

Influence of Selenization Pressure on Properties of CIGS Absorber Layer Prepared by RF Sputtering

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ABSTRACT: The effects of selenization pressure on the structural, optical and electrical properties of the CIGS thin films prepared by RF magnetron sputtering using a single quaternary target were investigated. At selenization pressures lower than atmospheric pressure, CIGS thin films formed non-stoichiometric compounds due to deficiencies of Se vapor. In contrast, when selenization process was conducted at above atmospheric pressure, the residence time of Se vapor inside the tube increased so that the Se element could be incorporated within vacant sites of the CIGS structure, resulting in the formation of stoichiometric CIGS thin films. High quality CIGS thin films could be obtained when the selenization process was performed at pressures greater than atmospheric and 550°C.

Key words: CIGS thin film, RF sputtering, Absorber layer, Selenization, Solar cells

1. Introduction

CuIn_{1-x}Ga_xSe₂ (CIGS) thin film is a promising material for the next generation photovoltaic solar cells. CIGS is a direct band gap semiconductor with the capacity to achieve high efficiency solar cells with a thickness of approximately 1~2 μm. CIGS is one of the materials with the highest absorption coefficients among currently available semiconductor materials due to its high absorption coefficient of 10⁵ cm⁻¹. Additionally, its high thermal stability makes the use of post-deposition heat treatment to improve its performance¹⁻³⁾.

CIGS thin films have been prepared by a variety of deposition methods including co-evaporation, sputtering, chemical spray pyrolysis and electrodeposition²⁻⁶⁾. Among these, CIGS thin films prepared by co-evaporation have yielded the highest efficiency; however, this method is difficult to scale up for large deposition areas owing to the complexity of controlling the composition of each element. Sputtering of CIGS quaternary targets has been proposed as a standard method for the fabrication of CIGS films to overcome these problems. The sputtering method has received a great deal of attention owing to its flexibility for mass production, fast deposition rates and stoichiometric transfer of target materials to films on the substrate²⁾. Nevertheless, CIGS films prepared by

sputtering have been shown to be Se deficient due to Se high vapor pressure⁷⁾. Therefore, selenization is frequently required to obtain accurate stoichiometric CIGS films and high cell efficiencies. The selenization process (in a Se/Ar atmosphere) can critically influence the properties of CIGS films; thus, further optimization of this process is required.

High efficiency CIGS films have been prepared by selenization in an H₂Se gas atmosphere; however, it is nearly impossible to effectively implement this process in industry due to the extreme toxicity of H₂Se gas⁷⁾. Currently, the evaporation of Se pellets or powder instead of toxic H₂Se gas is being widely researched⁸⁻¹⁰⁾. The selenization process has made it possible to obtain high quality CIGS thin films and high efficiency solar cells by controlling certain selenization process parameters such as the amount of Se, furnace temperature, time and pressure. Previous studies have extensively investigated the effects of selenization process temperature on the grain growth of the CIGS films; however, the effects of selenization process pressure on the properties of CIGS films have not yet been investigated.

In this study, we evaluated the effects of selenization process pressure on the structural, optical and electrical properties of CIGS films as absorber layers for photovoltaic devices. The films were deposited by RF sputtering using a quaternary Cu(In_xGa_{1-x})Se₂ target and then subjected to selenization in a tube furnace. The effects of selenization pressure on the properties of the CIGS film were investigated at pressures below and above atmospheric pressure.

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2. Experimental

CIGS thin films were prepared by an RF magnetron sputtering system using a single quaternary target on $15 \times 15 \times 2 \text{ mm}^3$ soda lime glasses coated with a $0.5 \text{ }\mu\text{m}$ thick Mo layer that had been deposited by DC sputtering. A 3 inch diameter target composed of the quaternary components of Cu, In, Ga and Se was employed. The compositional ratio of the target was 25:17.5:7.5:50 in at% for Cu, In, Ga and Se, respectively. The chamber was evacuated to base pressures around $0.93 \sim 1.20 \times 10^{-4} \text{ Pa}$ using a turbo-molecular pump backed by a mechanical pump. The substrate temperature was set at 500°C and Ar was used as a sputtering gas. The RF power and process pressure used in this study were 80 W and 0.67 Pa, respectively. The distance between the target and the substrate was fixed at 6 cm and the substrate was rotated at 15 rpm for uniform deposition. All deposited CIGS films were prepared to a thickness of $1 \text{ }\mu\text{m}$. Prior to film deposition, pre-sputtering was carried out for 15 min to remove contaminants from the target surface. The selenization was conducted in a one step process, in which the pressure range of the selenization process was varied from 71.33 to 133.3 kPa inside of the tube for 1 h at high temperature of 550°C in Se vapor under an Ar atmosphere. When the tube furnace pressure increased due to the formation of Se vapor, the pressure was adjusted using a bellows valve that controlled the mechanical pump flow rate.

The thickness of the CIGS films was measured using a surface profiler (Tencor-P1), while X-ray diffraction (XRD) analysis (Philips X'Pert PRO XRD system, Cu $K\alpha$ irradiation, $\lambda = 1.50405 \text{ \AA}$) was employed to examine the crystalline structure of the films. The microstructure and surface morphology of the films were observed using field emission scanning electron microscopy (FESEM) (Hitachi S-4300). Energy dispersive x-ray spectroscopy (EDS) (INCA Energy) was utilized to investigate the contents of each element on the films. An operating voltage of 15kV was employed for both SEM and EDS analysis. The band gap of the CIGS films was evaluated based on the optical transmittance of the films deposited on bare glass using UV-Vis spectroscopy (Lambda 55). The carrier concentration and resistivity of the films were measured using the Van der Pauw method through the Hall effect measurement system (HMS-3000) in a 0.55 T magnetic field at room temperature and Indium soldering was applied to the film's surface as the ohmic contact.

3. Results and discussion

XRD patterns of the CIGS films selenized at various pressures for 1 h at 550°C are shown in Fig. 1. Fig. 1(A) shows all films which exhibited (112), (220) and (312) diffraction peaks at 2θ of 26.8° , 44.65° and 52.8° , respectively, corresponding to the polycrystalline chalcopyrite structure of the $\text{Cu}(\text{In}_{0.7}\text{Ga}_{0.3})\text{Se}_2$ (JCPDS card (35-1102)). The CIGS film selenized at 71.33 kPa showed slightly reduced peaks and shifted to lower diffraction angles, which implied insufficient substitution and/or incorporation of Se and Ga ions into proper lattice sites.

As the selenization pressure increased from 71.33 kPa to 111.3 kPa, the peaks of CIGS films, excluding the peak of Mo substrate, shifted towards higher diffraction angles than those of CIGS films treated at 71.33 kPa. It is suggested that the incorporation Ga ion into CIGS films occurs via substitution of In ions due to the different ionic radii of Ga (0.047 nm) and In ions (0.062 nm)¹⁰. On the other hand, for CIGS films treated at 131.3 kPa, the peaks shifted back towards lower diffraction angles. Moreover, the very weak diffraction peak of CIGS film treated at 71.33 kPa

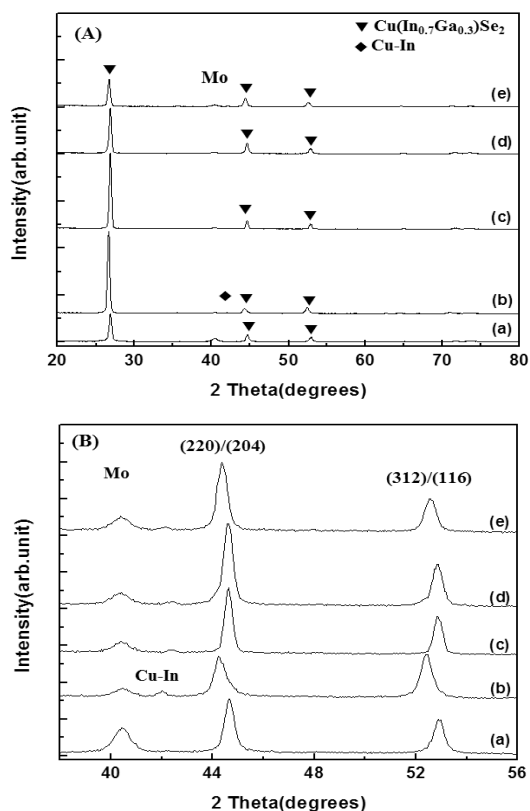


Fig. 1. XRD pattern (A) 2 theta from 20 to 80 degrees and (B) 2 theta from 38 to 56 degrees of (a) as-deposited and selenized CIGS thin films at various pressures for 1 h at 550°C : (b) 71.33 kPa, (c) 101.3 kPa, (d) 111.3 kPa, and (e) 131.3 kPa

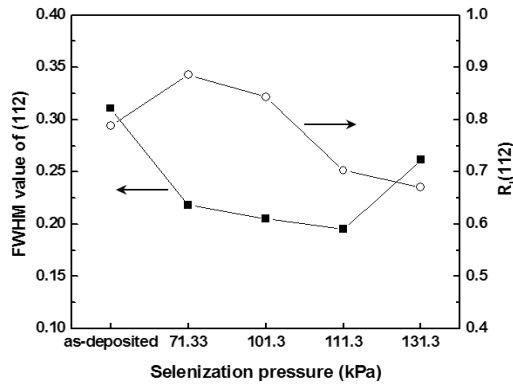


Fig. 2. FWHM and $R_{I(112)}$ value of CIGS thin films selenized at various pressures for 1 h at 550°C

displayed at 42.44° which corresponded to the Cu-In phase (Fig. 1(B)). Indium was segregated on the precursor surface owing to its low melting temperature and high surface mobility. The Cu-In phase was generated due to the diffusion of Ga toward Mo substrate in response to increased pressure¹¹⁾. As a result, the peak of the Cu-In phase gradually decreased as pressure increased and the (112) peak decreased with increasing pressure, which was likely to be related to changes in crystallinity.

Fig. 2 shows the full width at half maximum (FWHM) values of the (112) peaks and preferential orientation degrees of the (112) plane ($R_{I(112)}$) of the CIGS films as a function of selenization pressure. The $R_{I(112)}$ was defined as the ratio of the (112) diffraction peak intensity to the sum of intensities of all the peaks in the XRD pattern [7]:

$$R_{I(112)} = \frac{I_{112}}{I_{112} + I_{204/220} + I_{116/312}} \quad (1)$$

$R_{I(112)} = 1$ implies a complete (112) texture of the layer. The CIGS film selenized at a pressure of 111.3 kPa achieved the smallest FWHM value and the best crystalline quality. Moreover, the decrease of $R_{I(112)}$ with increasing pressure indicated that the preferred orientation was along the (112) direction at low pressure, while the preference changed to the (220) direction as pressure increased due to more incorporation Se into CIGS film. For the

purpose of solar cell fabrication, it is known that the (220) preferential orientation of CIGS films will result in higher efficiency devices. This can be directly attributed to lattice matching of CIGS absorber layer with the CdS buffer layer¹²⁾.

EDS analysis was used to explain the variation in the (112) and (220) peaks and the values of $R_{I(112)}$ with increasing pressure. The EDS data of CIGS films selenized at various pressures is shown in Table 1. The as-deposited CIGS film was Cu-rich, with a Cu/III ratio of 1.23 and Se/Cu ratio less than 2. When the selenization pressure increased, the content of Cu decreased from 29.45 at% to 25.57 at% and the contents of Se increased from 44.41 at% to 48.68 at%. These findings indicate that Se vapor can reside for a longer time on the CIGS films surface, resulting in a reaction between Se vapor and CIGS precursor. In particular, the In content on selenized CIGS films increased compared to that on as-deposited CIGS films. It can be estimated that In was more abundant than Ga on the CIGS surface owing to the diffusion of Ga towards the Mo substrate, causing a different reactivity of In and Ga with Se by thermodynamically favoring the reaction between In and Se rather than with Ga. The (112) and (220) peaks of the selenized CIGS films were confirmed to shift towards a lower diffraction angle at 71.3 kPa and 133.3 kPa (Fig. 1).

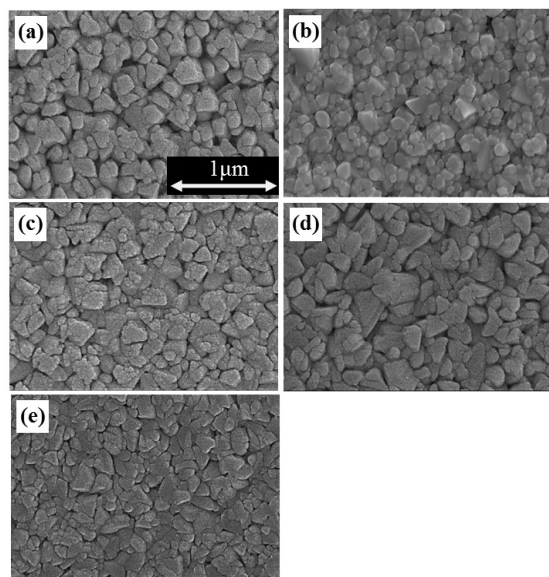
Table 2 shows the results of lattice constant (a and c), grain size, dislocation density and strain of the CIGS films calculated from the XRD patterns. Since the structure of the CIGS film is tetragonal, the deviation of c/a from 2 indicates distortion of the tetragonal structure. As a result, as-deposited CIGS films must have an appropriate stoichiometry to avoid distortions in the tetragonal structure. EDS analysis of the CIGS films revealed Ga and Se deficiencies, which can be explained by the low c/a ratio at low pressures of 71.33 kPa. At a pressure of 111.3 kPa, the Cu/(In+Ga), Ga/(In+Ga) and Se/Cu ratios of the CIGS films were close to their empirical stoichiometric values; hence, the c/a ratio was 1.998. The dislocation density (L) and strain (e) in the CIGS films were calculated using the formula¹³⁾:

Table 1. Chemical composition of as-deposited and selenized CIGS thin films at various pressures for 1 h at 550°C as determined by EDS

Selenization pressure (kPa)	Cu	In	Ga	Se	Cu/(In+Ga)	Ga/(In+Ga)	Se/Cu
As-deposited	29.28	16.39	7.50	46.83	1.23	0.31	1.60
71.33	29.45	20.10	6.04	44.41	1.13	0.23	1.51
101.3	28.10	17.60	7.55	46.75	1.12	0.30	1.66
111.3	26.60	17.67	8.27	47.46	1.03	0.32	1.78
131.3	25.57	19.81	5.93	48.68	0.99	0.28	1.90

Table 2. Variation of lattice parameter, grain size, dislocation and strain of as-deposited and selenized CIGS thin films at various pressures for 1 h at 550°C

Selenization pressure (kPa)	Lattice parameter		c/a	Grain size (nm)	Dislocation density (L) ($\times 10^{14} \text{ m}^{-2}$)	Strain (d) ($\times 10^{-4}\%$)
	a (Å)	c (Å)				
As-deposited	5.762	11.579	2.010	263	14.46	0.318
71.33	5.842	11.909	2.039	374	7.147	9.269
101.3	5.774	11.629	2.014	400	6.309	8.709
111.3	5.731	11.453	1.998	420	5.695	8.274
131.3	5.775	11.633	2.014	370	7.316	9.379

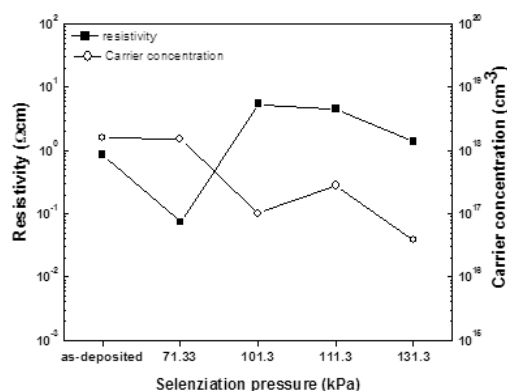
**Fig. 3.** SEM morphologies of (a) as-deposited and selenized CIGS thin films at various pressures for 1 h at 550°C: (b) 71.33 kPa, (c) 101.3 kPa, (d) 111.3 kPa, and (e) 131.3 kPa

$$L = \frac{1}{D^2} \quad (2)$$

$$\varepsilon = \frac{\beta \cos \theta}{4} \quad (3)$$

Dislocation density and strain of the selenized CIGS films decreased with increasing pressure. As pressure increased, the lattice defects decreased due to enhancement of the crystalline size and simultaneous movement of atoms from the grain boundary to the crystalline form.

Fig. 3 depicts the surface morphologies of as-deposited CIGS film and selenized at various pressures. As-deposited CIGS film revealed a non-uniform morphology with faceted crystallites of around 260 nm, with low density and high porosity (Fig. 3(a)). The CIGS film selenized at 71.33 kPa showed small, shiny and rugged grains compared to other films. As the selenization pressure

**Fig. 4.** Resistivity and carrier concentration of as-deposited and selenized CIGS thin films at various pressures for 1 h at 550°C

increased, the crystallite size increased, with triangle and tetrahedral shapes being formed, and the surface morphology became smoother, denser and more compact. The CIGS film selenized at 111.3 kPa showed the largest grain of 420 nm. According to the grain boundary carrier-trapping theory, grain boundaries work as trapping centers and therefore hinder the transport of charge carriers towards the pn-interface¹⁴. To reduce the recombination rate and improve the quality of the films and cell performance, the grain size should be bigger.

Fig. 4 shows the electrical properties of the CIGS thin films selenized at different pressure. All films exhibited p-type conductivity, and the electrical resistivity of the as-deposited CIGS thin film was $8.67 \times 10^{-1} \Omega \text{ cm}$. Selenized CIGS thin films resistivity increased from $7.33 \times 10^{-2} \Omega \text{ cm}$ to $1.4 \sim 5.4 \times 10^0 \Omega \text{ cm}$, while the carrier concentration decreased from $1.57 \times 10^{18} \text{ cm}^{-3}$ to $3.85 \times 10^{16} \text{ cm}^{-3}$ with increasing selenization pressure. Previous studies have reported that a CIGS thin film carrier concentration of 10^{16} cm^{-3} and resistivity ranging from $10^0 \sim 10^1 \Omega \text{ cm}$ are necessary to obtain high efficiency solar cells¹⁰.

NIR-UV-Vis spectroscopy was conducted to understand the optical properties of selenized CIGS thin films. Fig. 5 shows the transmittance and the band gap of films calculated from the

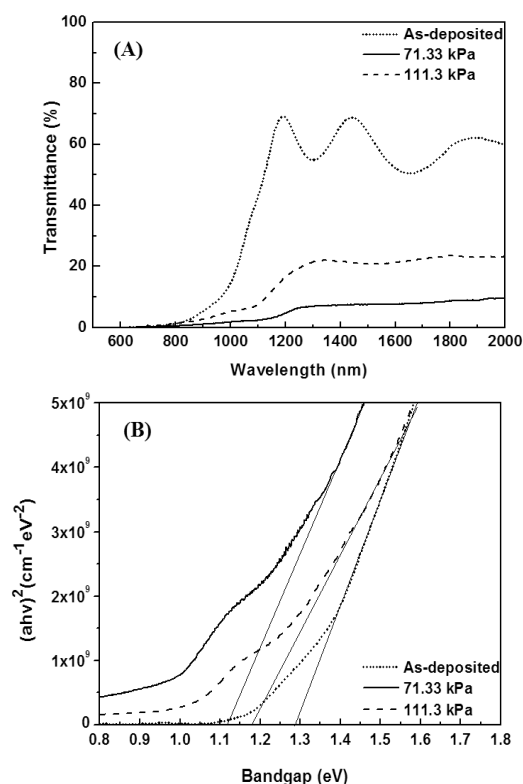


Fig. 5. (A) Transmittance and (B) $(ahv)^2$ vs. $h\nu$ for as-deposited and selenized CIGS thin films at various pressures for 1 h at 550°C

transmittance spectrum measured at various pressures. The transmittance in the NIR region of the selenized CIGS thin film rapidly decreased relative to the as-deposited CIGS thin film, suggesting the formation of a strong absorber layer after selenization. The transmittance of selenized CIGS thin films at 71.33 kPa appeared to be lower than at 113.3 kPa owing to the difference in crystallinity and grain size of the two films (Fig. 1 and Table 2). The transmittance of the CIGS thin films selenized at 71.33 kPa decreased due to an increase in the scattering produced by the small grains. Band gap energy values of 1.3 eV were obtained for as-deposited CIGS thin film; however, lower band gap energy values of 1.12 and 1.19 eV were obtained for CIGS thin films selenized at 71.33 kPa and 113.3 kPa, respectively. The ratio of Ga/III of the CIGS thin films selenized at 71.33 kPa was low (0.23), while at 111.3 kPa it was 0.32, which is closer to the ratio of Ga/III of as-deposited film (0.31). Conversely, the ratio of Cu/III of the CIGS thin film selenized at 111.3 kPa was 1.03, which was much lower than the ratio of Cu/III of as-deposited CIGS thin film (1.23). The variation in the Ga and Cu contents of the CIGS thin films caused the band gap to deviate from its reported value of about 1.1–1.3 eV. A band gap of CIGS thin films of 1.1–1.3 eV has been reported to yield high efficiency

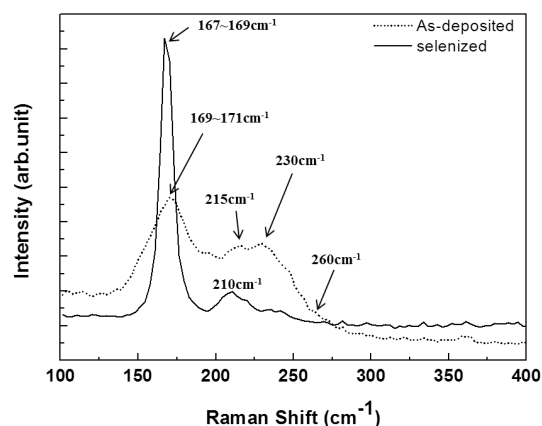


Fig. 6. Raman spectra of as-deposited and selenized CIGS thin films for 1 h at 550°C and 111.3 kPa

solar cells¹⁵.

Fig. 6 shows the Raman spectra of the as-deposited and selenized CIGS thin films at 111.3 kPa. As deposited film exhibited intense peaks within 169–171 cm^{-1} which is assigned to the A_1 mode, also at 215 and 230 cm^{-1} assigned to the B_2/E modes, respectively. Additionally, we detected a very weak peak at 260 cm^{-1} , which is generally attributed to binary Cu-Se structure¹⁶. The A_1 mode peak for the as-deposited CIGS thin films was very broad and showed low intensity, while the A_1 mode peak for the selenized CIGS thin films significantly increased. These findings suggest that heat treatments reduce the defects and binary phases, improving both the film structure and composition and resulting in the formation of single-phase chalcogenides¹⁷. Based on these results and discussion, the effects of selenization pressure on the properties of CIGS thin films could be elucidated and the optimal selenization process for CIGS precursors could be made for high efficiency of the cells.

4. Conclusions

CIGS thin films were prepared by RF magnetron sputtering using a single quaternary target. The Se content of the CIGS thin films selenized at pressures below atmospheric pressure was considerably lower than those selenized at pressures above atmospheric due to the shorter residence time of Se vapor inside of the tube. XRD analysis and Raman spectroscopy revealed an improvement in the crystallinity of CIGS thin films as selenization pressure increased, while SEM showed that the grains became larger and smoother. The energy band gap of the CIGS thin film increased from 1.12 to 1.19 eV and the resistivity increased from 10^{-2} to $10^0 \Omega \text{cm}$, which was likely to be due to reduced

defects in the CIGS structure. The structural, optical and electrical properties of CIGS thin films improved at a selenization pressure of 111.3 kPa, because the residence time of Se vapor was sufficient enough to allow a better incorporation of Se into the CIGS thin film. It can be concluded that good quality CIGS thin films, deposited using a single target, can be obtained when selenization using Se pellets was conducted at pressures greater than atmospheric and 550°C.

Acknowledgments

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