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THE VARIATION OF ELECTRICAL CONDUCTIVITY WITH TEMPERATURE FOR Cu-DOPED ZnS ALLOY

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ABSTRACT

The variation of the electrical conductivity of copper (Cu) – doped zinc sulphide (ZnS) alloy with temperature has been investigated. The electrical conductivity of the samples increases with temperature and obeys the Arrhenius relation, $\sigma = \sigma_0 \exp(-E_g/2kT)$ which is characteristic of semiconductors. The energy gaps determined from this empirical relation are 3.91, 3.82, 3.74, 3.60 and 3.58 eV for the various samples. The result shows that the energy gaps of the samples decrease with increase in the incorporation of Cu in the intrinsic ZnS. The narrowing of the band gaps facilitates the ease of electronic transition from the valence band to the conduction band thereby enhancing the conductivity of the samples. All the samples investigated are characterized by wide band gaps which make them invaluable for the fabrication of optoelectronic devices that utilize wide band gap materials.

KEYWORDS: Electrical conductivity, temperature, zinc sulphide copper, energy gap.

INTRODUCTION

The properties of the materials used for the fabrication of semiconductor devices are essential in determining the characteristic of the completed devices. The value of conductivity is important in many devices. Hence, the electron transport property of thin films may be characterized by the conductivity of the film. Therefore, a study of the temperature dependence of the conductivity is essential in the understanding of the carrier-scattering mechanism responsible for the transport property. Furthermore, the present study was undertaken to find out the effect of varying temperatures on the electrical conductivity of Cu-doped ZnS samples in order to determine their suitability for the fabrication of semiconductor devices.

Zinc sulphide is of considerable interest because of its application in optoelectronic devices such as electroluminescence or light emitting diodes (Hiroshi and Koji 1985; Masakazu et al 1985; Richard and Frank 1985; Fernandez and Sebastian 1993). Some of the properties which make it an attractive material for optoelectronic device applications are its direct band gap and it is transparent over a wide range of the visible spectrum (Berg and Dean 1976; Thomas 1981; Koppensteiner et al 1993). Also, ZnS is used in the production of fluorescent and luminous paints (Berg and Dean 1976). Furthermore, it is a prospective material for the passivation of the surfaces of some semiconductors and for the modulation of optoelectronic device (Osasona et al 1997). In addition, it can be used as a cathodoluminescent material for coating the screens of cathode ray tubes (Berg and Dean 1976; Sybil 1982). The present work was therefore partly inspired by these applications and the need to search for more applications for ZnS and Cu-doped ZnS.

Copper is an important impurity in wide band gap zinc chalcogenides. In ZnS and ZnSe, the incorporation of copper results in a variety of characteristic visible bands (Stringfellow and Bube 1968; Satoh and Igaki 1983). However, there is a long-standing uncertainty about the role of copper in the afore-mentioned materials. Hence, there is need to develop new experimental techniques for incorporating copper into zinc chalcogenides in order to provide additional information on the behaviour of this important impurity. It is necessary to gain a clear understanding of the effect of incorporating copper in ZnS on the electrical conductivity of ZnS.

MATERIALS AND METHODS

a. **Compounding of the Cu-doped ZnS alloy.**

The materials used in this investigation were 99.99% pure copper II nitrate trihydrate ($Cu/NO_3)_2 . 3H_2O$) and zinc sulphide (ZnS) powder obtained from the British Drug House (BDH). 5 ml of different concentrations of aqueous solution of $Cu(NO_3)_2 . 3H_2O$ were prepared and added drop by drop to 100ml of ZnS suspension prepared in four different beakers and the stoichiometric composition of the samples is presented in Table 1.

Thereafter, the mixture was stirred continuously and precipitates were formed. The precipitates obtained were then filtered and air-dried overnight. The samples were later annealed in a stream of argon gas at a temperature of 300^{0}C for 5 hours and at an argon flow rate of 20ml min^{-1}. After the annealing, the samples were cooled in an argon gas at room temperature.

Subsequently, they were crushed with a mortar and pestle and sieved through a mesh to obtain fine ground powders. Then thin pellets of the samples were formed from the finely ground powders of the synthesized materials by powder compression method using a vacuum pump aided powder presser. The pellets were then sintered at a temperature of 300^{0}C for 4 hours in an electric furnace to correct the imperfections that might have resulted from voids in the materials. The prepared pellet has a diameter of 10mm and thickness of 0.38mm. Silver paste was used to make contacts on the samples.

b. **Investigation of the variation of Electrical Conductivity with Temperature.**

Each sample with contacts was inserted in a thin walled test tube. The lower part of the test tube was immersed in a lagged heatable water bath. The water bath was maintained at the desired temperature with the aid of a temperature controller, while uniformity of temperature was ensured with the aid of a magnetic stirrer immersed in the bath. The insulated electrical leads from the contacts were taken out of the test tube via ports which were vacuum sealed with araldite. They were connected to a digital electrometer (Keithley 160B) and a digital millivoltmeter (Hewlett – Packard 3465A) which measured the current and voltage respectively. The actual sample temperature and that of the water bath were determined with copper – constantan thermocouples whose cold junctions were maintained at 0^{0}C. Effective

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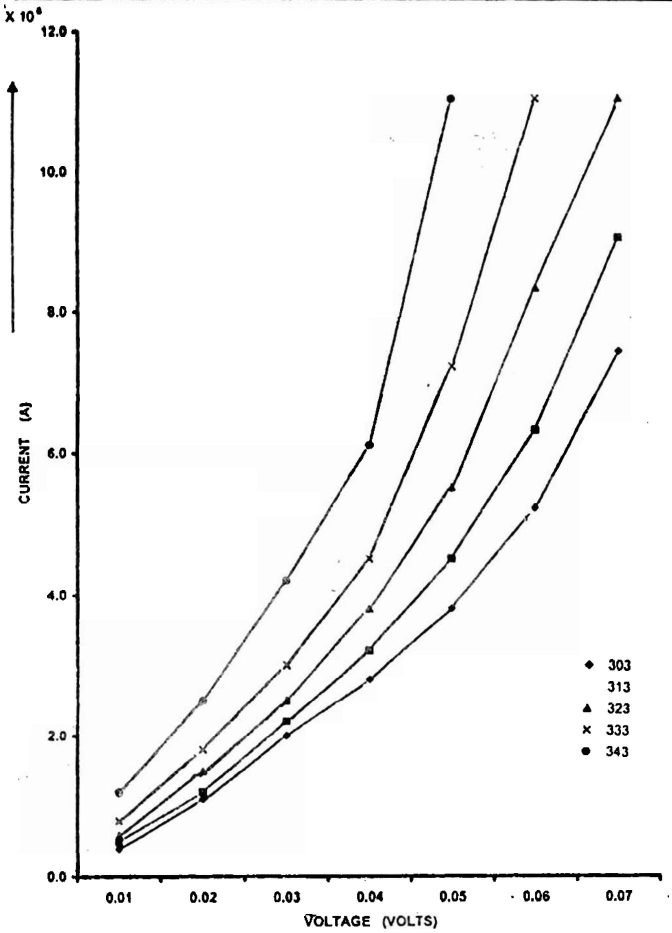

Fig. 1. I – V characteristics of pure ZnS at various temperatures.

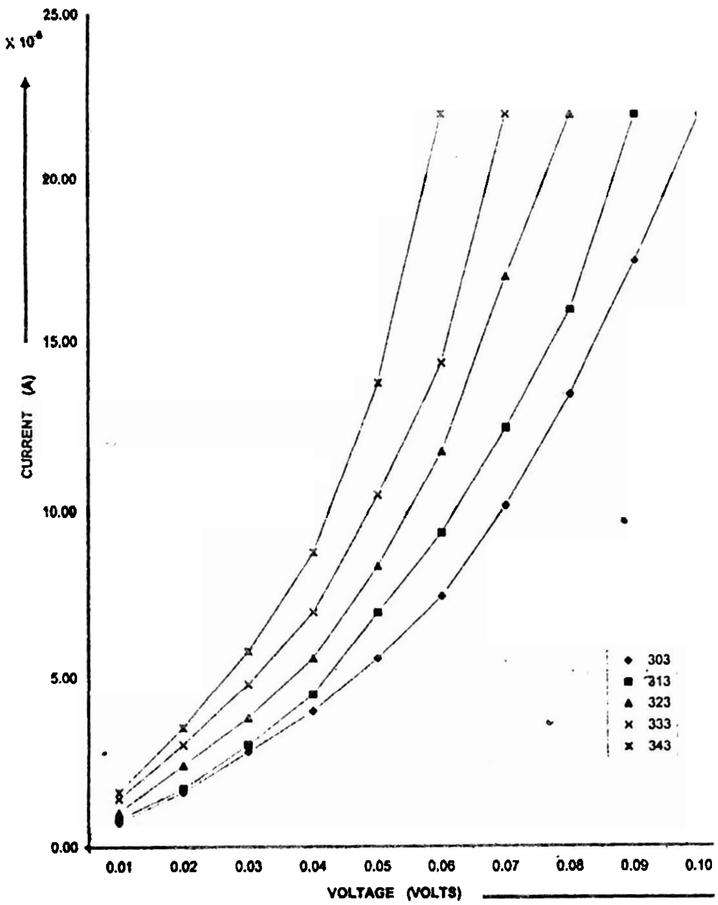

Fig. 2. I–V characteristics of Cu-doped ZnS at various temperatures for sample A

temperature control was achieved by connecting both the sample thermocouple and the heater leads to the temperature controller. All the measurements were carried out at a number of temperatures between 303 and 343K.

At any desired temperature, the currents were measured by varying the voltage from 0.01 to 0.10V. From the current – voltage (I-V) data, the electrical conductivity of the sample was determined. This process was repeated for the various samples.

c. **Determination of the carrier type of Cu-doped ZnS sample with the Hot Probe Method.**

The surface of each sample was touched by two identical metal probes between which a galvanometer was connected. One of the probes was heated while the other was at room temperature. Thereafter, the galvanometer was observed for the direction of current flow which determined the type of carrier.

RESULTS AND DISCUSSION.

The result of measurements of the current – voltage characteristics of the Cu-doped ZnS samples at various temperatures are summarized in Figures 1 to 5. The I – V characteristics of the samples obey the following relation given by Bethe (1942), Henisch (1957), Padovani and Stratton (1966), Krupanidhi et al (1983):

$$I = I_s \exp\left(\frac{qV}{nkT} - 1\right) \qquad (1)$$

Where

$$I_s = A^{**}ST^2 \exp \frac{\quad}{kT}$$

I_s is the saturation current
A^{**} is the effective Richardson's constant.
k is the Boltzmann constant.
S is the area of the contact.
T is the temperature.
Φ_b is the barrier height of the contact.
q is the electronic charge.
V is the applied voltage and
n is the ideality factor of the contact.

Table 1: Stoichiometric composition of the various samples of Cu-doped ZnS alloy.

Sample	Mole fraction of $Cu(NO_3)_2\ 3H_2O$
Pure ZnS	0.00
A	0.05
B	0.10
C	0.20
D	0.40

Table 2: The Energy Gaps of pure ZnS and the various samples of Cu-doped ZnS.

Sample	Energy Gap (eV)
Pure ZnS	3.91
A	3.82
B	3.74
C	3.60
D	3.58

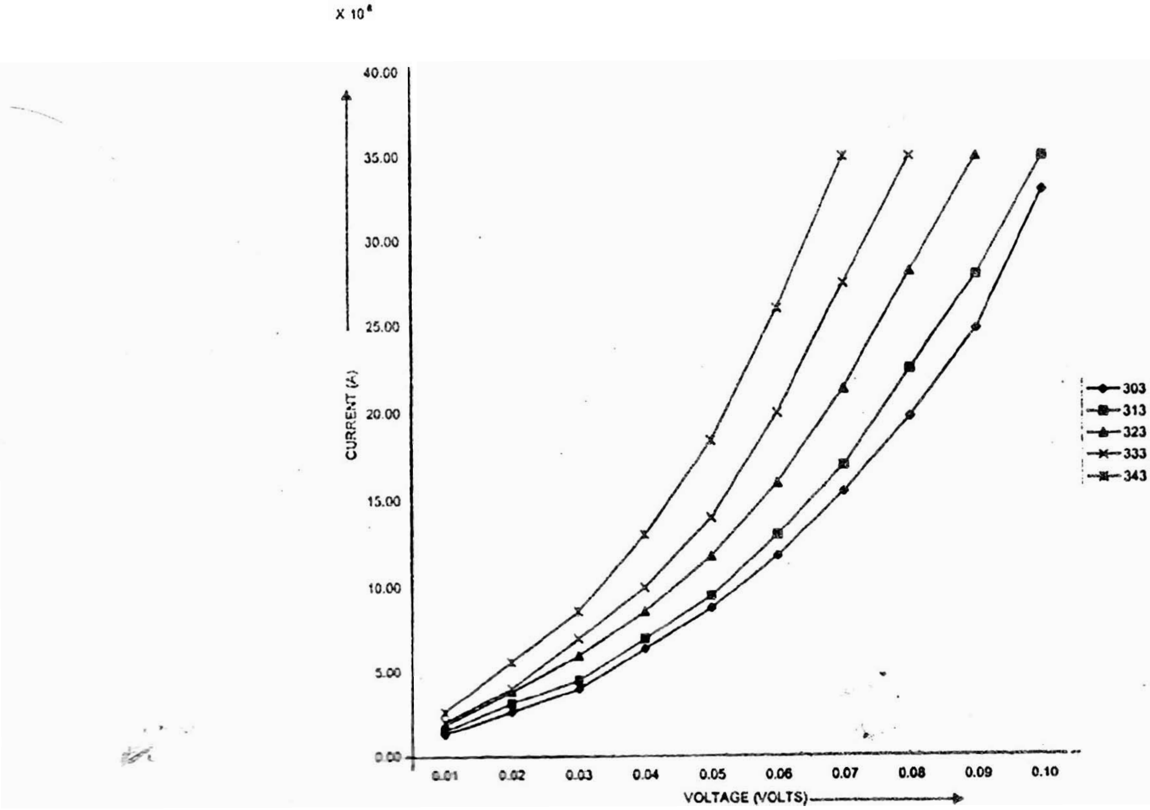

Fig. 3. I–V characteristics of Cu-doped ZnS at various temperatures for sample B

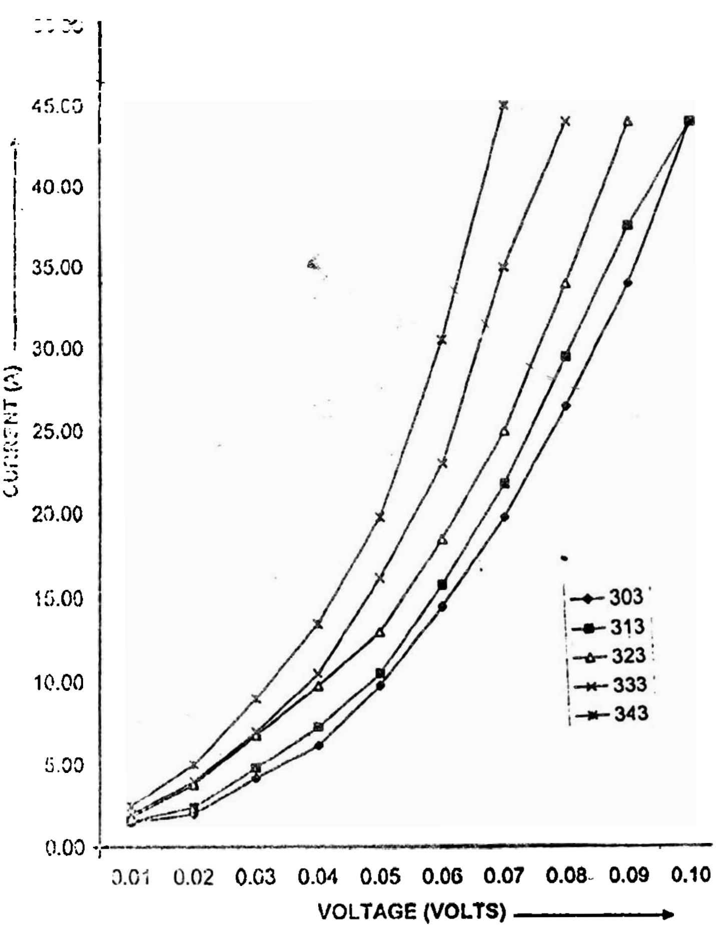

Fig. 4. I–V characteristics of Cu-doped ZnS at various temperatures for sample C

The figures show that current increases with temperature. A higher temperatures there is sufficient thermal activation fo some electrons to be excited from the valence band to the conduction band and consequently leading to an increase ir current.

Figure 6 shows the variation log of conductivity (ln σ of .he sample with inverse of temperature (1/T). This plo displays a linear variation between ln σ and 1/T, indicating tha the different plots obey the Arrhenius relation:

$$\sigma = \sigma_0 \exp(-E_g/2kT) \quad (2)$$

(Thornton and Colangelo 1985).

Where,

σ_0 = proportionality constant.
E_g = energy gap
k = Boltzmann constant and
T = temperature.

This type of variation could result in case of semiconductors o ionic solids. The energy gap was determined from the slopes of these plots using equation 2 and the values for the various samples are presented in Table 2. From Table 2, it is observed that the energy gap of each sample decreases with increase in dopant concentration due to the strong interactions either among the introduced Cu impurities themselves or with the host lattice atoms which broaden the discrete impurity levels into a band and the band tail gradually moves into the energy gap, resulting in the narrowing of the band gap of the sample under investigation. This facilitates the ease of electronic transition from the valence band to the conduction band leading to an improvement in the conductivity of the material.

In the course of the determination of the carrier type of the Cu-doped ZnS samples with the hot probe method, the hot probe heats the samples immediately under it, with a

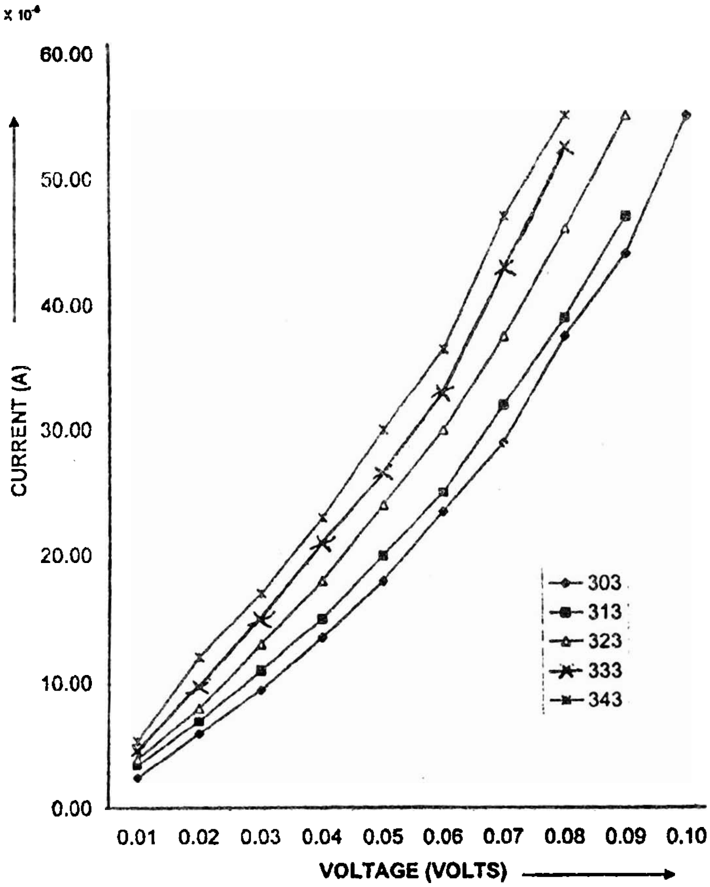

Fig. 5. I–V characteristics of Cu-doped ZnS at various temperatures for sample D

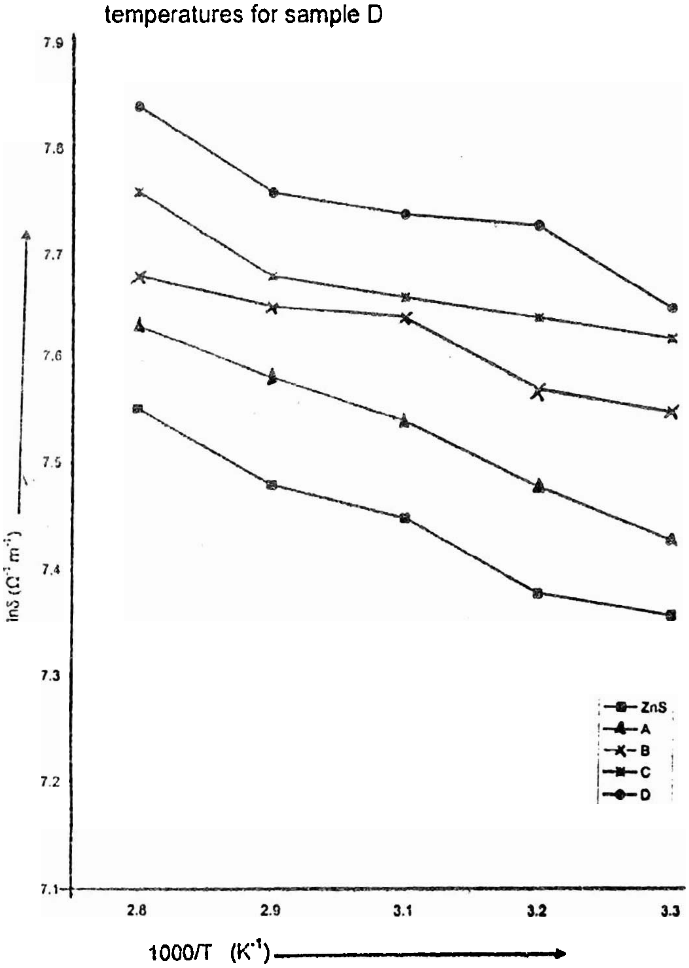

Fig. 6. ln σ versus 1/T for pure ZnS and the various samples of Cu-doped ZnS.

consequent rise in the kinetic energy of the free carriers there. These then move with higher velocities than their cooler neighbours. Therefore, the majority carriers at the hot probe diffuse out to the cold probe. This results in the hot region becoming slightly depleted of majority carriers and acquiring the potential of the ionized impurities there while the vicinity of the cold probe remains neutral. Current flows in the galvanometer, the direction of which depends on the sign of the charge of the ionized impurity. Since the hot probe was more negative with respect to the cold probe, it shows that the sample investigated behaves like a p – type semiconductor (Bar-Lev 1993).

CONCLUSIONS

The results obtained from this investigation show that:

1. The electrical conductivity of the Cu-doped ZnS alloy increases with temperature and obeys the Arrhenius relation,

$$\sigma = \sigma_0 \exp(-E_g/2kT)$$

which is characteristic of semiconductors.

2. The gradual decrease in the band gaps of intrinsic ZnS as a result of the incorporation of copper, facilitates the ease of electronic transition from the valence band to the conduction band which consequently enhances the conductivity of the material.
3. All the samples investigated are characterized by wide band gaps which make them attractive for the fabrication of optoelectronic devices.

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