STRUCTURAL, OPTICAL AND ELECTRICAL PROPERTIES P-TYPE QUATERNARY CHALCOGENIDES OF $CuIn(S_{1-x}Se_x)_2$ THIN FILMS

H. YANUAR[a*], U. LAZUARDI[a], J. COPRIADY[b]
[a]*Department of Physics, FMIPA University of Riau, Pekanbaru 28293 Indonesia.*
[b]*Department of Chemistry, FKIP University of Riau, Pekanbaru 28293 Indonesia.*

$CuIn(S_{1-x}Se)_2$ (CISS) thin films have been deposited successfully using a Close-Spaced Vapor Transport method. The films were grown on soda-lime glass substrates using a polycrystalline $CuIn(S_{1-x}Se_x)_2$ ingot as the source of the deposition material with x=0.3, x=0.4 and x=0.5. Effect of substrate temperature on the properties CISS films has been investigated using X-ray diffraction, scanning electron microscopy, energy dispersive spectroscopy, ultraviolet-visible spectrophotometer and Hall effect measurement. The results from XRD characterization confirmed the formation of chalcopyrite crystal structure with a strong preferred (112) orientation. We find that when Cu/In ration from EDS was 1.09 (Cu-rich) on the XRD observed a Cu_2Se peak at the substrate temperature 450°C, which corresponds to a surface morphology. Single phase chalcopyrite obtained when the substrate temperature was increased from 480°C and 520°C. CISS films showed uniformity large grains size of 10 microns and highly compact. The band gap of CISS films was found to be between 1.05 to 1.18 eV. The electrical properties are all p-type conductivity and carrier concentration varying between 10^{16} to 10^{17} cm^{-3} obtained at different film composition x between 0.27 to 0.55.

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1. Introduction

In the field of absorber materials suitable for photovoltaic conversion, silicon is still the most competitivematerial. But in order to reduce the cost of the modules, other materials such as $CuIn(S,Se)_2$ is being investigated by several researchers. With an absorption coefficient greater than 10^4 cm^{-1} in the range of UV-visible wavelengths, the $CuIn(S,Se)_2$ is already one of the most promising for a good photovoltaic conversion, a broad industrial application with lower cost prices. The band gap energies of $CuIn(S_{1-x}Se_x)_2$ solid solution alloys (~1-1.5 eV) are in the range of optimum band gap energies for single junction solar cells [1]. Crystallographic and optical properties of $CuIn(S_{1-x}Se_x)_2$ has been observed with $0 \leq x \leq 1$ that shows the band gap energy linearly increased from 1-1.5 eV [2]. The substitution of selenium by sulfur in thin film solar cells still is a challenging topic [3]. The commercial competitiveness of thin film materials depends mainly on the technique used. Arnou*et al.*[4] have developed an atmospheric solution-based process approach for the deposition of $CuIn(S,Se)_2$ absorbers in power conversion efficiencies of up to 8%. Some researcher [5-10] have been investigated by a number of different methods to grow $CuIn(Se_{1-x}S_x)_2$ thin films including spray pyrolysis, ion cluster beam, solution growth, mixture reaction, sputtering and microwave radiation. Another method for $CuIn(S,Se)_2$ thin film solar cells have been fabricated by selenizing $CuInS_2$ nanocrystals synthesized using a nanocrystal inks precursors [11].

The close-spaced vapor transport (CSVT) technique very rarely used extensively for the growth of compounds $CuIn(S,Se)_2$. CSVT is a simple technique and low cost for fabricating thin film material. This technique has been used to grow thin film $CuInSe_2$. The thermodynamical

*Correspondingauthor:yanuar.hamzah@lecturer.unri.ac.id

study to growth of $CuInSe_2$ films by CSVT technique has recently been reported by Masse *et al.*[12]. Here we demonstrate the application of the CSVT technique in vertical tube reactor for the deposition of $CuIn(S_{1-x}Se_x)_2$ thin film on soda lime glass substrate by using a $CuIn(S_{1-x}Se_x)_2$ source compound with differences in the composition x and solid iodine as a transporting agent. A major advantage of this technique is a simple process and it does not require high vacuum systems, deposition time was very fast around 10-15 minutes and the resulting film without selenization or sulfurization step. The challenge of this technique is preventive the impurity of iodine can act as a dopant which increases recombination or reduced mobility of film. A brief outline of the experimental technique will be described, as well as an analysis of the results obtained in this study. The aim of this work is to study the characteristics of this material obtained by CSVT according to different substrate temperature deposition and using different source $CuIn(S_{1-x}Se_x)_2$ composition. These results analysis is in the form of X-ray diffraction (XRD), scanning electron microscopy (SEM), and energy dispersive X-ray spectroscopy (EDS), UV-vis and Hall effect which were characterized to investigate the structural, optical and electrical properties of the films. The results showed that this technique is perfectly adapted to the growth of thin film $CuIn(S_{1-x}Se_x)_2$.

2. Experimental

Different composition of $CuIn(S_{1-x}Se_x)_2$ were synthesized by a direct combination of the element Cu, In, S and Se in the desired proportions (0.3<x<0.5). The elements were placed in a quartz tube (10 mm diameter, 200 mm length and 1.2 mm thick). The tube was cleaned by using a mixture of HF and rinsed with distilled water. Cu (5N from Balzers), In (6N from Balzers, S (6N from Koch Ligth) and Se (N from Sogemet) were a mixture in proportion to obtain compounds with a chosen composition x. Then the tube was sealed under a vacuum of 10^{-3} Torr. The quartz tube was placed in a horizontal furnace at a temperature higher than the melting temperature of the compound at 1150°C. The heating and cooling program has the duration of about 100 hours [13]. The source of $CuIn(S_{1-x}Se_x)_2$ polycrystalline crush into powders with grains (~10 microns) was compressed by the pressure of 300 kg/cm^2 using a hydraulic press with a diameter 2 mm and a thickness of 1 mm. $CuIn(S_{1-x}Se_x)_2$ thin films were grown on soda-lime glass substrates using CSVT vertical tube reactor and solid iodine as a transporting agent system is described in figure 1.

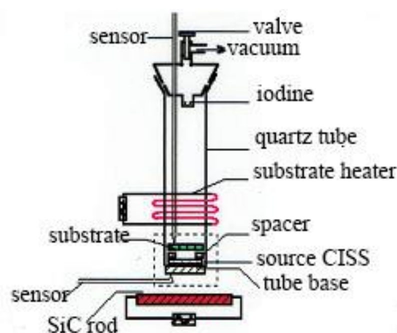
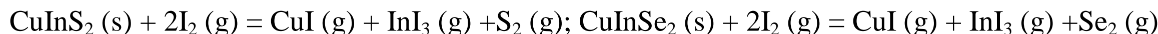


Fig.1. Schematic diagram of the CSVT.

CSVT method consists of a vertical reactor made of quartz glass with a length of 20 cm and a diameter 2 cm. Thin film deposition carried out in the reactor zone where the source and the substrate placed facing each other the bottom of the reactor separated by a quartz spacer thickness of 0.7 mm. Iodine as a transporting agent to accelerate the evaporation of the substrate to a source with the pressure of about 10^2 atm. The substrate was heated by an applying current to a rod of silicon carbide (SiC). The temperatures were controlled using thermocouples mounted near the substrate and the source. The temperature gradient is the driving force for the growth of thin films.

In this study of $CuIn(S_{1-x}Se)_2$ films growth condition have controlled at a substrate temperature T_{sub} (450°C, 480°C and 520°C) with a deposition time for 15 minutes. The substrate temperature is about 50°C lower than from the source temperature T_{sou}. The transport reactions of the $CuInS_2$ and $CuInSe_2$ compounds by the iodine are :



$CuInS_2$ (s) + $2I_2$ (g) = CuI (g) + InI_3 (g) +S_2 (g); $CuInSe_2$ (s) + $2I_2$ (g) = CuI (g) + InI_3 (g) +Se_2 (g)

It is necessary to determine the temperature range between source and substrate temperature. The growth conditions for each film are listed in tabel 1.

Table 1. The growth conditions for CISS thin films.

Source	T_{sou} (°C)	T_{sub} (°C)
$CuIn(S_{0.3}Se_{0.7})_2$	500	450
$CuIn(S_{0.4}Se_{0.6})_2$	530	480
$CuIn(S_{0.5}Se_{0.5})_2$	570	520

The films were characterized by the structural, optical and electrical properties by using XRD, SEM/EDS, UV-vis, and Hall effect measurement. The electrical properties (conduction type, mobility and carrier density of samples were determined by resistivity and Hall effect at room temperature using four point probe method.

3. Results and discussion

We studied different compositions source of $CuIn(S_xSe_{1-x})_2$. The samples we present the depositing conditions and compositions of the thin layers prepared from the sources of $CuIn(S_{0.3}Se_{0.7})_2$, $CuIn(S_{0.4}Se_{0.6})_2$ and $CuIn(S_{.5}Se_{0.5})_2$. Under the deposition conditions used such as substrate temperature (T_{su}), the distance between source to the substrate (0.7 mm) and time of deposition (15 minutes), the element of iodine present in our films was not detectable from the EDS analyzes. Deposition conditions and thin film compositions prepared from the sources a shown in tables 2.

Table 2. The deposited film composition $CuIn(S_{1-x}Se_x)_2$ thin films

x=S/(S+Se)	Cu/In	Source/Film	(S+Se)/(Cu+In)	$CuIn(S_{1-x}Se_x)_2$ composition			
				Cu	In	S	Se
0.3	1.0	Source		24.63	24.73	15.48	35.16
0.27	1.1	Film	1.02	25.38	24.15	13.84	36.63
0.4	1.0	Source		24.93	24.70	19.82	30.55
0.41	1.1	Film	0.97	27.18 Cu-rich	23.56	20.25	29.01
0.5	1.0	Source		25.07	25.25	24.65	25.03
0.55	1.1	Film	0.96	26.65 Cu-rich	24.60	26.76	21.99

We show the relationship between the atomic ratio [S]/[S + Se] of the thin film and that of the source material from EDS analysis. The deposited film composition (base on the source materials) were $CuIn(S_{0.28}Se_{72})_2$, $CuIn(S_{0.41}Se_{59})_2$ and $CuIn(S_{0.55}Se_{45})_2$, with a composition varied from 0.28 to 0.55. The thin films with almost the different composition as the source material are made due to the high deposition rate of the CSVT. It assumed that S is fully displaced by Se or vice versa. Previous work on $CuInSe_2$ thin films was sulfurized in H_2S/Ar at 320°C for 10 min in Se ambient showed that the presence of the binary phases of CuSe and InSe [14]. Another indication is allsamples increased the ratio Cu/In (rich-Cu).A slight excess of copper is noted with

respect to the sourcematerial compositionwhen the substrate temperature increases from 450 to 520°C, Cu/In increases from 1 to 1.1. Figure 2 represents the XRD spectrum of all three films $CuIn(S_{0.27}Se_{0.73})_2$, $CuIn(S_{0.41}Se_{59})_2$ and $CuIn(S_{0.55}Se_{45})_2$ indicate the chalcopyrite phase with a highly preferred (112) orientation. Only diffraction peaks (112) dan (312/316) are derived from the same plan of CISS detected and there is a peak of the binary Cu_2Se phase is observed when substrate temperature at 450°C, without CuI diffraction peak (Fig. 2).

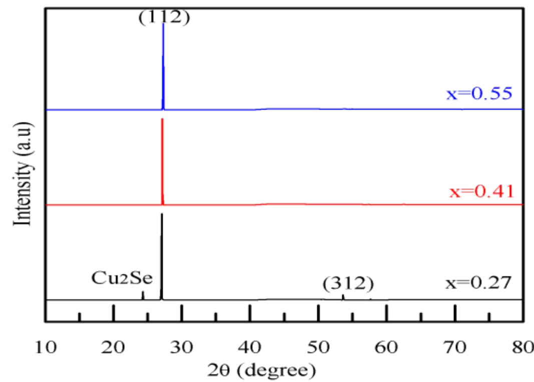


Fig.2. XRDof the CISS for x=0.27, 0.41 and 0.55 films deposited at substrate temperature 450℃, 480℃ and 520℃ respectively, peaks are indexed with standard JCPD 36-1311 for CISS.

The presence of Cu_2Se phase may be enhanced Se diffusion from the source to the substrate in the reaction surface etching $_2CuI^{(g)} + {}_{1/2}Se^{(g)} = Cu_2Se^{(s)} + I_2^{(g)}$. It was observed from EDS analysis sample for Cu/In > 1 (Cu-rich). This Cu_2Se phase is observed by a study of post-deposition sulfur incorporation into the $CuInSe_2$ thin film[14]. Figure 1 shows the spectra of $CuIn(S_{0.41}Se_{0.49})_2$ film is similar (112) and (321)/(116) peak and the Cu_2Se phase has been disappeared (removed). There is a displacement of this peak, which can be due to a variation of the composition. Using the Vegard law taking into account the position of the $CuInSe_2$ peak (112) and the $CuInS_2$ peak according to the chalcopyrite structure (JCPD 36-1311), the composition would vary from x between 0.27 and 0.55. We point out that all peaks shift to higher angle with increasing the sulfur content S in the film and good agreement with Yamamoto *et al.*[15]. The position of the peak (112) corresponding to the polycrystalline source material which the source was fabricated also shows in Figure 1 (b). It corresponds to the reduction in the lattice constants, caused S substituting for Se. It shows a displacement of the peak (112) higher angle when the content sulfur increases, wherein 2θ = 27.06° for $CuIn(S_{0.3}Se_{0.7})_2$ and 2θ = 27.19° for $CuIn(S_{0.5}Se_{0.5})_2$. From the variation of the lattice parameters *a*and*c*quaternary alloy systems $CuIn(S_xSe_{1-x})_2$ as a linear function of the composition x in the reference [13].

We studied different compositions source of $CuIn(S_xSe_{1-x})_2$. The samples we present the depositing conditions and compositions of the thin layers prepared from the sources of $CuIn(S_{0.3}Se_{0.7})_2$, $CuIn(S_{0.4}Se_{0.6})_2$ and $CuIn(S_{0.5}Se_{0.5})_2$. Under the deposition conditions used such as substrate temperature (T_{sub}), the distance between source to the substrate (0.7 mm) and time of deposition (15 minutes), the element of iodine present in our films was not detectable from the EDS analyzes. The elemental thin film composition prepared from the sources a shownin Figure3. We show the relationship between the atomic ratio [S]/[S + Se] of the thin film and that of the source material from EDS analysis. The thin films with almost the different composition as the source material are made due to the high deposition rate of the CSVT. According to the chemical transport reaction, the gaseous phase contains CuI, InI_3, S_2, Se_2 and I_2. The last three compounds are gaseous at T > 300°C under our pressure conditions (the tube is sealed under vacuum), but CuI might be soild at temperature of order 500°C. The iodine pressure is also important for the stoichiometry of films.

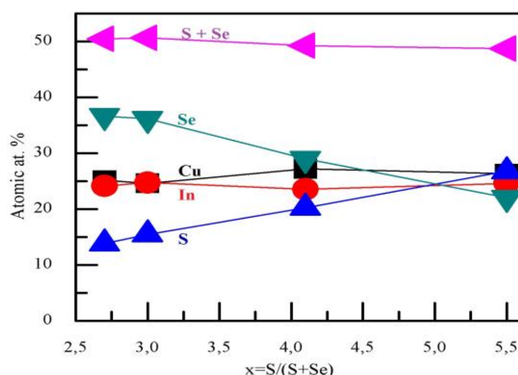


Fig.3. The Compositional CISS thin films at different composition.

Another indication is all the samples increased the ratio Cu/In (rich-Cu). A slight excess of copper is noted with respect to the source material composition when the substrate temperature increases from 450 to 520 °C, Cu/In increases from 1 to 1.1 The SEM image in Fig. 4(a) showed that the surface of a Cu-rich film prepared at substrate temperature (T_{sub}) 450°C (Cu/In) = 1.1 and (S+Se)/(Cu+In) ≈ 1. This morphology is dominated by a big triangular crystal with sizes up to 10 µm characteristic of the binary phase Cu_2Se, separated by a bottom consist of small crystalline 5 µm and more joined corresponding to the stoichiometric CuInSSe phase. All the films composition is rich in Cu. It has been noted, however, that the size of the crystal of Cu_2Se decrease when the substrate temperature is increased. Results of EDS analysis indicate that the surface of the layers consists of Cu_2Se phase and that the lower part consists of CuInSS phases (Table 1). On the other hand Fig. 4(b-d), the films deposited (T_{sou}) ≥ 500°C have a surface of smaller but very contiguous polyhedral grains giving it a more various shapes and well crystallized faces with size is of the order of 5 µm. The images obtained by SEM on these films show the $CuIn(S_xSe_{1-x})_2$ phase with different surface shapes and size of a more homogenous layer in the bottom. The difference in the substrate temperature deposition of the two phases (Cu_2Se and CuInSS) is partly responsible for this disparity in the shape and size of the grains.

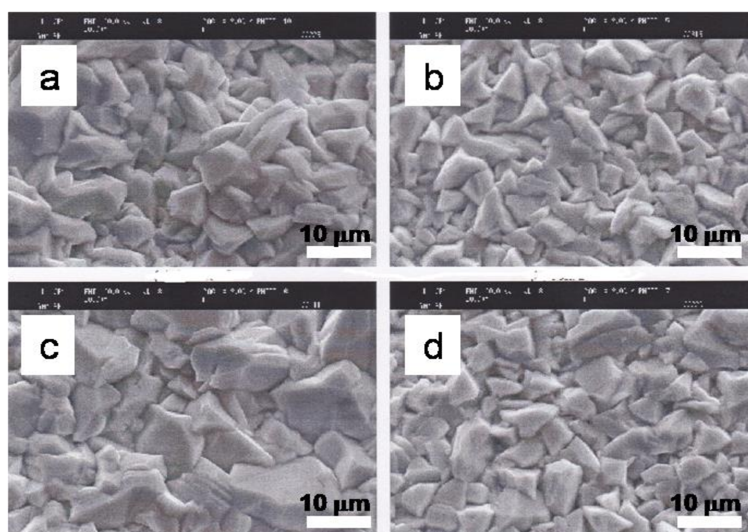


Fig.4.SEM images with composition (a) x=0.27, (b) x=0.28 (c) x=0.41 and (d) x= 0.55.

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It is important to characterize the optical properties of our thin film samples in order to verify the optical transmission and reflection (see Fig.5). The absorption coefficient α was

evaluated from the optical transmission and reflection data. The absorption coefficient of $CuIn(S_{1-x}Se_x)_2$ thin films is more than 10^4 cm^{-1} above the fundamenta1 band edge. These thin films are suitable for solar cells absorber. Fig. 5 indicates an allowed direct optical transition our films, the band gap E_g can be fitted approximately by using Tauc relation from extrapolation of the linear portion of the curve $(\alpha h\nu)^2$ to the interception of photon energy axis $(h\nu)^2$ [16]. The straight line indicated that the gap energy for samples was found to be 1.05, 1.08, 1.14 and 1.18 eV at room temperature. It is clear that the incorporation of sulfur content in an effort to increase the energy gap from $CuInSe_2$.

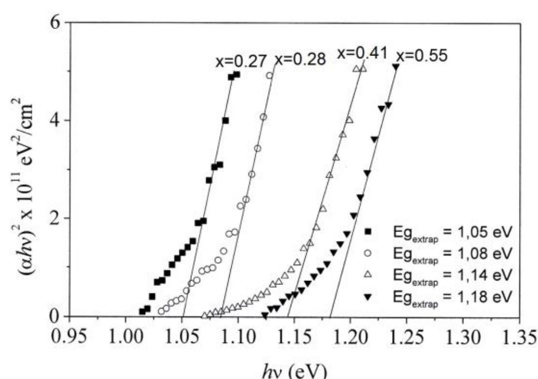

Fig.5. Band gap for CISS filmswith composition x=0.27, x=0.28, x=0.41 and x= 0.55.

The variation in band gap as a function of the composition x where the value of energy gap increases linearly with increasing x, our results are more close to obtained by Walter *et al.* [17] for composition x=0.55 our results are slightly different 0.06 eV. There is a noticiable shift toward higher wavelength corresponding to the presence of a high content of sulfur in the films.

The samples studied are all p-type, have a hole density varying between 10^{16}-10^{17} cm^{-3} and very low mobilities of a few tenths of cm^2/Vs. These results are close to observed by sulfurization [18]. The resistivity of $CuIn(S_{1-x}Se_x)_2$ with x = 0.27, 0.41 and 0.55 films by CSVT is of order 10^2-10^3 Ω cm.

4. Conclusions

CISS thin films have been deposited at a substrate temperature in the range from 450°C to 520°C. Deposited films founddifferent phases when copper and indium ratio from EDS was 1.09 on the XRD spectra obtained a Cu_2Se peak at the substrate temperature 450°C and CISS as chalcopyrite when the substrate temperature increases from 480°C to 520°C. All the sample increased the ratio Cu/In (rich-Cu) is partly responsible for this disparity in the shape and size of the grains.

The bandgaps of $CuIn(S_{1-x}Se_x)_2$ has been observed linearly from 1.05 to 1.18 eV with an increase of the atomic ratio x=[S]/[S+Se] of the thin films, in addition to a better electrical conductivity indicating that the samples have shown are all p-type. A small mobility of a few tenths of cm^2/Vs and the resistivity of films is of order 10^2-10^3 Ω cm was found by four point probe method. Further workis needed to study these effects and improve electrical properties. However, these values could be improved by annealing. Finally, CSVT is a simple and low cost technique very promising for solar cells absorber material.

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