INFLUENCE OF THE [Cu]/[In] RATIO ON THE PROPERTIES OF $CuInSe_2$ THIN FILMS

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This study examined the influences of the [Cu]/[In] ratio on the properties of $CuInSe_2$(CIS) thin films prepared by precursor deposition using pulsed laser deposition(PLD) and selenization, in which the [Cu]/[In] ratio of the films was varied from 0.36 to 2.31. Chalcopyrite CIS films formed at all ranges of [Cu]/[In] ratios of the experiment. The films with [Cu]/[In] $\geq$ 0.99, [Cu]/[In] = 0.55 and [Cu]/[In] $\leq$ 0.42 formed CIS with Cu_xSe_y, a CIS single phase and CIS with InSe, respectively. Structural compression of CIS caused by Cu vacancies in a Cu poor composition was observed and relieved near stoichiometry. All films exhibited p-type semi-conductivity and showed high absorption coefficients of ~10^{4-5} cm^{-1}. The band gap increased (0.98-1.34eV) and the carrier concentration decreased (3.46×10^{20}-1.58×10^{18} cm^{-3}) with decreasing [Cu]/[In] ratio. The film morphology varied with the [Cu]/[In] ratio, in which large grains were grown at Cu-rich ratios of [Cu]/[In] $\geq$ 0.99, small and compact grains were grown at a Cu- poor ratio of [Cu]/[In] = 0.55 and CIS grains with InSe nano-rod microstructures were grown with Cu very poor and In very rich ratios of [Cu]/[In] $\leq$ 0.42.

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1. Introduction

CIS has high light absorption properties over a wide range of the solar spectrum and is expected to be a good candidate for solar absorber layer applications [1]. Siemens Solar began to industrialize the process in 1998 since CIS solar cells have achieved conversion efficiencies up to 14.1%[2,3]. In CIS solar cells, the [Cu]/[In] ratios have a significant influence on the properties, such as the optical and electrical properties. [4,5].

A Cu- poor, In- rich composition from CIS stoichiometry is a good solar light absorber composition for CIS thin film solar cell applications, and many studies have focused on the development and characterization of the structural and opto-electrical properties of Cu- poor, In-rich CIS absorbers at [Cu]/[In] ratios ranging from 0.8 to 0.9 for CIS solar cells [6].

On the other hand, the properties of CIS films over a wide range of [Cu]/[In] ratios beyond [Cu]/[In] = 0.8 - 0.9 are not studied systematically for investigating the properties. This study examined the influences of the [Cu]/[In] ratio over a wide range, 0.36 - 2.31, on the CIS film properties including the structure, optical-electrical properties and morphology as a semiconductive materials.

2. Experimental details

Thin film preparation was performed in two-stages: precursor preparation using the PLD and CIS formation by selenization. Characterization involved structural identification, examinations of the optical-electrical properties and morphological observations of the film.

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2.1 Precursor preparation

Soda lime glass substrates, 1.3 cm × 1.2 cm in size, were cleaned by an ultrasonic cleaner (Branson 2510, 40 kHz) and washed with acetone, ethanol and de-ionized water. The precursor films were stacked sequentially by the PLD of an In_2Se_3 powder (99.9%) compacted target and Cu targets (99.99%) at room temperature. In the stacking model, Cu encapsulation is designed to prevent Cu oxidation, i.e. Cu diffusion to the glass substrate and In evaporation during selenization. The precursor composition was controlled by adjusting the deposition time of each target.

The In_2Se_3 and Cu targets were 1 cm and 2.5 cm in diameter, respectively, with corresponding substrate to target distances of 38 mm and 35 mm. A pulsed Nd:YAG laser (λ = 1064 nm) with a 270 µs laser pulse delay and 0.45 W was used as the PLD deposition source. The working pressure in the chamber was 4.8×10^{-4} Pa.

2.2 Selenization

The precursors were placed into an alumina crucible with Se pellets (99.99% purity) for selenization. The crucible was covered to maintain a sufficient Se atmosphere during selenization. Selenization was carried out in Ar ambient using two temperature profiles: 156 °C for 20 min for In melting and 500 °C for 40 min for selenization.

2.3 Characterization

The structure was identified by X-ray diffraction (XRD, PANalytical) using Cu K_α radiation (λ = 0.15418 nm). The film morphology was observed by scanning electron microscopy (SEM, SEM-4800, Hitachi). The film composition was determined by electron dispersive X-ray spectroscopy (EDX, HORIBA). The optical properties of the film were examined by UV-Vis-NIR (Cary 500) spectrophotometry. The carrier concentration was measured using a Hall Effect measurement system (HMS-3000, ECOPIA).

3. Results and discussion

Table 1 shows CIS thin film compositions with various [Cu]/[In] ratio gradient from 2.31 to 0.36, consisting of a Cu very rich-In poor CIS ([Cu]/[In] ratios ≥ 1.6), near-stoichiometric CIS ([Cu]/[In] ratio = 0.99), Cu poor-In rich CIS ([Cu]/[In] ratio = 0.55) and Cu very poor-In very rich CIS ([Cu]/[In] ratios ≤ 0.42) prepared, respectively.

Table 1. Composition, non − stoichiometry and thickness of the film.

Film ([Cu]/[In])	[Cu] (at.%)	[In] (at.%)	[Se] (at.%)	Non-stoichiometry $\frac{2[Se]}{([Cu]+3[In])} - 1$	Thickness (nm)
A (2.31)	34.7	15.0	50.3	0.26	770
B (1.60)	30.3	18.9	50.8	0.17	595
C (0.99)	24.2	24.3	51.5	0.06	823
D (0.55)	15.9	28.7	55.4	0.09	620
E (0.42)	13.3	31.9	54.8	0.01	764
F (0.36)	11.8	32.6	55.6	0.02	838

3.1 Structure

Figure 1 shows XRD patterns of the films. The all films prepared were identified as chalcopyrite CIS by the Joint Committee on Powder Diffraction Standards (JCPDS) from their main diffraction peaks of the (112), (204/220) and (116/312).

The film with a Cu very rich-In poor composition of [Cu]/[In] $\geq$ 1.6 formed CIS with Cu_xSe_y because the [Cu]/[In] ratios are higher than the stoichiometric composition ratio. The films with near stoichiometric CIS ([Cu]/[In] = 0.99) formed CIS but Cu_xSe_y still remained. This agrees with the Gödecke result showing that the stoichiometric composition of CIS, consists of a two-phase mixture of CIS and Cu_2Se [7]. A CIS single-phase was formed at a Cu-poor In-rich of [Cu]/[In] = 0.55, respectively. The phase diagram of the Cu_2Se-In_2Se_3 pseudobinary section of the Cu–In–Se chemical system showed a single phase CIS, in which the lattice is enriched with an excess of In at the off the stoichiometric composition [8]. Finally, CIS with InSe was formed at a Cu very poor In very rich composition of [Cu]/[In] $\leq$ 0.42 because of the excess In. All films formed a CIS compound with a chalcopyrite structure [Cu]/[In] ratios ranging from 0.36-2.31.

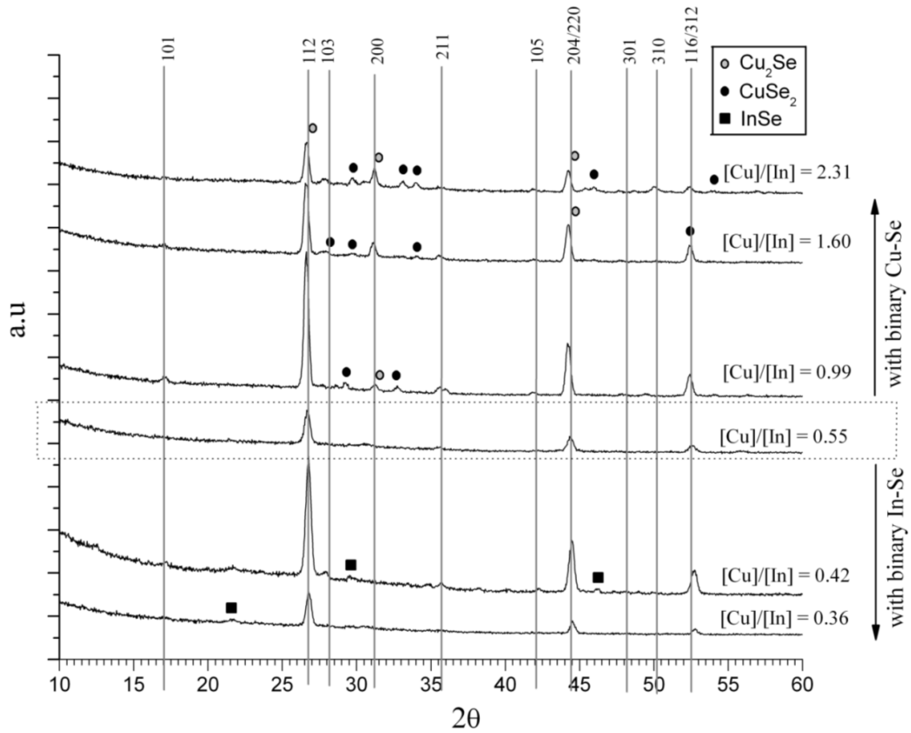

Fig. 1. XRD patterns of the films with [Cu]/[In] ratios = 2.31, 1.60, 0.99, 0.55, 0.42, and 0.36.

The *d* spacing increased with increasing [Cu]/[In] ratio from 0.36 until 0.99 because the XRD pattern of CIS showed a shift to a lower diffraction angle with increasing [Cu]/[In] ratio of the film and became saturated at [Cu]/[In] $\geq$ 0.99.The *d* spacing increasing of the thin film with [Cu]/[In] $\geq$0.99 saturated due to the formation of Cu_xSe_y as a secondary phase after CIS formation of the film. The *d* spacing compression of the CIS structure occurred at [Cu]/[In] < 0.99. This is because of the development of $(2V_{Cu}^{-} + In_{Cu}^{2+})$ defect pairs. When the [Cu]/[In] ratio of the film decreased from stoichiometry, the Cu vacancy (V_{Cu}) has the lowest formation energy and the formation of a V_{Cu} defect will lead to an anti-site defect (In_{Cu}) formation for an electrically neutral arrangement due to $(2V_{Cu}^{-} + In_{Cu}^{2+})$ development in CIS. The calculation by Zhang showed that this defect pair has low formation energy, enabling this defect pair cluster formation in large structures (super cluster), which is the reason for the compositional tolerance in CIS [9-10]. If the [Cu]/[In] ratio of CIS composition is smaller from stoichiometry, the defect pair cluster will be large, which is evidence of a CIS single phase at the thin film at [Cu]/[In] = 0.55, respectively.

3.2 Optical and electrical properties

Table 2 lists the optical and electrical properties of the films, such as the light absorption coefficient (α), optical band gap (E_g), semiconductor type, and electrical carrier concentration. The composition effect on the electrical properties can be modeled by their non-stoichiometry (Δy), where $\Delta y > 0$ and $\Delta y < 0$ indicates *p*-type and *n*-type conductivity, respectively [11-13].

$$\Delta y = \frac{2[\mathrm{Se}]}{([\mathrm{Cu}]+3[\mathrm{In}])} - 1 \tag{1}$$

Table 1 lists the non-stoichiometry (Δy) of the films. All films had $\Delta y > 0$, which indicates p-type semiconducting behavior from non-stoichiometry.

Table 2. Absorption coefficient (α), optical band gap energy (E_g), semiconductor type and carrier concentration of the film

Film (Cu/In)	α (cm^{-1})	E_g (eV)	Semiconductor type	Carrier concentration (cm^{-3})
A (2.31)	3×10^4	0.98	*p*	3.46×10^{20}
B (1.60)	9×10^4	0.98	*p*	-
C (0.99)	8×10^4	1.01	*p*	8.56×10^{19}
D (0.55)	4×10^4	1.34	*p*	1.58×10^{18}
E (0.42)	6×10^4	1.31	*p*	-
F (0.36)	6×10^4	1.02	*p*	1.61×10^{18}

The all films exhibited high absorption coefficients of ~10^4 cm^{-1}.The films with a Cu very rich composition of [Cu]/[In] > 1.60 showed a band gaps of 0.98eV with a high carrier concentration and conductor-like properties. The conductor-like properties were attributed to the Cu_xSe_y secondary phases behaving like a metal [14-15]. The film with a near stoichiometric composition ([Cu]/[In] = 0.99) showed a band gap of 1.01 eV, which is similar to the reported value of 1.04 eV [16]. The band gap of the films with a Cu-poor, In-rich composition of [Cu]/[In] = 0.55 and 0.42 was 1.34 and 1.31 eV, respectively, which is higher than the band gap of stoichiometric CIS. This is caused by defect pair development in the film because a ($2V_{Cu}^{-} + In_{Cu}^{2+}$) defect pair developed as the [Cu]/[In] ratio decreased away from stoichiometry in a super cluster arranging "ordered defect compounds" (ODC), i.e., $CuIn_5Se_8$, $CuIn_3Se_5$, $Cu_2In_4Se_7$, and $Cu_3In_5Se_9$, as a repeat of a single defect pair ($2V_{Cu}^{-} + In_{Cu}^{2+}$) unit of CIS, respectively. The band gaps of the CIS films with Cu-poor, In- rich $CuIn_5Se_8$ and $CuIn_3Se_5$ agree with Zhang's results of 1.34 eV and 1.26 eV, respectively [9].

On the other hand, the low band gap (1.02 eV) at [Cu]/[In] = 0.36 is considered by the defect pair saturation in the effect of InSe phase formation. The carrier concentration of the films with [Cu]/[In] = 1.60 and 0.42 was expected to be in the range, 3.46×10^{20} cm^{-3} to 1.58×10^{18} cm^{-3}, if the carrier concentration of the films are changing regularly, respectively.

3.3 Morphology

Fig. 2 shows a surface and cross section image of the film according to the [Cu]/[In] ratio. All films showed good adhesion with the substrate. Large grains were grown in the films with a Cu-rich and near stoichiometric composition with [Cu]/[In] ≥ 0.99, respectively, by assisting Cu_xSe_y and a sufficient Cu content promoted CIS growth [7,8,17]. Magnified images of a small area on the surface of the film with [Cu]/[In] = 2.31, revealed a granular microstructure that was distributed well over the surface, which was identified as Cu_2Se. The arbitrary shaped particles at the surface of the film with [Cu]/[In] ratio = 1.6 was identified as $CuSe_2$, which have a hexagonal microstructure on the surface. This agrees with the identification of Cu_2Se and $CuSe_2$ by the granular microstructure and hexagonal microstructure, respectively [18].

The film with [Cu]/[In] = 0.55 showed fine, compact grains with homogeneity, revealing polycrystalline CIS only. This suggests that a homogenous film can be prepared with a Cu-poor, In-rich CIS composition of [Cu]/[In] = 0.55. Many nano-rod phases on the CIS surface were observed on the films with a Cu-very poor, In-very rich composition of [Cu]/[In] ≤ 0.42, and were assigned to an InSe phase.

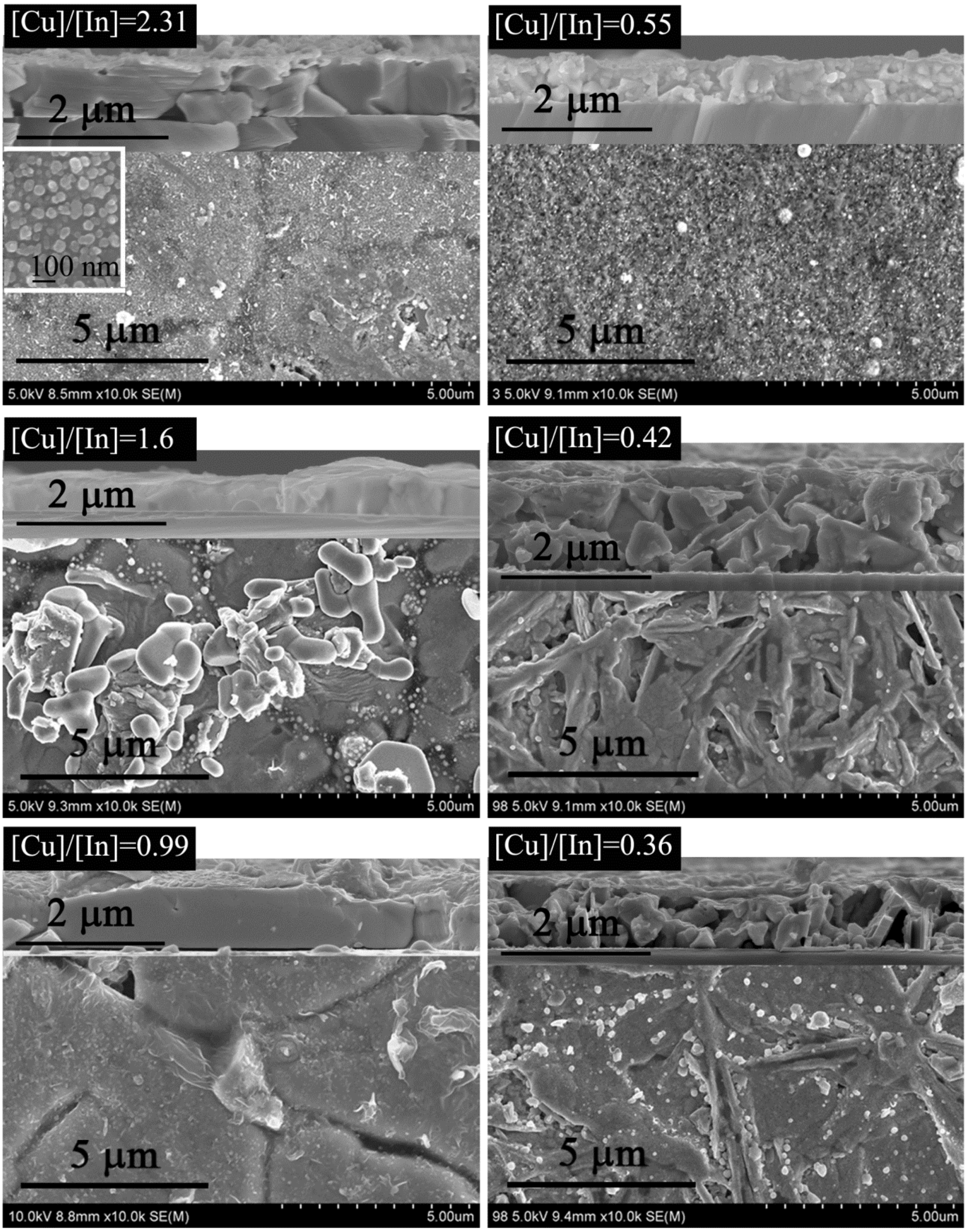

Fig. 2. Surface and cross section morphology of the films with [Cu]/[In] = 2.31, 1.60, 0.99, 0.55, 0.42, and 0.36.

4. Conclusion

This study examined the effects of the [Cu]/[In] ratio on the properties of CIS thin films prepared by PLD deposition and selenization, in which the [Cu]/[In] ratio of the films was varied from 0.36 to 2.31. A CIS phase was formed in thin films with a wide range of [Cu]/[In] ratios, from 0.36 to 2.31, in which thin films with [Cu]/[In] ≥ 0.99 formed CIS with Cu_xSe_y, thin films with [Cu]/[In] = 0.55 formed a CIS single phase and thin films with [Cu]/[In] ≤ 0.42 formed CIS with InSe. CIS structural compression at a Cu poor composition was relieved near stoichiometry. All films prepared exhibited p type semi-conductivity and showed high absorption coefficients of ~10^4 cm^{-1}. The band gap increased gradually (0.98-1.34eV) and the carrier concentration (3.46 x 10^{20}-1.58 x 10^{18} cm^{-3}) decreased with decreasing [Cu]/[In] ratio, which was affected by the ordered defect compounds(ODC) and the existence of secondary phases due to the effects of the [Cu]/[In] ratio gradient. The film morphology varied according to the [Cu]/[In] ratio gradient, in which large CIS grains were grown in the films with a Cu-rich and near stoichiometric composition of [Cu]/[In] ≥ 0.99, small and compact CIS grains were grown in the films with Cu-poor, In-rich composition of [Cu]/[In] = 0.55, and small CIS grains with InSe nano-rod microstructures were grown in the films with a Cu-very poor, In-very rich composition of [Cu]/[In] ≤ 0.42.

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