Effect of annealing, film thickness and deposition rate on dc conductivity of co-evaporated Cu-GeO₂ thin cermet films

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dc Conductivity measurements were carried out using van der Pauw four probe technique for 20 vol% Cu films in the temperature range 200-573 K. Increase in conductivity during temperature cycling of as-deposited films was observed and explained as the removal of defects. Annealing and preparing the film at elevated substrate temperature make the dc conductivity reversible on temperature cycling; the latter has an enhanced dc conductivity. The variation of dc conductivity with thickness was consistent with the Neugebauer-Webb model whereas deposition rate variation was explained on the basis of the concept of localized states in the band gap.

1 Introduction

Cermet films, also known as granular metal, have been studied for more than half a century and the many new properties have revealed a continuing interest in such films [1]. The temperature dependence of dc conductivity combined with optical absorption measurements yields valuable information about the transport mechanism in amorphous semiconductors. At low metallic concentration it is widely believed that a multi-component system, such as a cermet film consists of metal islands dispersed through a continuous insulating matrix [1]. These films have a similar structure to a discontinuous metal film with negative temperature coefficient of resistance. 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.

2 Experimental Procedure

Cu-GeO₂ cermet thin films were prepared by the technique of thermal co-evaporation as described by Hogarth and Wright [2] using a Speedivac 19A/122 vacuum coating unit and were deposited on clear Corning 7059 substrates. Molybdenum boats were used for the evaporation of both Cu and GeO₂ and a tungsten spiral for Al electrodes. dc Electrical conductivity was measured using van der Pauw four-probe technique [3]. The samples were circular of diameter 10 mm with four symmetrically placed circles of diameter 2 mm each and were contacted by four rectangular shaped 100 mm thick evaporated aluminium electrodes. An auto-ranging Keithley 617 programmable digital electrometer having input impedance of 200 T ohm was used for all voltage measurements. A power supply unit (Farnell stabilised power supply E350) produced current and a Keithley 485 auto-ranging pico-ammeter was used for current measurement. The film was connected to the current source and the electrometer via four highly polished small copper blocks fixed under the front corners of two pyrophyllite blocks to sit exactly on the contacts. The connections were held in place using a spring loaded screw which passed through the other end of the pyrophyllite block. This type of contact is necessary because at high temperatures the sample could become contaminated if silver conductive paint is applied to the film contacts. It is necessary to measure across different pairs of contacts in order to correct the geometrical effects [4]. This requires the sample current and voltage to be reversed to the sample. For this purpose an external mechanical switching arrangement was used to connect the electrometer, current source and ammeter. The switch-box consists of three switches, one single pole single throw switch (S₁) and two double pole double throw switches (S₂ and S₃). S₁ was used to provide power to the circuit. S₂ altered the direction of the current between contact pairs and S₃ changed the contacts for voltage measure-
LUCY: CU-GeO₂ THIN CERMET FILMS

2.6 mm. The film was placed in the groove of the substrate holder block and the residual pressure was reduced to \(10^{-6}\) Torr. The resistance \(R_{CD,AB}\) was calculated by applying current through contact pair A and B (\(I_{AB}\)) and measuring the voltage developed between contact pair C and D (\(V_{CD}\)). The direction of the current was then reversed from B to A (\(I_{BA}\)) and the voltage developed at contact pair D and C (\(V_{DA}\)) noted. The values of the resistances \(R_{CD,AB}\) and \(R_{DA,BC}\) were determined and averaged. The ratio \(R_{CD,AB}/R_{DA,BC}\) was calculated and the corresponding value of function \(f\) was obtained from the graph. The factor \(f\) was found to be close to unity and remained almost constant with temperature. The resistivity of the sample was calculated as a function of temperature in steps of 5-10 K.

The resistivity of the sample is given by:

\[
\rho = \frac{\pi d}{\ln 2} \left( \frac{R_{CD,AB} + R_{DA,BC}}{2} \right) f
\]

where \(R_{CD,AB} = V_{CD}/I_{AB}\) and \(R_{DA,BC} = V_{DA}/I_{BC}\), and \(V_{CD}\) and \(V_{DA}\) are the measured voltages between contacts C and D, and D and A, respectively, and \(I_{AB}\) and \(I_{BC}\) are the corresponding currents flowing via contacts A and B, and B and C, respectively. The thickness of the sample is \(d\), and \(f\) is a geometrical correction factor which depends upon the ratio of \(R_{CD,AB}\) and \(R_{DA,BC}\) only. The factor \(f\) is given by:

\[
R_{CD,AB} - R_{DA,BC} = f \frac{\exp (\ln 2/f)}{R_{CD,AB} + R_{DA,BC}} \ln 2
\]

3 Results and Discussion

3.1 Temperature cycling

The variation of dc conductivity with temperature (200-573K) during the heating and cooling cycles for as-deposited samples of 20 vol% Cu is shown in Fig. 1. The graph shows an irreversible change to higher conductivity values occurred during the first heating and cooling cycles. During the second heating and cooling cycles further irreversible increases in conductivity occurred. A stable conductivity was obtained after the third/fourth temperature cycle.

The increase in conductivity during temperature cycling can be explained as follows: some structural defects, such as voids, vacancies, grain boundaries and dislocations produced during co-evaporation of the films, are partially annealed out during repeated temperature cycling; scattering of electrons at grain boundaries decreases; coalescence of islands occurs and continuous/semi-continuous metal bridges may form between metal particles. Some additional metallic oxide phase, e.g. CuO may also form.

The grain size in vacuum-deposited thin films depends on the deposition parameters. The average grain
size in thin films is smaller than in bulk materials, hence thin films have a larger grain boundary surface area. If the grain size is smaller than the mean free path for electrons, internal diffuse scattering at the surface area will reduce the conductivity. Large grain sizes are obtained on depositing the films at elevated temperatures, because of an increase in surface mobility, as confirmed by transmission electron microscopy. This allows the total energy of the film to decrease by reducing the grain boundary surface area\(^7\), thus leading to a more stable configuration of the film.

3.2 Annealing

The effect of annealing was investigated by raising the temperature of the as-deposited film to 573 K and maintaining this temperature for 5 h in vacuum. Fig. 2 shows how the conductivity increases with time at 573 K. It has been observed that the dc conductivity is reversible after annealing.

Vand\(^8\) explained that the decay of structural defects, such as vacancies and interstitials incorporated during evaporation of metallic thin films in vacuum, especially at low substrate temperatures, are responsible for the irreversible changes occurring during the heating and cooling cycles. In order to obtain a reversible change in conductivity, a critical energy is required for interstitial atoms and lattice vacancies to combine. This energy is available in the film at a sufficiently high annealing temperature.

3.3 Elevated substrate temperature during deposition

To observe the effect of elevating the substrate temperature during deposition, a film containing 20 vol% Cu was prepared at 600 K. The conductivity was found to be reversible from the beginning of the temperature cycles but the values were higher by a factor of 10-15 over those obtained after annealing samples of the same composition.

At an elevated temperature, deposited particles have a higher probability of reaching preferable lattice sites than at room temperature. The disordered structure is unable to rearrange itself quickly on annealing as it does during deposition at an elevated temperature because it is already locked into an amorphous structure. Thus films deposited at higher temperatures have fewer defects incorporated into them than post-annealed films made at room temperature. Thus films prepared at elevated temperatures are expected to have an enhanced dc conductivity.

3.4 Effect of thickness

Fig. 3 shows graphs of natural logarithm of dc conductivity versus inverse temperature for 20 vol% Cu films of three different thicknesses. These films were deposited at 600 K at a rate of 1 nm/s. It can be seen that the conductivity increases as thickness increases. The temperature-dependent activation energy \(E_a\) is defined as

\[
E_a(T) = -k \left(1/dn\sigma/1d(1/T)\right)
\]

![Graph showing the effect of annealing on dc conductivity](image)
and can be calculated from the local gradients of In $\sigma$ versus $1/T$ graphs. Fig. 3 also shows 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 $E_\alpha$, such as $\sigma = \sigma_0 \exp (-E_\alpha / kT)$ since the slope of In $\sigma$ versus $1/T$ graphs are changing gradually with changing temperature. In the present work all the graphs fit second order polynomials such as $E_\alpha = 3A/T + 2B/T + C$

Thus dc conductivity fits the expression

$$\sigma(T) = \sigma_0 \exp \left\{ - \left( A/kT^3 + B/kT^2 + C/kT \right) \right\}$$

where $A$, $B$ and $C$ are constants.

Fig. 4 shows that the dc conductivity decreases with increasing thickness. The variation of $E_\alpha$ with thickness can be explained using the Neugebauer-Webb model in which it is assumed that the activation energy is proportional to the reciprocal of the average linear dimension ($r$) of a Cu particle. Neglecting distant-site contributions and assuming that charge transport occurs between nearest spatial neighbours, $E_\alpha$ is proportional to $e^2/r$. In the present case, thermally-activated conduction is assumed to take place between two Cu islands separated by a space filled with GeO$_2$. As the film thickness increases the inter-island separation decreases whilst the island size increases, leading to smaller activation energies. This same trend in activation energy with thickness was observed by Rahman$^{10}$ with electron-beam evaporated Cu-GeO$_2$ films and by Neugebauer and Webb$^8$ with Pt films. So the thickness variation of dc conductivity of co-evaporated and electron-beam evaporated Cu-GeO$_2$ film shows good agreement.

3.5 Effect of deposition rate

To observe the effect of deposition rate, Cu-GeO$_2$ films of 200 nm thickness and of different rates were prepared at a substrate temperature of 600 K. Fig. 5 shows that the dc conductivity increases with increasing deposition rate. Fig. 6 demonstrates that dc activation energy is a decreasing function of deposition rate for 20 vol% Cu film, 200 nm thick.

An increasingly amorphous structure is expected to occur with increase in deposition rate because the deposited particles have insufficient time to move toward preferred lattice sites. This, in turn, increases the localized state density and band tailing in the band gap. Thus

![Fig. 3 — Variation of natural logarithm of dc conductivity with inverse temperature for various thicknesses of 20 vol% Cu films.](image)
dc conductivity may be expected to be higher at higher deposition rates. Increasing values of dc conductivity with increasing deposition rate were also observed by Beyer and Stuke\textsuperscript{31} with amorphous Ge and by Schepis \textit{et al.}\textsuperscript{22} with Fe films. From optical measurements\textsuperscript{9} it is observed that $E_{\text{opt}}$ decreases, and band tailing increases.
with increasing deposition rate. Increasing values of activation energy with decreasing deposition rate also indicate that the conduction is moving away from the Fermi level as the localized states are decreasing at lower deposition rates.

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References
2 Khan M I. Studies of the electrical and structural properties of some thin oxide films, PhD Thesis, Physics Department, Brunel University, UK. (1976).
19 Lucy I B. Electrical and optical properties of Cu-GeO thin solid films prepared by vacuum co-evaporation, PhD thesis, Department of Physics, Brunel University, UK. (1995) 125.