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Conduction mechanisms in Cu–GeO_2 thin cermet films

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

Much research has been carried out on metallic, semiconducting, insulating, and cermet thin films. Among these cermet films have been studied for more than half a century [1–8] and the many new properties revealed have led to a continuing interest in such films. Compared with pure metallic films, thin cermet films display some interesting electrical properties. These include a widely varying resistivity and temperature coefficient as a function of composition, and high stability when exposed to normal atmospheric conditions. The presence of dielectric provides a considerable degree of passivation and temperature stability. Cu–GeO_2 films are not strictly cermets because they do not consist of two discrete phases throughout the whole composition range; CuO may also be present [5].

Electrical characterizations were studied of cermet films with various metal and dielectric compositions such as Cu–GeO_2 [2], Mn–SiO [4], Cu–SiO_x [6], and Au–SiO_2 [7], which were prepared by various deposition techniques. The characteristics of the films depend strongly on the technique employed and the deposition parameters: film thickness, substrate temperature, deposition rate, and residual pressure. Various techniques have been used: thermal evaporation, sputtering, electron beam evaporation, etc.; the coevaporation technique has been used for preparing Cu–GeO_2 for the present investigation. It has the advantage over single boat evaporation in that deposition parameters can be closely controlled and as a result film properties are more reproducible.

Rahman [9] obtained results on Cu–GeO_2 prepared by electron beam evaporation. The investigations include optical absorption, dc and ac conductivity, and Hall effect. No work was carried out on thermoelectric properties of thermally evaporated Cu–GeO_2 cermet films. Hall effect and thermoelectric power give an independent measurement of the nature of the charge carriers and together with direct current (d.c.) conductivity allow the conduction mechanisms operative in the films to be investigated. According to Mott and Davis [10] the sign of 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 techniques for obtaining thermoelectric power data: the integral and differential [11]. A characteristic of the integral technique is that one junction is maintained at constant temperature while the temperature of the other is varied. It also allows samples of extended length (∼3 to 5 cm) to be used. However as the length of the sample increases the resistance also increases. This problem was overcome using an electrometer whose input impedance is 10^3 times higher than the highest sample resistance investigated. This paper deals with the results of thermoelectric power measurements on coevaporated Cu–GeO_2cermet films containing 30 and 40 vol% Cu. Combining with d.c. conductivity results [15], the band structures were also proposed.

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 coevaporation 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). 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. 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 variance before taking the data. No noise was recorded on switching the heater on or off. The basic dimension of the sample was 3 cm × 0.7 cm. Fig. 1 shows the appearance of the structure onto the substrate. To obtain 200-nm-thick 30 vol% Cu film, 60 nm of Cu was mixed with 140 nm of GeO_2 by controlling the deposition rates of the sources.

The thermoelectric power, S, was measured *in vacuo* in the temperature range 300–600 K on planar samples of 30 and 40 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

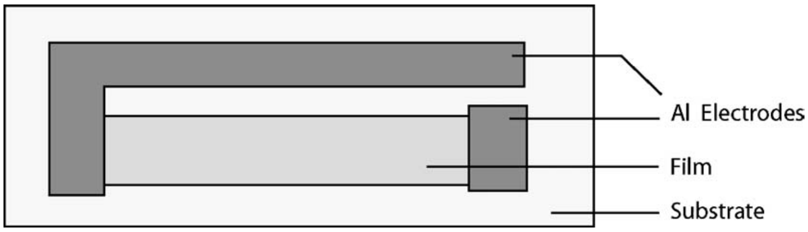

Figure 1 Evaporated planar device on substrate for thermoelectric power measurements.

T produced by Cu–GeO$_2$ and Al contact films. S_{Al} is -40 nVK^{-1} [12], which is negligibly small compared to S_{film}. Hence

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

The thermoelectric power of the sample was calculated by fitting polynomials to the measured Seebeck voltage data points and then taking slopes at various hot junction temperatures. The samples were prepared at 600 K at a rate of 0.8 nm/s and were 200 nm thick.

Fig. 2 shows the variation of Seebeck voltage with temperature for 30 and 40 vol% Cu. In Figs 3 and 4, thermoelectric power vs. temperature are plotted for 30 and 40 vol% Cu, respectively. The samples in this investigation can be divided into two temperature regions.

Region-1 For temperatures 300–430 K for 30 vol% Cu and 300–400 K for 40 vol% Cu.

It may be seen that the thermoelectric power in this region decreases slowly with increasing temperature up to 430 K (Fig. 3) and 400 K (Fig. 4), respectively, before increasing again above it. According to Buchy *et al.* [13], a positive thermoelectric power that decreases with increasing temperature suggests that a valence band transport mechanism is taking place via p-type carriers. The thermoelectric power has the general form

$$S = \frac{k}{e}\left[\frac{E_{\text{F}} - E_{\text{V}}}{kT} + f(T)\right]$$

where E_{F} is Fermi energy, k is Boltzmann's constant, e is the electronic charge, T is the absolute temperature, and E_{V} is assumed to be the mobility shoulder energy. The exact form of $f(T)$ is unknown, but following Buchy *et al.* [13], it is assumed to be a slowly varying function of T. Mott and Davis [10] state that in amorphous semiconductors $f(T)$ only makes a small

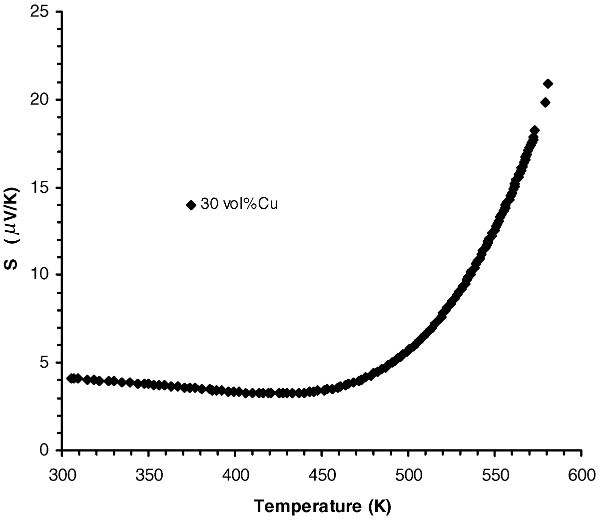

Figure 3 Thermoelectric power vs. temperature for 30 vol% Cu.

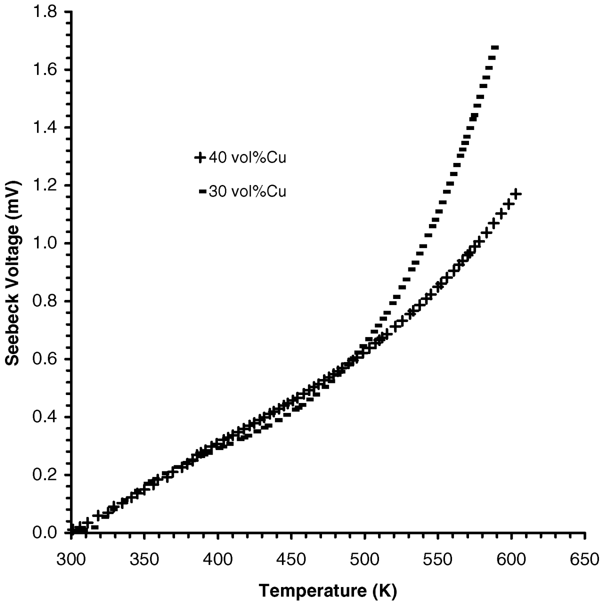

Figure 2 Seebeck voltage vs. temperature for 30 and 40 vol% Cu.

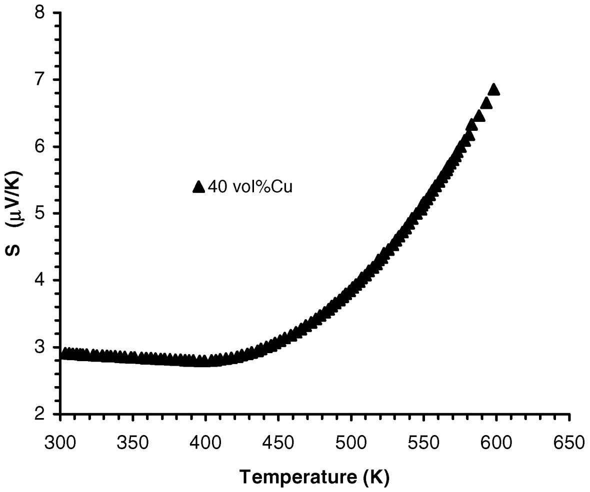

Figure 4 Thermoelectric power vs. temperature for 40 vol% Cu.

TABLE I Values of d.c. activation energy (E_σ) [15] and thermoelectric power activation energy (E_s) for 30 and 40 vol% Cu samples

Vol% Cu	Temperature (K)	E_σ (meV)	E_s (meV)
30	300–430	83–122	1.02
40	300–400	54–75	0.14

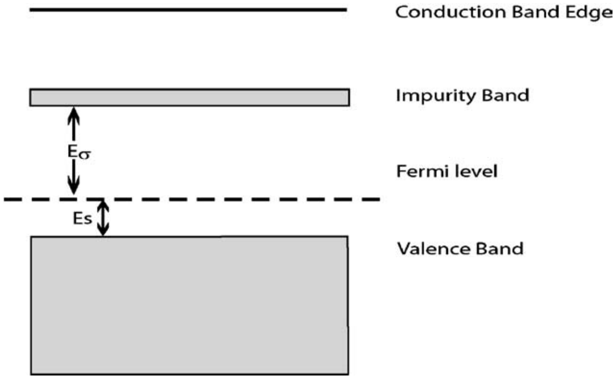

Figure 5 Proposed band diagram for samples in region-1.

contribution to S. Thus Figs 3 and 4 suggest that holes in the valence band are the dominant charge carriers between 300 and 430 K and 300 and 400 K for 30 and 40 vol% Cu samples, respectively. In this lower temperature region where the thermoelectric power is activated, the activation energy was calculated using the relation

$$E_s = \frac{dS}{d(1/T)}$$

Values of E_s are listed in Table I. A comparison of the experimental thermoelectric power activation energy E_s with d.c. conductivity activation energy E_σ below 430 K (for 30 vol% Cu) and 400 K (for 40 vol% Cu) indicates that $E_s \ll E_\sigma$. This suggests that the charge carriers are probably small polarons [10]. The band structure for 30 and 40 vol% Cu in this region is shown in Fig. 5.

Region-2 For temperatures 430–600 K for 30 vol% Cu and 400–600 K for 40 vol% Cu.

In this region the thermoelectric power shows metallic-like behavior. The thermoelectric power is nonlinear with values much higher than higher metallic content films [14]. In this region d.c. conductivity is activated [15], whereas thermoelectric power is nonactivated.

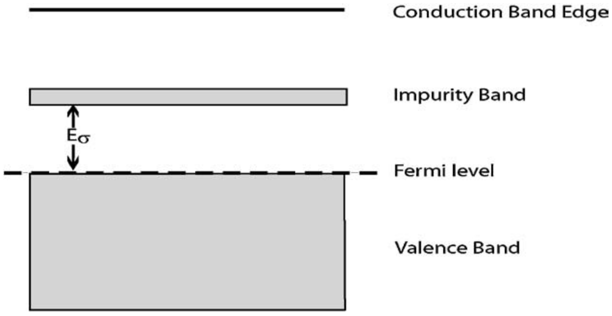

Figure 6 Proposed band diagram for samples in region-2.

The band structure for 30 and 40 vol% Cu in this region is shown in Fig. 6.

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