

STRUCTURAL AND ELECTRICAL CONDUCTIVITY STUDIES OF POLYCRYSTALLINE COPPER SELENIDE AT LOW TEMPERATURE

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ABSTRACT

This paper reports the structural and electrical conductivity characterization of the copper selenide (CuSe) metal chalcogenide semiconductor in bulk form. In situ X-ray powder diffraction analysis of CuSe at low temperature (100 – 300 K) is studied to support the electrical conductivity analysis. The electrical conductivity of the polycrystalline CuSe was measured and analyzed at low temperature (100 to 286 K) using 4 point probe technique. The electrical conductivity values obtained were in the range of 1.69×10^3 to 2.58×10^3 S/cm.

INTRODUCTION

Metal chalcogenide compounds having semiconductor structure are important materials for electronics and electro-optical devices. They show continuous change of physical properties with the change in chemical composition [1]. Copper selenide (CuSe) is a metal chalcogenide semiconductor with various applications in solar cells, super ionic conductors, photo-detectors, photovoltaic cells and Shottky-diodes [2, 3]. The attraction of copper selenide also lies in the feasibility of producing ternary material, CuInSe₂ by incorporating indium into this binary compound [4]. Copper selenide is a metal chalcogenide semiconductor with a wide range of stoichiometric compositions (CuSe, Cu₂Se, Cu₃Se₂, Cu₇Se₄, Cu₅Se₄, Cu₂Se) and non-stoichiometric composition (Cu_{2-x}Se) [4, 5]. Cu_{2-x}Se or Cu₂Se are treated as copper (I) selenide and CuSe, Cu₃Se₂ and CuSe₂ are treated as copper (II) selenide [6-8]. Copper (II) selenide in Cu₃Se₂ form is often reported as an impurity phase along with CuSe [3, 7]. The copper selenide exists in various crystallographic forms even at room temperature. This includes orthorhombic, monoclinic [9], cubic [6, 10], tetragonal and hexagonal [9, 11] forms, depending on the method of preparation.

In this study we investigated the structural and electrical conductivity studies of the polycrystalline copper selenide at temperature ranging from 100K to 286 K using X-ray diffraction (XRD) and four point probe technique respectively. The clarification of the

electrical properties of the copper selenide is important in the context of their use as precursor materials for forming CuInSe₂ thin films, and other multinary materials for thin film solar cell application [12, 13].

EXPERIMENTAL METHOD

Copper (II) Selenide 99.5% metal basis powder supplied by Alfa Aesar were used as received without any further purification or drying. The powder were characterized by X-ray power diffraction, XRD (Philips X'pert PRO PW3040) using Cu K α ($\lambda = 1.5418$ Å) radiation. A scan rate of 0.005°/s was used to record the pattern in the 2 θ range of 20° - 60°. The low temperature camera system TTK 450 allows in situ temperature studies by XRD at temperatures from 100K -300K. The low temperature measurements were made under vacuum. The diffraction patterns were then compared to the patterns found in the JCPDS index.

The electrical properties of the sample under study were measured by a standard collinear four point probe technique. The measurements were made on pressed pellets which was prepared by pressing CuSe powders in a 8mm diameter mould using a hydraulic press (SPECAC USA, model 15011) at 3 ton pressure. Thickness of pellet was measured with a digital micrometer. Currents were applied to the pellets using a source measure unit (Keithley 236) and the resulting potentials measured using a voltmeter (Picotest, M3500A) with the accuracy of ± 0.001 mV. The resistivity of the semi-infinite volume sample can be obtained through expression [14]

$$\rho_o = 2\pi s \frac{V}{I} \quad (1)$$

where s is the spacing of the probe in cm, I is the test current, and V is the measured voltage. The equation (1) indicates the measured value of the resistivity is equal to the actual value, ρ , only if the sample is of semi-infinite volume. Practical samples usually are of finite size, where the sample thickness, L is $\leq 5s$. Hence, the correction factors derived by Valdes [14] as shown in equation (2) is consider.

$$G_7\left(\frac{L}{s}\right) = 1 + 4 \frac{s}{L} \sum_{n=1}^{n=\infty} \left(\frac{1}{\sqrt{\left(\frac{s}{L}\right)^2 + (2n)^2}} - \frac{1}{\sqrt{\left(2\frac{s}{L}\right)^2 + (2n)^2}} \right) \quad (2)$$

Thus the surface resistivity of the CuSe can be calculated using the expression $\rho = \rho_o/G_7(L/s)$ [14] and the surface conductivity, σ was calculated from $\sigma = 1/\rho$.

For low temperature measurement, cryostat system (Cryogenics, NVT-152-DOT) was used to place the sample at specified measurement temperature. The temperature was controlled by auto tuning temperature controller (LakeShore 321). The pressure in the chamber was reduced to $\approx 10^{-3}$ torr by using a rotary vane pump.

RESULTS AND DISCUSSION

Figure 1 shows the in-situ low temperature x-ray diffraction analysis for CuSe powder. All the peaks obtained for CuSe from 100 K to 300 K are well matched with the Joint Committee on Powder Diffraction Standards (JCPDS) data (File No. 49-1457) as copper selenium, which belongs to the hexagonal system. Figure 2 shows the I–V curves for CuSe sample measured at 100 K. The sample exhibits a linear I–V behavior for both forward and reverse bias condition. The slope of the curve provides the resistance value which is used to calculate the surface conductivity of the sample.

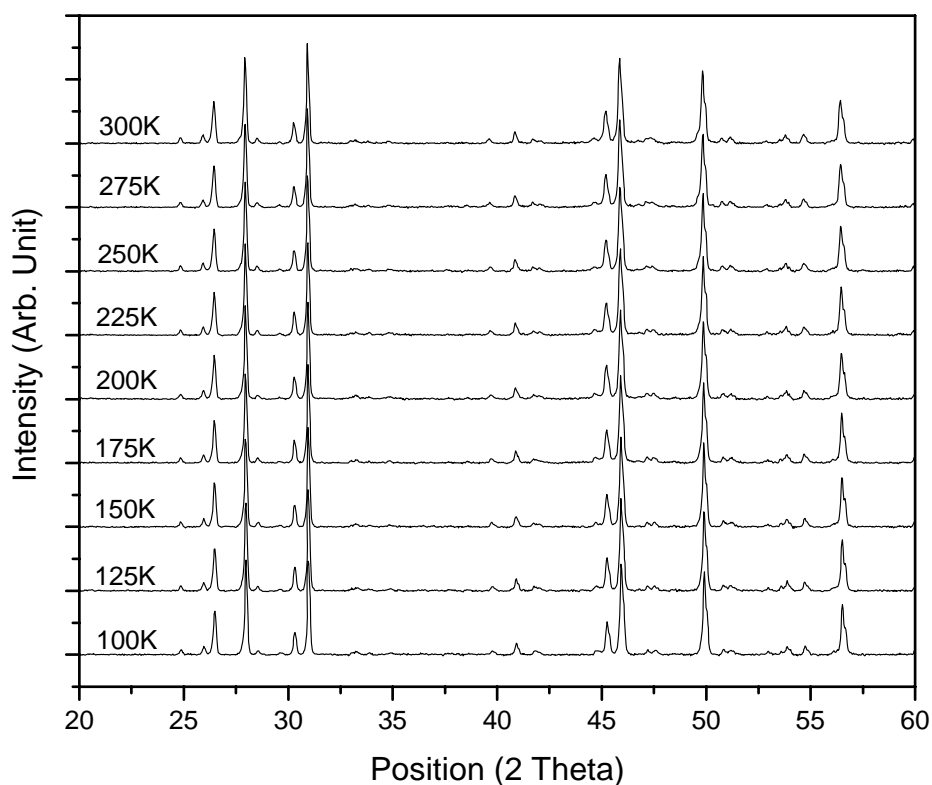


Figure 1: In-situ XRD pattern of CuSe powder at 100 K – 300 K.

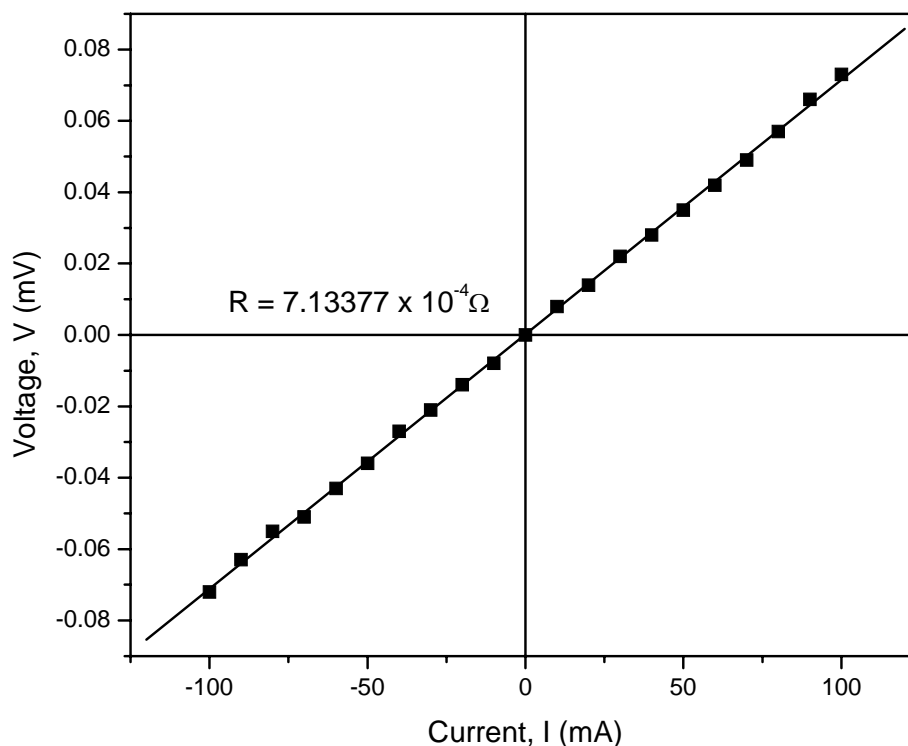


Figure 2: I-V characteristic for CuSe sample at 100 K

Figure 3 shows the variation of DC electrical conductivity as a function of temperature for CuSe in bulk form with sample thickness of 0.1653 cm. The measured surface conductivity values of CuSe were in the range of 1.69×10^3 to 2.58×10^3 S/cm.

From Figure 3, it was observed that the variation of the surface conductivity with temperature for CuSe sample shows the pattern of an extrinsic semiconductor. The variation of surface conductivity with temperature can be divided into two distinct temperature zones with two characteristic regions. At region I which started from 100K up to 220K, all the impurity atoms are ionized, but the intrinsic carrier is not yet excited to a marked degree and therefore the density of carriers remains approximately constant and equal to the impurity concentration. Since the conductivity is dependent on the number of carriers per unit volume, n , carrier charge, q as well as the carrier mobility, μ , $\sigma = nq\mu$, the reduction of the surface conductivity is directly related to the carrier mobility since the n and q are constant in this region. The main scattering mechanism caused by thermal vibrations of the lattice reduced the carrier mobility with rising temperature, and subsequently reduced the surface conductivity value [15]. This situation is exactly shown in Figure 3 at region I.

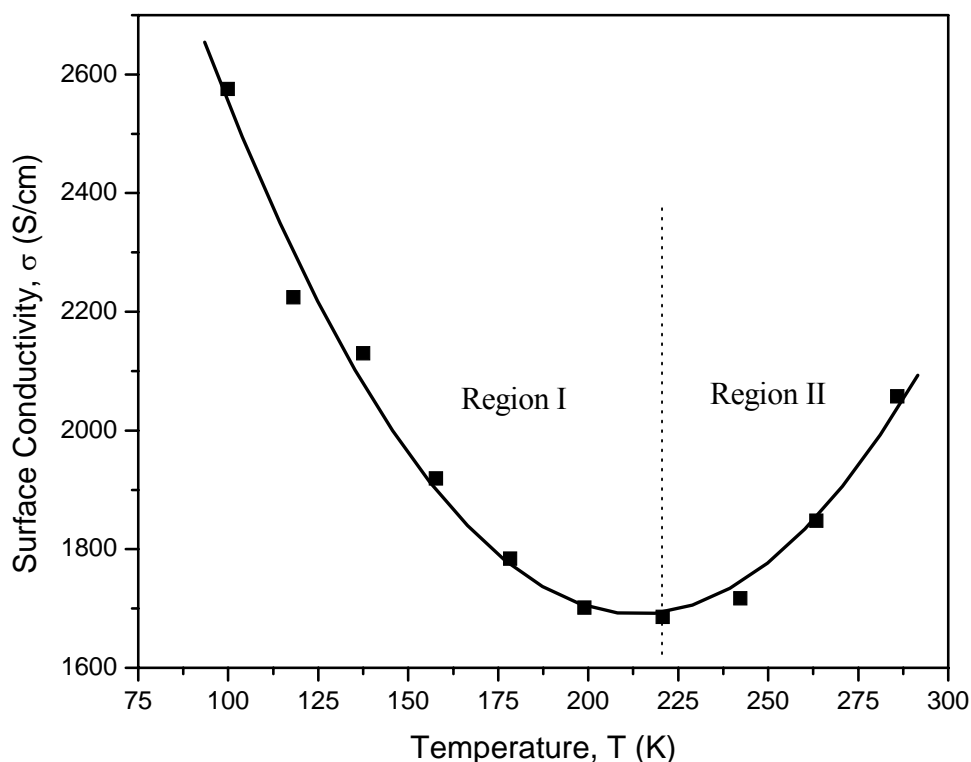


Figure 3: Electrical conductivity as a function of temperature for polycrystalline CuSe.

The region II in Figure 3 from 220 K up to 286 K is identified with the transition to intrinsic conduction in a semiconductor. Within this region, the density of hole carriers is equal to that of intrinsic carriers. When intrinsic effects set in, it will increase the number of carriers and therefore enhance the conductivity [16].

CONCLUSIONS

In-situ low temperature X-ray diffraction analysis for CuSe powder shows that the structure of the CuSe was stable at the temperature range 100 – 300 K. The electrical conductivity of copper selenide metal chalcogenide was characterized in the temperature range from 100 to 286 K using four point probe technique. The electrical conductivity value of CuSe were determined to be in the range from 1.69×10^3 to 2.58×10^3 S/cm. The variation of electrical conductivity with temperature for CuSe sample reveals that, the samples follow the pattern of an extrinsic semiconductor. The experiment shows that there are two distinct temperature zones with two characteristic regions.

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