Structural and transport mechanism studies of copper selenide nanoparticles

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Abstract

Copper selenide (CuSe) nanoparticles were successfully prepared via chemical precipitation method at room temperature. The field emission scanning electron microscopy (FESEM), transmission electron microscopy (TEM) and atomic force microscopy (AFM) micrograph showed the synthesized CuSe powder is nanoparticles. The energy dispersive x-ray (EDX) analysis and inductively coupling plasma (ICP) analysis showed the formation of the stoichiometric CuSe compound. In-situ x-ray diffraction (XRD) at temperatures ranging from 100 to 473 K was performed to study the structure stability of the CuSe compound. The electrical conductivity, Hall mobility, carrier sheet density and thermal diffusivity of the CuSe compound have been investigated at various temperatures to study the electron-phonon transport mechanism in the compound.

Keywords: CuSe nanoparticles, electrical conductivity, thermal diffusivity, chemical precipitation method

(Some figures may appear in colour only in the online journal)

1. Introduction

The physical properties of metal chalcogenide compounds with semiconductor structure have the capacity to change continuously as the chemical composition of the compound is altered [1]. This behaviour makes them important for sensor and laser materials, thin film polarizers, thermoelectric cooling materials [2, 3]. The unique properties of the metal chalcogenide compounds have encouraged a lot of work on the synthesis and characterization of chalcogenide of different groups.

Among the metal chalcogenide that has received extensive attention is copper selenide (CuSe). CuSe has a wide range of stoichiometric compositions (CuSe, Cu₂Se, Cu₃Se₂, Cu₇Se₄, Cu₅Se₄, Cu₂Se) and non-stoichiometric compositions (Cu₂₉₋ₓSe) [4–7]. Cu₂₋ₓSe or CuSe belongs to the group of copper (I) selenide, while CuSe, Cu₃Se₂ and CuSe₂ belong to the group of copper (II) selenide [8, 9]. CuSe can exist in various crystallographic forms such as orthorhombic, monoclinic [10], cubic [8, 11], tetragonal and hexagonal [3, 10]. It has the ability to form a ternary compound, CuInSe₂, or other multinary materials by integrating indium into the binary compound [12, 13]. Various applications such as solar cells, super ionic conductors, photo-detectors, photovoltaic cells and Shottky-diodes have been associated with the metal chalcogenide compound [14–17].

A variety of methods have been explored and reported on the synthesis of CuSe in the form of nanostructure (including...
nanoparticles, nanowires, nanotube and nanoplates) such as solvothermal method [18], hydrothermal method [7, 19, 20], hot injection method [6, 15, 21] and chemical aqueous route [22]. There is very limited research on synthesizing CuSe through chemical precipitation technique.

CuSe was demonstrated to be a good precursor for fabricating CuInSe$_2$- based nanostructures [23, 24]. Li et al [25] have investigated the evolution of hierarchically ordered dendritic Cu$_2$Se and bunchy CuSe nanocrystals and found out that the differences in stoichiometric compositions and crystals phase were mainly resulted from the release and diffusion effect of Cu cations towards Cu-Se reaction interface. Cu$_2$Se (generally with $1 \leq x \leq 2$) with lower $x$ value represents a higher Cu deficiency. The copper vacancies act as electron acceptors and make them behave as p-type semiconductors [26]. As yet, the exploration on transport properties such as the electrical conductivity and thermal diffusivity of CuSe has rarely been investigated especially in bulk form. Most of the researcher study the transport properties of Cu$_2$Se [27–32] and found out that Cu$_2$Se show potential candidate as p-type thermoelectric materials at medium temperature. In order to evaluate the potential device applications of CuSe nanoparticles, the transport properties of this materials in bulk form are needed.

Therefore, this paper reports the CuSe nanoparticles synthesized through the chemical precipitation technique. We utilized the route proposed by Zhang et al [33] using selenium alkaline aqueous solution as a selenium source to form CuSe compound at room temperature under atmospheric pressure. The structural, morphological and transport properties of the synthesized CuSe nanoparticles were investigated in details as it is believe that the current research on studying the basic fundamental properties of CuSe nanoparticles in bulk form will fill the information gap and may open new opportunities for device applications.

2. Materials and methods

All chemicals used were of analytical grade and used without further purification. Manipulations and reactions were carried out in air. CuSe nanoparticles were synthesized by the chemical precipitation method. The selenium alkaline aqueous solution was prepared by dissolving 3.948 g of elemental Se (BDH) in 12 M NaOH (Fisher Scientific) solution. The color of solution turned into orange red immediately upon the dissolution of elemental selenium. Upon complete dissolution of elemental selenium, Cu$_{2+}$ solution obtained from CuCl$_2$.2H$_2$O (Fisher Scientific) was added drop wise to the selenium alkaline aqueous solution and stirred rapidly. The black precipitate obtained was centrifuged and washed with distilled water to remove the excessive alkaline solution. The powder precipitation was then dried in an oven at 343 K. The calculation of the electrical conductivity, Hall mobility, carrier sheet density and thermal diffusivity were characterized by four point probe technique using a source measure unit (Keithley 236) and a voltmeter (Picotest, M3500A) with an accuracy of $\pm 0.001$ mV. Measurements were taken in the range from 100 to 300 K for low temperature measurement and from 300 K to 523 K for high temperature measurement. For low temperature (100–300 K) measurement, the CuSe pellet was placed in a cryostat system (Cryogenics, NVT-152-DOT) with the temperature controlled by auto tuning temperature controller (LakeShore 321), while the measurement of electrical conductivity at high temperature was carried out by placing the sample holder with the CuSe pellet in a furnace (Nabertherm model L3/C6) capable of controlling the temperature to within $\pm 1$ K. To avoid the errors produced from the Peltier effect, the average values of both positive and negative current directions were taken into consideration. The calculation of the electrical conductivity has been discussed elsewhere [34]. Variable temperature Hall effect measurements were performed in van der Pauw configuration to determine the carrier sheet density and Hall mobility of the CuSe from 100 to 300 K with the temperature controlled and monitored by LakeShore 340.
were performed for field strengths 0.8 T driven by LakeShore Model 642 electromagnet power supply. The ohmic contact of the CuSe was formed by indium beads (Aldrich 99.9%) in a van der Pauw configuration with minimum noise [35]. Thermal diffusivity measurement at temperatures between 100 to 300 K was done by photoflash technique using a camera flash (Maxxum flash 5400HS) as an energy pulse source. A K-type thermocouple was used to monitor the temperature at the rear surface of the sample. The signal was then amplified by a preamplifier (SR560) and was transferred to a digital oscilloscope (Tektronix TDS 220). For measurements of thermal diffusivity above room temperature to 523 K, laser flash (Netzsch LFA 457 MicroFlashTM) with Nd: YAG laser was used. The calculation of the thermal diffusivity and its correction factor is found in the literature [36].

3. Results and discussion

The compositional analysis of the synthesized CuSe nanoparticle was carried out using the EDX analysis technique and inductively coupled plasma (ICP) Analysis. A representative EDX spectrum for synthesized CuSe nanoparticle is shown in figure 1 with three prominent peaks corresponding to the Cu, Se and Au element. The Au signal detected in the EDX spectrum is the results of gold coating on sample to prevent charging. In addition, small signal of C and O observed is expected from the background environment and carbon tape holding the powder sample. There are no other impurities elements were found by EDX spectrum. The EDX analysis revealed that the average atomic percentage of Cu:Se was 52.38: 47.62 in the ratio range 1:1.1. The ICP analysis was also done in order to confirm the expected trend in composition variation of Cu and Se as shown in EDX. The analysis shows a Cu:Se ratio of 1:1.1. The composition ratios determined from both EDX and ICP method shows that the synthesized CuSe nanoparticle appear to be nearly stoichiometric (1:1) which revealed that successful formation of CuSe compound was achieved in the precipitation preparation.

In-situ low and high temperature x-ray diffraction spectra of synthesized CuSe nanoparticles are shown in figures 2 and 3 respectively. All the peaks obtained for temperatures up to 398 K are well matched with the JCPDS data (File No. 34-0171) as Klockmannite, which belongs to the hexagonal system [37]. The peaks observed at 2θ = 39.6° and 46.0° which overlapped with CuSe peak presented in the spectra shown in figure 3 are due to the platinum heating strip of the high temperature camera system. An additional peak which is observed starting at temperature 423 K at 2θ = 45.40° and shifted to smaller peak angles as the temperature increased indicating the changes in d-spacing due to heating effect. The shifting pattern of the peaks in d-spacing may be due to the phase transformation from CuSe to Cu2Se structure.

In order to investigate the compositional change and phase evolution at elevated temperature involved with the CuSe nanoparticles, TGA experiment has been performed in the temperature range between 300 to 1273 K as shown in figure 4 in order to check the dehydration, sublimation or decomposition process. The first weight loss stage (1.76%) was observed from 324 to 548 K with 2 small DTG peaks at 324 and 445 K due to the vaporization of loosely bound surface water molecules and vaporization of Se respectively during the heating process. The TGA curves displayed onset
of decomposition temperatures at 548 K and the total weight loss around 28.81\% as shown in Figure 4.

Based on the DTG curve with peak at 657 K as shown in Figure 4, phase transformation has been further investigated by annealing the synthesized CuSe powder in N2 atmosphere at 653 K for 12 h. Figure 5 shows the XRD spectra of CuSe transformed into Cu2Se after the heat treatment process. All peaks observed in the pattern are identified to the standard pattern as stoichiometric Cu2Se (JCPDS 03-065-2082) with no further CuSe peaks are visible. The initial phase of hexagonal copper (II) selenide is changed to cubic phase copper (I) selenide due to the heat treatment process. This observation corresponds to theoretical expectations as proposed by Shafizade et al [9]. The phase transition of CuSe into Cu2Se phase is favourable thermodynamically above 653 K in an oxygen free atmosphere [38]. During the heat treatment process on the CuSe nanoparticles, a gradual volatilization of selenium occurs that results in copper enrichment of the specimens up to the Cu2Se composition where CuSe $\rightarrow$ Cu$_{2-x}$Se $\rightarrow$ Cu2Se.

The mean crystallite size ($L_g$) of the CuSe nanoparticle was calculated at various temperatures using the Scherrer’s formula [12, 39, 40],

$$L_g = \frac{0.89 \lambda}{\beta \cos \theta}$$  \hspace{1cm} (1)

where $\beta$ is the full-width half maximum (FWHM), $\lambda$ the wavelength of the x-ray used and $\theta$ the Bragg angle corresponding to the peak that was being analyzed. The dislocation density ($D_\delta$) defined as the length of dislocation per unit volume of the crystal can be generated using the calculated mean crystallite size ($L_g$) by the relation $D_\delta = \frac{1}{L_g^2}$ [12, 40]. The calculated mean crystallite size, $L_c$ and the dislocation density $D_\delta$ of the synthesized CuSe nanoparticle as a function of temperature are shown in Figure 6. The mean crystallite size and the dislocation density remain at fairly constant values of $\approx 30$–$36$ nm and $(7.8$–$10.4) \times 10^{14}$ lines/m$^2$ respectively at temperatures between 100 and 398 K. Starting from 423 until 473 K, the $L_g$ increases to $\approx 40$–$45$ nm while the $D_\delta$ decreases to $\approx (5.0$–$5.8) \times 10^{14}$ lines/m$^2$. The increase of the crystallize size and decrease of the dislocation density of the compound may be due to the heat treatment effect or transformation of the Cu2Se phase which promoted grain growth [40].

Figure 7(a) shows the FESEM micrograph of the synthesized CuSe powder at 50 000 $\times$ magnification with various size of rod like shape particles. Rod like shape particles with the highest count of diameter size range in 30–40 nm range and average diameter size distribution of (54.1 $\pm$ 3.4) nm are observed from the histogram of the size distribution for synthesized CuSe nanoparticle as shown in figure 7(b). The data for the histogram were obtained from direct measurement of the diameters of the rod-like shape particles with a representative group of 196 particles on the FESEM photograph as shown in figure 7(a). The length of the rod like shape varies from 60 to 680 nm. The formation of different size of rod like shape particle indicates that the synthesized powder is not uniform and not homogeneous. The observed average particle size of synthesized CuSe powder in FESEM is larger than the...
crystallite size calculated from the XRD result. This may be due to the aggregation of the smaller particles because of the high surface energy of the particles.

The size and morphology results of the FESEM have been further confirmed through TEM and AFM imaging. The result represented by TEM images in figure 8 show that the CuSe particles formed are with the diameter size range in between 20–40 nm. In addition, AFM has been conducted to further confirm the result obtained from TEM imaging. Figures 9(a) and (b) shows the 2D AFM image and size distribution of the CuSe nanoparticles disperse in chloroform respectively.

The average particle size evaluated by TEM $(32.5 \pm 1.6 \text{ nm})$ observation and AFM $(31.2 \pm 0.8 \text{ nm})$ are in good agreement with the crystallite size $(34.5 \pm 0.3 \text{ nm})$ obtained from XRD measurements.

The electrical conductivity of the CuSe nanoparticle pressed into pellets using 3 ton pressure was measured in the temperature range between 100 and 473 K using four point probe technique. The conductivity of the CuSe nanoparticles was measured only up to 473 K since the structural change due to phase transformation from CuSe to Cu$_2$Se structure as shown in figure 3 would render the conductivity measurement insignificant [41]. Figure 10 displays the variation of dc conductivity as a function of temperature for CuSe nanoparticle with two distinct temperature zones, where the conductivity decreases as the temperature increased and reaches a minimum at 349 K and then started to increase. The electrical conductivity of the CuSe was found to be in the range of $8.24 \times 10^2$ to $1.03 \times 10^3 \text{ S cm}^{-1}$. In region I, started from 100 K up to 349 K, the decrease of electrical conductivity can be explained by the reduction in Hall mobility, $\mu_H$ with rising temperature as shown in figure 11. The decrease of Hall mobilities as the temperature increased may be due to the influence of impurity, defect scattering, lattice scattering or surface scattering [42–45].

In region II, above 349 K and up to 449 K, the increase of the electrical conductivity with the temperature as shown in figure 10 is related to an increase in crystallite size and reduction of the dislocation density of the CuSe compound as indicated by XRD measurement in figure 6. As the study has been carried out on pellets, electrical conductivity can also be much affected by grain boundary phenomena [46]. The conductivity begins to increase with temperature at region II can be explained as a consequent of thermal activation of the electrons which gained enough energy to jump across the depletion layers at the crystallite boundaries which act as potential barriers for conduction electrons [47, 48].

The carrier sheet density and Hall mobility for the CuSe pellet was calculated directly from the Hall effect measurement using standard equations [49]. The carrier sheet density of the CuSe pellet as shown in figure 11 increase from $2.54 \times 10^{19}$ to $3.08 \times 10^{19} \text{ cm}^{-2}$ with increasing temperature which corresponds to the behaviour normally observed in a non-degenerate semiconductor trend. This behaviour can be explained by the usual impurity concentration in which the excitation of conduction electrons occurs from impurity
The increase in carrier sheet density is reflected in the decrease in the Hall mobility. The Hall mobility of the CuSe pellet decreases from 92.9 to 5.6 cm$^2$ V$^{-1}$s$^{-1}$ as the temperature increased from 100 to 300 K with the slope varies as $-2.52$. The Hall mobility is related directly to the mean free time between carrier collisions which is determined by the various scattering mechanisms such as lattice scattering, neutral or ionized impurity scattering and grain boundary scattering [51, 52]. The influence of acoustic lattice scattering as a dominant effect in the carrier transport can be deduced by analyzing the dependent of mobility with temperature according to $\mu \propto T^{-1.5}$ by theory and $\mu \propto T^{-2.5}$ by experimental [51, 53]. From the obtained result of $T^{-2.52}$, lattice scattering is suggested as the domain effect over the measured temperature range which also being proved by the reciprocal thermal diffusivity results in figure 12.

It is well known that the transport of heat in semiconductor solid is by the flow of lattice vibrational energy or phonons and carriers (holes and electrons) along the specimen [54–56]. The thermal diffusivity measurement results of the CuSe nanoparticle tested from 100 up to 473 K are shown in figure 12. It is observed that the average thermal diffusivity value of the CuSe nanoparticle shows a decreasing trend from $1.20 \times 10^{-2}$ to $6.01 \times 10^{-3}$ cm$^2$ s$^{-1}$ as temperature increased from 100 to 473 K, which is a characteristic of crystalline materials. The observed variation in thermal diffusivity can be explained based on the basis of various phonon scattering mechanisms such as structural scattering, stray scattering and chain defect scattering [57]. Since the thermal resistance arising from both phonon-phonon Umklapp process and phonon-defect scattering becomes less important at low temperature, the thermal diffusivity value will be higher at lower temperature. In addition, the decrease in thermal diffusivity with increasing temperature may be due to the
decrease in the mobility of free charge carriers arising out of scattering and phonon collisions as shown in the Hall mobility results in figure 11. In an attempt to analyze the role of phonon scattering, the reciprocals of the thermal diffusivity (1/α) are plotted against the absolute temperature (T) as shown in figure 12. Phonon scattering is separate into two areas, the temperature dependent intrinsic scattering factor and the temperature independent extrinsic scattering factor. It can be seen that the reciprocal thermal diffusivity increases linearly with increasing temperature especially at temperature range 100–350 K which suggested that the lattice heat transfer is dominant in this temperature range following the equation 1
\[ \frac{1}{\alpha} = A'T + B' \] [58]. The slope A' = 3.04 \times 10^{-1} \text{ cm}^2\text{K}^{-1} is the intrinsic scattering factor of phonons, while the intercept value B' = 5.30 \times 10^{1} \text{ cm}^{-2}\text{K}^{-1} is the extrinsic scattering factor of mean free path. Above 400 K, it is believed that both intrinsic and extrinsic scattering occurred. This has been proved by the XRD measurement (figure 3) where an additional peak which acts as impurities was observed starting at temperature 423 K.

4. Conclusion

Copper selenide nanoparticles have been successfully synthesized via chemical precipitation method. EDX, ICP and XRD patterns confirmed that the synthesized CuSe nanoparticles were stoichiometric. The SEM, TEM and AFM micrographs showed the synthesized CuSe nanoparticles in powder formed with diameter size range between 30 and 40 nm. The CuSe nanoparticles exhibited a stable structure at the temperature range of 100 K to 398 K with no selenium peaks, unassigned, or additional peaks observed. The appearance of additional peaks corresponding to Cu2Se is expected to be due to the continuous loss of the Se at higher temperatures. The mean crystallite size has been determined to be \( \approx 30–36 \text{ nm} \) and the \( D_\delta \approx (7.8–10.4) \times 10^{14} \text{ lines/m}^2 \), respectively, between temperatures of 100 and 398 K. The \( D_\delta \) increases to \( \approx 40–45 \text{ nm} \) while the \( D_\delta \) decreases to \( \approx (5.0–5.8) \times 10^{14} \text{ lines/m}^2 \) between temperatures of 423 to 473 K. The electrical conductivity of the CuSe was found to be in the range of \( 8.24 \times 10^{-2} \) to \( 1.03 \times 10^{5} \text{ S}^{-1} \). The decrease of electrical conductivity can be explained by the reduction in Hall mobility while the increase of the electrical conductivity is related to the effect of grain boundary phenomena, increased in crystallite size and reduction of the dislocation density. The increase in carrier sheet density is reflected in the decrease in the Hall mobility. The average thermal diffusivity value of the CuSe nanoparticle decreased from \( 1.20 \times 10^{-2} \) to \( 6.01 \times 10^{-3} \text{ cm}^2\text{s}^{-1} \) as temperature increased from 100 to 473 K. Lattice scattering is suggested as the domain effect at temperature range 100–350 K from the Hall mobility and reciprocal thermal diffusivity results.

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Disclosure statement

No potential conflict of interest was reported by the author.

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