Enhancing Precursor Quality of Cu-In-S Ternary Thin Films by Applying More Appropriate Deposition Procedure

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Research Article

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Enhancing precursor quality of Cu-In-S ternary thin films by applying more appropriate
deposition procedure

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Abstract

Copper indium sulphur (CIS) thin films were electrochemically grown from an acidic aqueous
solution including 10 mM CuCl$_2$, 10 mM InCl$_3$, 20 mM Na$_2$S$_2$O$_3$ and 200 mM LiCl. Deposition
potential is determined by means of cyclic voltammetry analysis. The precursor CIS thin films are
produced at -1.10 V for 600 s, -0.90 V for 300 s and a mixed potential of -0.25 V for 150 s and -
1.10 V for 150 s. It is reported that surface morphology and film stoichiometry vary remarkably
with the deposition parameters. SEM images show a variation in the grain shape, homogeneity and
agglomeration due to the different Cu/In ratio. The produced films have XRD peaks belonging to
both CIS$_2$ crystalline phase and S element. The produced CIS material at -1.1 V has a band gap of
1.66 eV. The CIS thin film produced at -0.9 V has three different band gaps such as 1.76, 2.59 and
2.85 eV. The CIS material produced by two steps has also three different band gaps between 1.59
and 2.74 eV. The CIS films are p-type, and resistivity and mobility data are in the range 6.56-8.61
Ωcm and 8.68-22.2 cm$^2$/Vs, respectively. It is found that the acceptor concentration of CIS thin
films varies between 2.48x10$^{17}$ and 1.06x10$^{18}$ cm$^{-3}$. In summary, this study reports a procedure to
produce high-quality precursor CIS thin films, highlighting a promising material to be used in
heterostructure photovoltaic devices as a p-type absorber layer.

Keywords: Electrodeposition, CIS thin films, Energy band gap, Hall-Effect measurements

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Introduction

Copper Indium Sulphide (CuInS\textsubscript{2}) is a member of I-III-VI\textsubscript{2} ternary chalcopyrite semiconductors which are mostly used in solar sell applications due to their direct band structures (Tell et al. 1971). The CuInS\textsubscript{2} materials have an optical energy band gap of 1.5 eV and a high absorption coefficient of $10^5$ cm\textsuperscript{-1} (Tell et al. 1971; Sun et al. 1978). CuInS\textsubscript{2} materials can be produced both n and p-type depending on the stoichiometry (Kazmerski et al. 1975). This property is desirable for homojunction production (Kazmerski and Sanborn, 1977). Different vacuum and non-vacuum methods have been applied to grow/deposition of CuInS\textsubscript{2} (CIS) thin films such as solvothermal growth (Yue et al. 2015), thermal evaporation (Scheer et al. 1993), single/multiple source deposition (Kazmerski and Shieh, 1977), flash evaporation (Neumann et al. 1981), spray pyrolysis (Oja et al. 2005), RF magnetron sputtering (Forbes et al. 2003), chemical vapor deposition (Hwang et al. 1981), chemical deposition (Padam and Rao, 1986), electrodeposition (Bouima et al. 2019; Yukawa et al. 1996; Nakamura and Yamamoto, 1997; Broussillou et al. 2011; Bhattacharya et al. 1984; Nakamura and Yamamoto, 2003; Hodes et al. 1985; Herrero and Ortega 1990). Among these processes, electrodeposition steps forward in recent years because it meets the demand of low-cost production of photovoltaic industry by providing non-vacuum, low temperature and large area production.

Based on the literature, the production of CIS thin films by electrodeposition is mainly performed in two methods: 1) single bath/one-step electrodeposition of precursor CIS films followed by an annealing (Bouima et al. 2019; Yukawa et al. 1996; Nakamura and Yamamoto, 1997; Bhattacharya
et al. 1984; Nakamura and Yamamoto, 2003), 2) electrodeposition of Cu-In bilayer precursors followed by annealing under hydrogen sulfide or sulfur atmosphere (Broussillou et al. 2011; Hodes et al. 1985; Herrero and Ortega 1990). Yukawa et al. (1996) have grown CIS thin films in an aqueous electrolyte containing CuSO$_4$, In$_2$(SO$_4$)$_3$ and Na$_2$S$_2$O$_3$ via electrodeposition. They have presented well-crystallized films by annealing in vacuum at 673 K (Yukawa et al. 1996). They have also reported that the conduction type of produced CIS films has changed from p-type to n-type as the In concentration increases in deposition solutions (Yukawa et al. 1996). Nakamura and Yamamoto (2003) have presented that CIS-based solar cells prepared by sulfurization of electrodeposited Cu-In precursors exhibit an efficiency of 1.3% (Nakamura and Yamamoto, 2003). They have reported that the morphology of the precursors can be improved when the deposition solution is prepared without HCl (Nakamura and Yamamoto, 2003). In the study done by Herrero and Ortega (1990), CIS thin films were produced by annealing electrochemically deposited Cu-In alloys in H$_2$S atmosphere (Herrero and Ortega, 1990). They have investigated the effect of annealing temperature and deposition time on the crystal quality (Herrero and Ortega, 1990). They have reported that the best CIS crystalline films are obtained for the annealing temperature of 400 °C and 500 °C and CuInS$_2$ phase is observed only for the films annealed for 60 min or longer (Herrero and Ortega, 1990). Broussillou et al. (2011) have presented 11% efficient CuInS$_2$-based solar cells with an active area of 0.421 cm$^2$ prepared by rapid thermal annealing (Broussillou et al. 2011). Bhattacharya et al. (1984) have produced CIS thin films on Ti substrates by electrodeposition from aqueous electrolytes of CuCl, InCl$_3$, thiourea, triethanolamine and ammonia (Bhattacharya et al. 1984). They have annealed the films in Ar and H$_2$S atmosphere (Bhattacharya et al. 1984). They have reported that deposited films have included both CuInS$_2$ (mainly) and CuIn$_5$S$_8$ phases (Bhattacharya et al. 1984).
Production of high quality CIS thin films depends on the properties of the precursor films. Therefore, it is first necessary to deposit high quality precursors. In this sense, this study focuses on growing of Cu-In-S ternary precursor thin films produced by electrodeposition technique. It is presented physical properties of CIS precursor thin films prepared by one-step and two-step electrodeposition methods in aqueous solutions at four different deposition potentials between -0.25 V and -1.1 V. The influences of deposition potential on the film stoichiometry, morphology and semiconductor properties are investigated.

2. Experimental Details

2.1. Materials

CuCl$_2$ (99.99%), InCl$_3$ (99.99%), Na$_2$S$_2$O$_3$ (99.99%) and LiCl (99.99%) were purchased from Sigma-Aldrich. Indium tin oxide (ITO) coated glass was used as substrate which has 0.5 cm x 1 cm surface area and 0–10 Ω/cm$^2$ sheet resistance. All experiments were performed in aqueous solutions using ultra-pure water. Substrates were individually sonicated in acetone and then isopropanol for 5 minutes and rinsed with ultra-pure water and dried in air prior the deposition.

2.2. Electrochemical Synthesis of Cu-In-S Ternary Materials

Cu-In-Se precursor thin films were electrochemically co-deposited on ITO substrates by a Gamry Reference 3000 Potentiostat/Galvanostat system. We used a three-electrode configuration in electrochemical cell. In this configuration, ITO substrate, platinum wire and saturated Ag/AgCl correspond to working, counter and reference electrode, respectively. Deposition electrolyte includes 10 mM CuCl$_2$, 10 mM InCl$_3$, 20 mM Na$_2$S$_2$O$_3$, 200 mM LiCl, and 50 cc ultra-pure water. Acidic solution medium was provided by adjusting pH of the electrolyte to ~2.0 with HCl.
Production of Cu-In-S ternary compounds was performed by using chronoamperometry method. In this study, three different films were produced depending on the deposition time and potential, and they were called as Films 1, 2 and 3. Films 1 and 2 were produced by single-step, while Film 3 was prepared by two-step electrodeposition technique. Film 1 was co-electrodeposited at a constant deposition potential of -1.10 V for 600 s. Film 2 was co-electrodeposited at a constant deposition potential of -0.90 V for 300 s. Film 3 was produced at -0.25 V for 150 s and -1.10 V for 150 s. Fig. 1 shows the chronoamperometry curves during the electrochemical synthesis of Cu-In-S precursor thin films. Determination of deposition potential is explained in Section 3.1. The current is near to 32 mA for the Film 1, while it is 0.37 mA for the Film 2 (Fig. 1). For the Film 3, the current at -0.25 V is near to zero, while it is near to 0.38 at -1.10 V. Therefore, it is noted that the applied deposition voltage of -1.10 V has main role on the formation of Cu-In-S for the Film 3.

2.3. Measurements

A Gamry Reference 3000 Potentiostat/Galvanostat/ZRA was used in electrodeposition of CIS precursor thin films. PHE200 Physical Electrochemistry software was used to carry out deposition experiments. The morphology of the films was characterized using Carl Zeiss Evo 40-type scanning electron microscope (SEM). Elemental composition of the films was investigated via Bruker AXS Microanalysis energy dispersive X-ray (EDX) analysis. Optical characterization experiments were conducted by Shimadzu-SolidSpec-2700 UV-VIS-NIR spectrophotometer. XRD studies were performed by using Bruker X-ray diffractometer D8 advance model. HMS-3000 Manual Ver. 3.5.1 Hall-Effect measurement system was used to determine the electrical properties
of the CIS materials. Thickness measurements of the precursor thin films were carried out by an optical profilometer (Zeta-20, Zeta Instruments, United States).

3. Results and Discussion

3.1. Determination of Electrodeposition Process

We try to explain the electrochemical mechanisms of the formation of Cu-In-S ternary thin films by means of cyclic voltammograms (CV) belonging to the individual Cu, In and Te constituents, and Cu-In-Te ternary system. In our early work [21], we have reported individual cyclic voltammograms of 10 mM CuCl$_2$ and 20 mM Na$_2$S$_2$O$_3$ aqueous solutions. For this reason, the cyclic voltammograms of Cu and S molecular sources are not given in this study due to the avoiding repetition. The reduction peak of Cu$^{2+}$ to Cu is reported at -0.35 V vs Ag/AgCl electrode, and deposition reaction can be given as (Yildirim and Peksoz, 2017):

\[ \text{Cu}^{2+} + 2e^- \rightarrow \text{Cu}, \quad E^0 = -0.35 \, V \]  

(1)

The reduction peak of S to S$^{-2}$ is reported at -0.90 V vs Ag/AgCl electrode, and the peak can be explained by the following reaction (Yildirim and Peksoz, 2017):

\[ S + 2e^- \rightarrow S^{-2}, \quad E^0 = -0.90 \, V \]  

(2)

The cyclic voltammogram of an aqueous electrolyte with 10 mM InCl$_3$ and 200 mM LiCl is recorded in a potential interval from -2 V to -0.25 V with a scan step of 20 mV/s (Fig 2a). Two cathodic peaks are observed at -0.96 V and -1.32 V (Fig 2a). The first peak is attributed to the reduction of In$^{3+}$ to In, and it can be described by the following reaction:

\[ \text{In}^{3+} + 3e^- \rightarrow \text{In}, \quad E^0 = -0.96 \, V \]  

(3)
The second peak at -1.32 V is due to the evaluation of H$_2$ gases (Fig. 2b). Fig 2b shows cyclic voltammogram of an aqueous solution consisting of 10 mM CuCl$_2$, 10 mM InCl$_3$, 20 mM Na$_2$S$_2$O$_3$ and 200 mM LiCl. The pH of solution is kept at ~2 using HCl. Two cathodic peaks are observed at -0.25 V and -1.22 V vs. Ag/AgCl reference (Fig. 2b). The peak at -0.25 V is due to the changing of S$_2$O$_3^{2-}$ ions in acidic solutions to S and of HSO$_3^-$ according to the following reaction (Broussillou et al. 2011):

$$S_2O_3^{2-} + H^+ \rightarrow S + HSO_3^- \quad (4)$$

The peak at -1.22 V is attributed to the formation of Cu-In-S ternary structure by the following reaction:

$$xCu + yIn + zS \rightarrow Cu_xIn_yS_z \quad (5)$$

It is noted that formation of CIS compound moves towards more negative potentials compared with individual deposition of Cu, In and S constituents (Fig. 2b). The formation of CIS compound starts at -0.85 V, reaches to maximum at -1.22 V, and finishes at -1.35 V (Fig. 2b). According to the CV studies, the selection of an appropriate deposition potential should be within this potential interval. Therefore, two constant potentials such as -0.90 V and -1.10 V were applied to obtain CIS compound. Afterwards, we want to test film production at the mixed potential of -0.25 V and -1.10 V, which are seen CV plot of the electrolyte including of Cu, In and S molecular sources.

3.2. Structural Studies

SEM images of the produced CIS thin films are shown in Fig. 3. Bean-shaped grains are seen on the surface of Film 1 (Fig. 3a). Film 2 has spherical grains, and distribution of these grains is
homogeneous (Fig. 3b). Size and shape of the grains on the surface of the Film 3 are irregular, and some aggregated formations and pores are seen on the surface (Fig. 3c). EDX data of the produced CIS materials are recorded from the whole surface seen in Fig. 3, and atomic percentages are listed in Table 1. The ratio of \([\text{Cu+In}]/\text{S}\) is 1.71, 1.34 and 1.13 for the Films 1, 2 and 3, respectively (Table 1).

XRD patterns of the produced CIS thin films are shown in Fig. 4. According to the XRD studies of the produced films, the peaks observed at \(2\theta=21.44^\circ, 30.40^\circ, 35.34^\circ, 40.09, 50.74^\circ\) and \(60.46^\circ\) belong to the ITO substrate (Fig. 4). Grindle et al. (1979) have calculated XRD parameters by considering \(\text{CuInS}_2\) to be a chalcopyrite crystal phase with \(a=5.51\) Å and \(c=11.05\) Å, and they have also supported these calculations with experimental observations (Grindle et al. 1979). Some of the peaks observed in our study are well matched with the XRD data given in the work done by Grindle et al. (1979). Film 1 has three weak peaks at \(2\theta=38.68^\circ, 45.52^\circ\) and \(69.64^\circ\), which can be attributed to \((2\ 1\ 1), (2\ 1\ 3)/(1\ 0\ 5)\) and \((4\ 0\ 0)/(0\ 0\ 8)\) due to the \(\text{CuInS}_2\) crystalline phase, respectively (Fig. 4a) (Grindle et al. 1979). Film 2 and Film 3 have a strong peak at \(2\theta=31.82^\circ\) and two small peaks at \(2\theta=37.52^\circ\) and \(45.42^\circ\), which are identified as \(\text{CuInS}_2\) crystalline phase with \((2\ 0\ 0)/(0\ 0\ 4), (2\ 1\ 1), \) and \((2\ 1\ 3)/(1\ 0\ 5)\) respectively (Fig. 4b and 4c) (Grindle et al. 1979). According to the JCPDS (Joint Committee on Powder Diffraction Standards) card no PDF 01-089-6764, the produced films have a peak at \(2\theta=22.40^\circ\) due to the triclinic lattice of Sulphur atoms. The crystallite size (\(D\)) of the precursor CIS materials is estimated by the Scherrer’s equation given as (Vadivel et al. 2013):

\[
D = \frac{0.9\lambda}{FWHM \times \cos\theta}
\]  

(6)
Where $\lambda$ is the wavelength of the X-rays used in the measurement (1.54056 Å), $\theta$ and FWHM correspond to the diffraction angle and the full width at a half maximum intensity of the related peak, respectively. Crystallite size values are calculated for each XRD peak via Eq. (6), and the obtained data are listed in Table 2. Crystallite size belonging to CIS$_2$ phase changes between 16 and 27 nm, 7 and 45 nm, and 14 and 29 nm for Film 1, Film 2 and Film 3, respectively (Table 2). Film 1 has two XRD peaks due to the sulphur element (Fig. 4a), while Film 2 and 3 have only a sulphur peak (Fig. 4b and 4c). Crystallite size of sulphur element is 16-21 nm, 4 and 17 nm for Film 1, 2 and 3, respectively (Table 2). Crystallite size of the main CIS$_2$ phase at $2\theta=38.68^\circ$ is 27, 7 and 19 nm for Film 1, 2, and 3, respectively. The crystallite size variation of this main CIS$_2$ phase with the biggest intensity is most probably due to the variation of indium percentage (Tables 1 and 2).

### 3.3. Optical and Electrical Properties

The physical thicknesses of the precursor CIS films are determined as 162 nm, 140 nm and 108 nm for Films 1, 2 and 3 respectively. Fig. 5a shows the absorbance spectra of the produced films in the range of 200 nm-1100 nm. To calculate energy band gap ($E_g$) of the films, absorbance data of the precursors are used in Tauc equation (Tauc et al. 1966),

$$\alpha \nu = \beta (\nu - E_g)^n$$  \hspace{1cm} (7)

Where $\alpha$ is the absorption coefficient, $\nu$ is the incident photon energy, $\beta$ is edge parameter, $n$ is a constant which takes the value 1/2 for direct transitions and 2 for indirect transitions. Here $n$ is 1/2 since CIS material has a direct band gap. The absorption coefficient $\alpha$ is calculated for each thin film using Beer-Lambert’s equation:
\[ \alpha = 2.303 \frac{A}{d} \]  

(8)

Where \( A \) is the absorbance of the films for a given wavelength and \( d \) is the thickness of the thin film. The \( E_g \) values of the CIS thin films were determined from where the extended linear part of the \((\alpha h\nu)^2 - h\nu\) curves hits the \( h\nu \)-axis (Fig 5b-d). While the \( E_g \) of the Film 1 is 1.66 eV, Film 2 and Film 3 have three different band-gap values that may be caused by different ternary or single crystal phases of Cu-In-S system involved in mentioned precursor thin films. The formation of \( E_{g2} \) and \( E_{g3} \) energy band gaps for the Films 2 and 3 is attributed to transitions from a copper valance band to conduction band edge. \( E_{g1} \) values can be explained by film stoichiometry (Table 1). Herein, \( E_{g1} \) values are 1.66, 1.76 and 1.59 eV for Films 1, 2, and 3, respectively. \( E_{g1} \) energy band gap varies proportionally with the compositional ratio of S/Cu ratio in the CIS films.

Conduction types of the electrodeposited precursor CIS films were measured by four probe Hall-Effect system. Some of the electrical parameters of the produced films are given in Table 3. All films show p-type conductivity. Hodes et al. (1984) have reported that if Cu/In is greater than 1 in the films, the conductivity of the film is p-type, and if the Cu/In is less than 1 then the conductivity of the film is n-type. Furthermore, Grindle et al. (1979) have reported that CIS films with excess sulphur exhibite p-type conductivity. The results reported by Grindle et al. (1979) support our results. However, the results in the present work are in conflict with those of Hodes et al. (1979). Some earlier literature summarization related with the structural, optical and electrical parameters of CIS ternary thin films is given in Table 4. The acceptor density is between \( 2.48 \times 10^{17} \) and \( 1.06 \times 10^{18} \) cm\(^{-3}\) (Table 3), which are in accordance with the literature as seen in Table 4. The mobility increases from 8.68 to 22.2 cm\(^2\)/Vs, as the [Cu+In]/S ratio decreases from 1.71 to 1.13 (Table 1 and 3). The obtained mobility values in this study are higher than those of the literature (Table 4).
Conclusions

The structural and electrical properties of the electrodeposited Cu-In-Se thin films are reported. The CV studies show that individual deposition of Cu, In and S elements on ITO substrate occurs at -0.35, -0.96 and -0.90 V, while electrodeposition of ternary CIS compound takes place at two deposition voltages such as -0.25 and -1.22 V vs. Ag/AgCl. According to the mentioned CV behavior, three different CIS materials are prepared, and called as Films 1, 2 and 3. The precursor Cu-In-S ternary thin films have polycrystalline structure. Films 2 and 3 show three optical band gaps most likely due to their polycrystalline structures. However, Film 1 has an optical band gap of 1.66 eV in spite of the fact that its polycrystalline nature. Optical band gap increases from 1.59 to 1.76 eV with increasing Cu/In ratio. Stoichiometry of Films 1, 2 and 3 is CuIn_{18.1}S_{11.2}, CuIn_{2.62}S_{2.70} and CuIn_{6.71}S_{6.83}, respectively. Films 1, 2 and 3 have a conductivity of 0.14, 0.12 and 0.15 1/Ωcm, respectively. The produced CIS materials exhibit p-type conductivity with the acceptor concentration range ~10^{17}-10^{18} cm^{-3}, which are well correlated with the literature data.

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Figure Captions

Figure 1

The current-time variation during the electrodeposition of the CIS ternary thin films.

Figure 2

Cyclic voltammogram of a) In and b) Cu-In-S on ITO substrate.

Figure 3

SEM image of a) Film 1, b) Film 2 and c) Film 3.

Figure 4

XRD patterns of a) Film 1, b) Film 2 and c) Film 3

Figure 5

a) Absorbance spectra of the CIS films, and Tauc plot of b) Film 1, c) Film 2 and d) Film 3.
Table 1

Atomic percentages of the produced Cu-In-S precursor thin films. Film stoichiometry is also given.

| Deposition Potential (V) | Cu (%) | In (%) | S (%) | (Cu+In)/S | Stoichiometry     |
|-------------------------|--------|--------|--------|-----------|-------------------|
| Film 1                  | 3.31   | 59.78  | 36.91  | 1.71      | CuIn_{18.1}S_{11.2} |
| Film 2                  | 15.82  | 41.45  | 42.73  | 1.34      | CuIn_{2.62}S_{2.70} |
| Film 3                  | 6.88   | 46.16  | 46.96  | 1.13      | CuIn_{6.71}S_{6.83} |
Table 2

Crystallite size of the produced CIS materials. Gaussian fit function is used to find out FWHM of each XRD peak.

| XRD peak position 2θ (°) → | 22.40 (S atom) | 31.8 (CIS$_2$) | 38.6 (CIS$_2$) | 43.4 (S atom) | 45.4 (CIS$_2$) | 69.7 (CIS$_2$) | Average crystallite size (nm) |
|----------------------------|----------------|----------------|----------------|----------------|----------------|----------------|-----------------------------|
| Produced Film ↓            |                |                |                |                |                |                |                             |
| Film 1                     | 16             | No peak        | 27             | 21             | 16             | 22             | 20                          |
| Film 2                     | 4              | 45             | 7              | No peak        | 20             | No peak        | 19                          |
| Film 3                     | 17             | 29             | 19             | No peak        | 14             | No peak        | 20                          |
Table 3

The optical and electrical data related with the produced CIS thin films

| Electrodeposited film → Film 1 | Film 2 | Film 3 |
|-----------------------------|--------|--------|
| Physical Parameters ↓        |        |        |
| Film thickness (nm)          | 162    | 140    | 108 |
| Energy band gap (eV)         | 1.66   | 1.76 to 2.85 | 1.59 to 2.74 |
| Acceptor density, x10^{17} (cm^{-3}) | 10.6  | 2.48   | 4.27 |
| Mobility, (cm^{2}/Vs)        | 8.68   | 20.9   | 22.2 |
| Resistivity, (Ωcm)           | 6.79   | 8.61   | 6.56 |
| Conductivity, (1/ Ωcm)       | 0.14   | 0.12   | 0.15 |
| Conductivity type            | p      | p      | p    |
Table 4.

Literature data related with the CIS materials. Production methods listed here are abbreviated such as: single source deposition (SSD), double source deposition (DSD), sputtering and sulfurization (SPS), Airless spraying (AS), thermal evaporation (TE), e-beam evaporation (EBE), electrodeposition (ED), chemical deposition (CD), modulated flux deposition (MFD), spray pyrolysis (SP), electrospinning (ES), pulse galvanostatic deposition (PGD), Photochemical deposition (PCD), heating-up polyol method (HPM)).

| References | Production method | Crystallite Size (nm) | Crystalline phase | Energy band-gap interval (eV) | Carrier density (cm$^{-3}$) | Mobility (cm$^2$/Vs) | Resistivity (Ωcm) | Conductivity type |
|------------|-------------------|-----------------------|------------------|------------------------------|-----------------------------|---------------------|------------------|-------------------|
| [3] SSD-DSD | -                 | CuInS$_2$             | 1.55             | 10$^{14}$ to 10$^{19}$       | 1 to 10                     | 0.1 to 800          | n-type           |
| [22] SPS   | 50-100            | CuInS$_2$ and In$_2$S$_3$ | 1.55           | 10$^{16}$                      | <0.2                        | 0.8 to 400          | p-type           |
| [26] AS    | -                 | CuInS$_2$ and In$_2$S$_7$ | 1.4              | 1.0-5.0x10$^{17}$               | -                           | -                  | n-type           |
| [27] EBE   | 50                | InS and CuInS$_2$     | -                | 3x10$^{20}$                     | 0.1                          | 0.03               | p-type           |
| [14] ED    | 1.9, 1.3 and 0.7  | CuInS$_2$, CuIn$_{11}$S$_{17}$ and In$_2$O$_3$ | - | - | - | - | p-type |
| [28] CD    | 4                 | CuInS$_2$, Cu$_2$S    | -                | -                             | -                           | 10                 | p-type           |
| [29] SP    | 7.85-24.36        | CuInS$_2$ and In$_2$S$_3$ | 1.31 to 1.49     | -                             | -                           | -                  | p-type           |
| [30] MFD   | 30-55             | CuInS$_2$, Cu$_2$S    | 1.42             | -                             | -                           | -                  | p-type           |
| [31] SP    | 6.2               | CuInS$_2$, Cu$_2$S    | 1.9              | -                             | -                           | -                  | p-type           |
| [32] ED    | -                 | CuInS$_2$, In$_2$O$_3$ | 1.40 to 1.45     | -                             | -                           | -                  | -                |
| [33] ES    | 23-56             | CuInS$_2$             | 1.53 to 1.60     | -                             | -                           | -                  | -                |
| [34] ED    | -                 | CuInS$_2$, Cu$_2$S    | 1.98 to 2.70     | -                             | -                           | -                  | -                |
| [35] TE    | 1500-2000         | CuInS$_2$ and CuS     | -                | 1x10$^{18}$ to 1x10$^{21}$    | 0.1 to 1.0                 | 0.1 to 10.0        | p-type           |
| [36] SP    | 17-34             | CuInS$_2$             | 1.53 to 2.16     | -                             | -                           | -                  | -                |
| [37] TE    | 100-200           | CuInS$_2$ and In$_2$O$_3$ | 1.5              | -                             | -                           | 15 to 288          | p-type           |
| [23] PGD   | 15-80             | CuInS$_2$             | 1.30 to 1.51     | 6.95 x10$^{18}$ to 39.98x10$^{18}$ | 2.45 to 15.54 | 0.1 to 3.67     | p-type           |
| [38] PCD   | 12-32             | CuInS$_2$, Cu$_2$S and In$_2$S$_3$ | 1.6 to 1.9 | 2.5x10$^{15}$ to 1.3x10$^{16}$ | 9.2 to- | - | 0.54 to 27.29 | p-type |
| [39] ED    | 20-50             | CuInS$_2$             | 1.5              | -                             | -                           | -                  | -                |
| [40] HPM   | 17-20             | CuInS$_2$, Cu$_2$S, Cu$_2$S | 1.46 to 1.57     | 4.2x10$^{20}$ to 8.31x10$^{21}$ | - | - | - | p-type |
| This work | ED 20             | S element, CuInS$_2$  | 1.59 to 2.85     | 2.48x10$^{17}$ to 10.6x10$^{17}$ | 8.68 to 22.2 | 6.56 to 8.61 | p-type |

This work
Figure 1

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