Structural investigation of the Al effect on CIAS thin films prepared in wide range metallic composition

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Abstract. Investigation was performed to one of the chalcopyrite materials, Cu(In,Al)Se2 (CIAS) to observed the Al effect on the structural properties. The investigation was done by CIAS preparation, i.e. pulsed laser deposition and selenization, and characterization, i.e. film composition and structure. The Al composition was 0%, 9%, 20%, 28%, 50%, and 67% of [Al]/[In+Al] ratio, and each Al composition had varied [Cu]/[In+Al] ratios for the detail investigation of Al effect. In the phase formation, the results show that Al hinders the CIAS chalcopyrite formation at Cu rich composition. CIAS diagram phase is close to the diagram phase of CIS system, which the more Al content in the film leads to a single phase formation of CIAS chalcopyrite.

1. Introduction

Cu(In,Al)Se2 (CIAS) was developed by Al addition into CuInSe2 (CIS). The Al substitutes a part of In composition which is in the same group of periodic table, group III. Since coming from the same group, Al was designed to keep the chalcopyrite formation with a little modification in the properties of CIS chalcopyrite, e.g. wider band gap energy from 1.0-2.7 eV, optically [1] and bigger grain size, morphologically [2].

CIAS is identified by using CIS and CAS because there is no CIAS joint committee on powder diffraction standards (JCPDS) until now [1,3-4]. The Al was reported having ability to shift the X-ray diffraction (XRD) pattern, i.e. XRD pattern will shift to the bigger diffraction angle, 2θ, by the more Al addition in CIAS film [3,5-11]. Then, some reports have counted the structural properties, such as d-spacing of 112 plane diffraction, a-lattice parameter, c-lattice parameter, distortion constant, and cell volume [4-5,7,12]. However, the structural investigation has not explained about Al effect on the CIAS chalcopyrite formation due to wide range of Cu composition, [Cu]/[In+Al] ratio. Therefore, this research was carried out to investigate the effect of Al in the chalcopyrite phase formation and further in the possible secondary phase rising at the thin film.

This investigation was done on CIAS thin films with varied Al composition, presented by [Al]/[In+Al] ratio. Since chalcopyrite material is compositional tolerance material [13], this
investigation was done at wide metallic composition variation by preparing some films with varied Cu composition, presented by [Cu]/[In+Al] ratio, for each Al composition. By this, the investigation of Al effect on the structure would be detail and valid, so that we could distinguish whether the modification generated by Al or other composition, e.g. [Cu]/[In+Al] ratio.

2. Materials and Methods
It was not easy to prepare the CIAS film with certain composition as designed. So that, we prepared varied film compositions and then classified according to the Al composition into many groups for this investigation. By this reason, we have un-uniform gradient of Al composition in the classification, i.e. 0, 9%, 20%, 28%, 50%, and 67% of [Al]/[In+Al] ratio.

2.1. Precursor preparation
The precursor films were prepared sequentially by pulsed laser deposition (PLD) using high purity targets (99.99% purity), i.e. bulk Al, bulk Cu, and powder-compact In-Se, [In]/[In+Se] = 0.25. The Al, Cu, and In-Se targets were 2.5 cm, 2.5 cm, and 1 cm in diameter and the distance from the Al, Cu, and In-Se target to the substrate were 3.5 cm, 3.5 cm, and 3.8 cm, respectively. A pulsed Nd:YAG laser (λ = 1064 nm) with a 270 µs laser pulse delay and 0.45 W was used as the deposition source. The working pressure in the PLD chamber was 4.8 × 10^-4 Pa.

The precursors were prepared at room temperature by tree layer deposition. The Al layer was deposited firstly on a glass substrate, then In-Se layer, and finally Cu layer was deposited on the top for capsulation. Al layer was deposited on the glass for film adhesivity to the substrate [14] and reducing the possibility of Al₂O₃ formation on the surface caused by an unincorporated Al to CIS during CIAS formation in selenization [6]. In-Se layer was deposited on the Al layer and under Cu layer to let In-Se binary form prior to CIAS formation and diffuse to other layer for film homogenization. Finally, Cu layer was deposited on the top to prevent Cu oxidation [14-15], i.e. Cu diffusion to the glass substrate, and reduce In evaporation during selenization. The precursor composition was controlled by adjusting the deposition time.

2.2. Selenization
The precursors were placed into an alumina crucible within Se drops (99.99% purity) as selenization source. The crucible was then covered with aluminum foil to ensure a sufficient Se atmosphere. The selenization process was run using a programmed heating profile in Ar ambient through two temperature holding steps: 156 °C for 20 min and 500 °C for 40 min. A temperature of 156 °C was used to melt the In, allow In diffusion into other layers at the liquid state, and then homogenize the precursor. A temperature 500 °C was used to form CIAS according to the conversion of CIS to CIAS which is initiated at 500 °C [16].

2.3. Characterization
Structural phase analysis was performed by XRD, PANalytical, using Cu Kα radiation (λ = 0.15418 nm). The film composition was determined by electron dispersive X-ray spectroscopy (EDX), HORIBA, built in scanning electron microscopy (SEM), SEM-4100 Hitachi. All characterizations were performed at room temperature.

3. Results and Discussion
3.1. Film composition
All films were designed to have constant Se composition, i.e. 48 at.% < [Se]/[Cu+In+Al+Se] ratio < 56 at.% to eliminated Se effect in the investigation. The metallic composition is in atomic ratio with [Cu]+[In]+[Al] = 100%, [Al]/[In+Al] ratio from 0-67%, and [Cu]/[In+Al] ratio = 0.04-2.72, respectively.
3.2. Structure

The XRD patterns were collected and presented using the PANalytical program, 10-60 °2θ. XRD patterns for all Al compositions show that CIAS can be formed by film composition of [Al]/[In+Al] ratio from 0-67%. Many articles in CIAS reports that the CIAS identification by XRD is dominated by 112 orientation in its growth [6-7,9-11,16-21]. XRD patterns show that the 112 orientation is not dominated in very low [Cu]/[In+Al] ratio. It might be the off-stoichiometry have particular orientation preference or overlap with secondary phase at the same diffraction angle. Further, the JCPDS is identification standard for powder and thin film does not have identification standard yet, so that the CIAS identification does not need following the sequential dominant peaks of the CIAS phase, i.e. 112, 204/220, and then 116/312.

Figure 1 shows the formed compounds from Cu, In, and Se. As chalcopyrite with I-III-IV₂ configuration, all group III sites were occupied by In. In this condition, the CIAS chalcopyrite were formed in single phase at composition 0.42 < [Cu]/[In+Al] ratio < 1.00 and presented by thin films with [Cu]/[In+Al] ratio = 0.56, respectively. The more Cu excess presented by the higher [Cu]/[In+Al] ratio affects the more Cu-Se formation as secondary phase, i.e. CuSe₂ and Cu₃Se. This can be seen clearly on the higher diffraction peak at 31.1 °2θ triggered by the higher [Cu]/[In+Al] ratio, from = 1.00 to 2.32, respectively. In other hand, the less [Cu]/[In+Al] ratio, meaning the more In excess, affects the In-Se formation as secondary phase, i.e. InSe phase.

![Figure 1. XRD patterns of the films with 0% Al substituting In and [Cu]/[In+Al] ratio = 0.36, 0.42, 0.56, 1.00, 1.60, and 2.32, respectively.](image)

Figure 2 shows the formed compounds from Cu, In, Al, and Se. As chalcopyrite with I-III-IV₂ configuration, 9% In sites were occupied by Al. In this condition, the CIAS chalcopyrite were formed in single phase at composition 0.43 < [Cu]/[In+Al] ratio < 1.05 and presented by thin films with [Cu]/[In+Al] ratio = 0.57, 0.58, 0.61, and 0.68, respectively.

The off-stoichiometry triggered secondary phase formation where at film with [Cu]/[In+Al] ratio = 0.04, the CIAS 112 and 204/220 diffraction peaks were detected at 27.123 °2θ which overlapped with In₂Se₃ and 44.733 °2θ which overlapped with InSe diffraction peaks. At this condition, In₂O₃ was also formed as a consequence of the very thin Cu capsulation in selenization from the very low [Cu]/[In+Al] ratio.
Figure 2. XRD patterns of the films with 9% Al substituting In and [Cu]/[In+Al] ratio = 0.06, 0.43, 0.57, 0.58, 0.61, 0.68, and 1.05, respectively.

Figure 3 shows the formed compounds with [Al]/[In+Al] ratio = 20%. The CIAS chalcopyrite were formed in single phase at composition 0.21 < [Cu]/[In+Al] ratio < 1.22 and presented by thin films with [Cu]/[In+Al] ratio = 0.33, 0.44, 0.45, 0.49, and 0.73, respectively. As the [Cu]/[In+Al] ratio = 2.09, Cu₂Se is more dominant than the CIAS.

Figure 3. XRD patterns of the films with 20% Al substituting In and [Cu]/[In+Al] ratio = 0.21, 0.33, 0.44, 0.45, 0.49, 0.73, 1.22, and 2.09, respectively.

Figure 4 shows the formed compounds at [Al]/[In+Al] ratio = 28%. In this condition, the CIAS chalcopyrite was formed in single phase at composition 0.04 < [Cu]/[In+Al] ratio < 1.25 and presented by thin films with [Cu]/[In+Al] ratio = 0.49 and 0.57, respectively. The same condition like at [Al]/[In+Al] ratio = 9%. In₂O₃ was formed at [Al]/[In+Al] ratio = 28% and very low [Cu]/[In+Al] ratio, i.e. 0.04 respectively, by the same reason of the very thin Cu capsulation.
Figure 4. XRD patterns of the films with 28% Al substituting In and [Cu]/[In+Al] ratio = 0.04, 0.49, 0.57, 1.25, and 1.47, respectively.

Figure 5 shows the formed compounds at [Al]/[In+Al] ratio = 50%. In this condition, the CIAS chalcopyrite were formed in single phase at composition $0.17 < [\text{Cu}]/[\text{In+Al}] < 2.72$ and presented by thin film with $[\text{Cu}]/[\text{In+Al}]$ ratio = 0.29 and 0.55, respectively. At this Al composition, $\text{In}_2\text{O}_3$ has been start to form on film with $[\text{Cu}]/[\text{In+Al}]$ ratio = 0.17 and $\text{Cu}_2\text{Se}$ is more dominant than the CIAS in film with $[\text{Cu}]/[\text{In+Al}]$ ratio = 2.72, respectively.

Figure 5. XRD patterns of the films with 50% Al substituting In and [Cu]/[In+Al] ratio = 0.10, 0.17, 0.29, 0.55, and 2.72 respectively.

Figure 6 shows the formed compounds at [Al]/[In+Al] ratio = 67%. In this condition, the CIAS chalcopyrite were formed in single phase at composition $[\text{Cu}]/[\text{In+Al}] < 1.16$ and presented by thin films with $[\text{Cu}]/[\text{In+Al}]$ ratio = 0.70, respectively. At this Al composition, $\text{Cu}_2\text{Se}$ is more dominant than the CIAS started in film with $[\text{Cu}]/[\text{In+Al}]$ ratio = 1.16, respectively.
Analyzing the XRD patterns of Figure 1-6 gives an interpretation that CIAS chalcopyrite can be formed by PLD and selenization at 500 °C from wide range metallic composition, i.e. [Al]/[In+Al] ratio from 0-67% and [Cu]/[In+Al] ratio = 0.04-2.72, respectively. The CIAS chalcopyrite was formed in single phase or with secondary phases depended on the element excess in selenization process. So that, the CIAS chalcopyrite would form along with Cu-Se binary compounds at thin film compositions from stoichiometry to Cu rich CIAS, i.e. [Cu]/[In+Al] ratio ≥ 1.00, respectively. Addition, the CIAS chalcopyrite would form with In-Se binary compounds at thin films with Cu poor CIAS composition, i.e. [Cu]/[In+Al] ratio < 1.00, respectively. The In$_2$O$_3$ would form as In oxide at very low Cu composition with [Cu]/[In+Al] ratio ≤ 0.17, respectively, that would not be depended on the Al composition in the film.

Cu$_2$Se formation was caused by the Cu rich CIAS composition, [Cu]/[In+Al] ratio ≥ 1, identified at 26.6 °2θ which overlaps with CIAS chalcopyrite of 112 diffraction peak and at 31.1 °2θ which overlaps with CIAS chalcopyrite of 200 diffraction peak. Although film has composition [Al]/[In+Al] ratio = 0 and [Cu]/[In+Al] ratio = 2.32, Cu$_2$Se is not the most dominant phase. Also, the Cu$_2$Se diffraction peaks at 31.1 °2θ is not the highest diffraction peak at film with [Al]/[In+Al] ratio = 9% and [Cu]/[In+Al] ratio = 1.05 and at film with [Al]/[In+Al] ratio = 20% and [Cu]/[In+Al] ratio = 1.22, respectively. However, this Cu$_2$Se starts to be the highest diffraction peak at film with [Al]/[In+Al] ratio = 20% and [Cu]/[In+Al] ratio = 2.09. This also becomes the highest diffraction peak at film with [Al]/[In+Al] ratio = 50% and [Cu]/[In+Al] ratio = 2.72. Moreover, this Cu$_2$Se becomes the highest at all Cu rich CIAS films with [Al]/[In+Al] ratio = 67%, even [Cu]/[In+Al] ratio = 1.16, respectively. Figure 1-6 show that the height of Cu$_2$Se diffraction peaks at 31.1 °2θ are higher with the increasing of Al content in the Cu rich films. Thus, Al decreases the stability of Cu$_2$Se, so that the Cu$_2$Se formation becomes easier at higher Al composition, in contrary, the CIAS chalcopyrite formation at Cu rich CIAS composition is more difficult at higher Al composition. The reason might come from the higher formation energy of CIAS than CIS chalcopyrite [22].

At stoichiometry and [Al]/[In+Al] ratio = 0, the phase formation is not single phase of CIAS chalcopyrite, but CIAS chalcopyrite with Cu-Se binary phases. However, the single phase of CIAS chalcopyrite was formed at [Cu]/[In+Al] ratio < 1 and any [Al]/[In+Al] ratio. By this we can conclude that the CIAS diagram phase is close to the diagram phase of CIS system that CIS consists of a two-phase mixture of CIS and Cu$_2$Se at stoichiometry and CIS single phase is formed at off-stoichiometry of In rich CIS composition which can be seen in phase diagram of Cu$_2$Se-In$_2$Se$_3$ pseudobinary section of CIS system [23].

The single phase of CIAS chalcopyrite at off-stoichiometric composition was supported by the defect pair (2V$_{Cu}$+In$_{Cu}$) development in the chalcopyrite tetragonal that the Cu poor condition led Cu
vacancy ($V_{Cu}$) development at low formation energy [24]. This $V_{Cu}$ was electrically neutralized by antisite defect point of Cu at In site ($In_{Cu}$). In CIAS chalcopyrite system with Cu poor condition, the formation energy of $Al_{Cu}$ antisite shall higher than that of $In_{Cu}$. This is an analogical interpretation from CIGS where the antisite of Ga in Cu site ($Ga_{Cu}$) defect point has higher formation energy than that of $In_{Cu}$ because the band gap energy of $CuGaSe_2$ (1.68 eV) is higher than that of CIS (1.04 eV) [25]. Thus, the formation energy of $Al_{Cu}$ will be higher than that of $In_{Cu}$ because the band gap energy of $CuAlSe_2$ (2.67 eV) is higher than that of CIS (1.04 eV). So that, the antisite defect point in compensating the composition for CIAS single phase formation is $In_{Cu}$, the same phenomenon between CIS and CIAS chalcopyrite system.

The effect of Al in CIAS single phase formation supported by defect pair can be analyzed by plotting the thin film compositions of Al composition, i.e. $[Al]/[In+Al]$, versus Cu composition, i.e. $[Cu]/[In+Al]$, Figure 7. The film compositions of CIAS chalcopyrite single phase were marked by grey circles. The limited data of thin films with $[Al]/[In+Al]$ ratio = 28% and 0.04 < $[Cu]/[In+Al]$ ratio < 0.49 gives possible interpretation of having CIAS chalcopyrite single phase at those film compositions. Therefore, we could make a limit line of CIAS single phase composition at off-stoichiometry of In rich CIAS compositions, Figure 7, that the more Al content in the film gives higher possibility to have single phase formation of CIAS chalcopyrite.

4. Conclusion
CIAS was developed by Al substituting the In in CIS to keep the chalcopyrite formation. This research investigated on how Al modifies the chalcopyrite formation in various Cu composition by CIAS thin film preparation and characterization. The results show that CIAS chalcopyrite can be formed in wide range metallic composition, i.e. $[Al]/[In+Al]$ ratio 0-67% and $[Cu]/[In+Al]$ ratio 0.04-2.72, in single phase or with secondary phases depended on the element excess in selenization process. Addition, CIAS chalcopyrite formation of high Al composition at Cu rich CIAS composition is difficult, CIAS diagram phase is close to the diagram phase of CIS system, and high Al composition in the film leads to a single phase formation of CIAS chalcopyrite.

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