.104
50	0.012	0.018	0.025	0.031	0.037	0.045	0.052	0.057

TABLE III Values of P and Q in accordance with equation (7)

Temperature (K)	P (10^{-3} eV)	Q
553	7.31	4.22
410	4.06	4.67
360	3.17	4.81
310	2.55	4.86
260	1.93	4.88

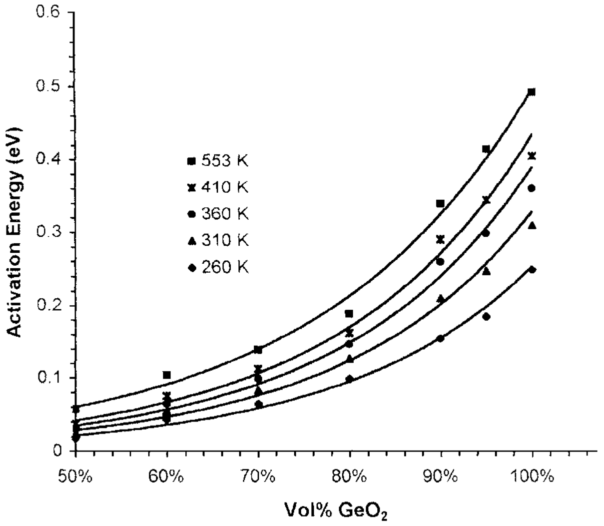

Figure 6 Variation of E_σ vs. vol%GeO_2 for selected temperatures.

of Q indicate that the rate of change of activation energy with GeO_2 content decreases as the temperature increases. Increasing values of P with temperature indicate that the activation energy increases with temperature.

Electronic conduction between metal particles separated by an insulator can take place in three ways : a) tunnelling, b) thermionic emission and c) hopping. At 50 vol%Cu, charge-transfer by tunnelling may be dismissed because the activation energy is a function of temperature. A small activation energy of the order of kT may be attributed to hopping in the quasi-continuous distribution of localized states in the band gap.

In the composition region less than 50 vol%Cu the film structure is predominantly island type. Transmission electron micrographs shown in Figs 7 and 8 support this statement [10]. The activation energies are higher than that for 50 vol%Cu and lie in the range 0.10 to 0.49 eV at 560 K. In this compositional region ($<$50 vol%Cu) the probability of conduction by direct tunnelling can probably be neglected because the metal particles are generally too widely separated.

Fig. 6 shows that the activation energy increases exponentially as the insulating content (vol%GeO_2) increases. Thus the probability of conduction via metallic localized states is expected to increase. At higher temperatures the carriers are activated to localized states. Increasing values of activation energy with temperature

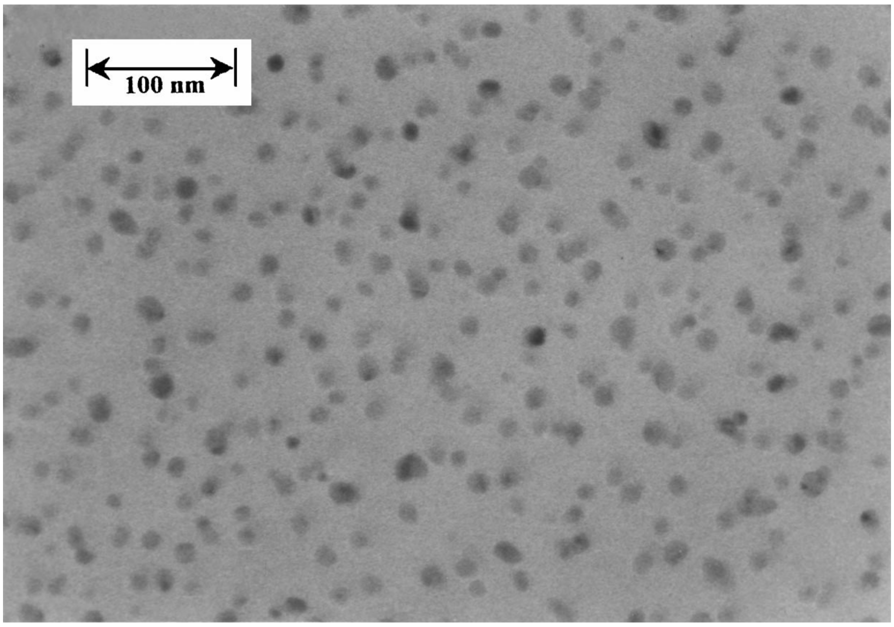

Figure 7 Transmission micrograph of 10 vol%Cu film, 200 nm thick, deposited at a rate of 0.8 nm/s, at a substrate temperature 600 K.

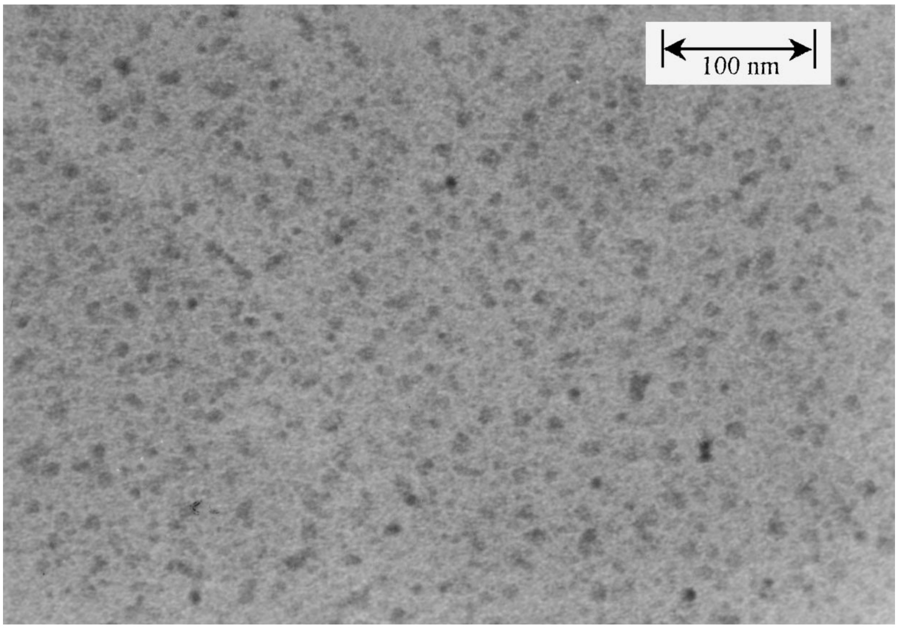

Figure 8 Transmission micrograph of 20 vol%Cu film, 200 nm thick, deposited at a rate of 0.8 nm/s, at a substrate temperature 600 K.

indicate that the conduction process is moving away from states near the Fermi level. The gradual increase in activation energy suggests that there are several impurity levels in the band gap. The increase in E_σ with decrease in metallic concentration that occurs at a given temperature (Table II) may be explained in terms of a decrease in the number of localized states near the Fermi level.

4. Conclusions

The conduction mechanism can be understood by combining optical and conductivity data. According to Devenyi *et al.* [14] when the metal particles are highly dispersed, bands of localized states are expected to appear in the energy band gap of the dielectric matrix. For 0,5 and 10 vol%Cu 150 nm films E_{opt} are 2.65, 2.35 and 1.9 eV respectively [6]. On comparing E_σ with E_{opt}, one can then deduce that E_σ should be less than $\frac{1}{2}E_{\text{opt}}$. This relation suggests that an impurity band created by the incorporation of Cu particles in the GeO_2 matrix must exist in the mobility gap.

Acknowledgements

I am grateful to my supervisor, 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. J. E. MORRIS, *Thin Solid Films* **11** (1972) 299.
2. R. M. HILL and T. J. COUTTS, *ibid.* **42** (1977) 201.
3. C. A. NEUGEBAUER and M. B. WEBB, *Appl. Phys.* **33** (1962) 74.
4. C. A. NEUGEBAUER, *Thin Solid Films* **6** (1970) 443.
5. C. A. HOGARTH and L. A. WRIGHT, in Proceedings of the International. Conference on the Physics of Semiconductors, Moscow (Nauka, Leningrad, 1968) p. 1274.
6. I. B. LUCY, J. BEYNON and D. N. WATERS, *J. Mat. Sci. Lett.* **15** (1996) 515.
7. L. J. VAN DER PAUW, *Philips Res. Repts.* **13** (1958) 1.
8. CRC Handbook of Chemistry and Physics, Editor in chief : David R Lide, 73rd Edition. (1992–1993)
9. C. A. NEUGEBAUER, "Handbook of Thin Film Technology," edited by L. I. Maissel and R. Glang (McGraw-Hill Book Co., New York, USA, 1970) p. 8.
10. I. B. LUCY, PhD thesis, Dept. of Physics, Brunel University, Uxbridge, Middlesex, UK, 1997, p. 79.
11. W. J. OSTRANDER and C. W. LEWIS, *Amer. Vac. Soc. (AVS)* **2** (1961) 881.
12. A. A. MILGRAM and C. S. LU, *J. Appl. Phys.* **39** (1968) 4219.
13. B. ABELES and P. SHENG, "Low Temperature Physics - LT 13," Vol. 3, edited by Timmerhause, O'Sullivan and Hammel (Plenum Press, New York, 1974) p. 578.
14. A. DEVENYI, R. MANAILA and C. RUSU, *Thin Solid Films* **41** (1977) 143.
15. M. R. RAHIM, PhD thesis, Dept. of Physics, Brunel University, Uxbridge, Middlesex, UK, 1993.
16. S. Z. A. ZAIDI, PhD thesis, Dept. of Physics, Brunel University, Uxbridge, Middlesex, UK, 1996.
17. C. B. STEELE and J. BEYNON, *Phys. Stat. Sol. (A)* **106** (1988) 515.
18. M. H. RAHMAN, A. M. AL-SAIE and J. BEYNON, *ibid.* **156** (1996) 397.

Received 6 August 1999
and accepted 7 March 2000