

Research Article

Manipulation of MoSe₂ Films on CuIn(Ga)Se₂ Solar Cells during Rapid Thermal Process

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In this study, the CuIn(Ga)Se₂ (CIGS) crystalline quality and MoSe₂ thickness of films produced by the rapid thermal selenization process under various selenization pressures were investigated. When the selenization pressure increased from 48 Pa to 1.45×10^4 Pa, the CIGS films were smooth and uniform with large crystals of varying sizes. However, the MoSe₂ thicknesses increased from 50 nm to 2,109 nm, which created increased contact resistivity for the CIGS/MoSe₂/Mo structures. The efficiency of CIGS solar cells could be increased from 1.43% to 4.62% due to improvement in the CIGS crystalline quality with increasing selenization pressure from 48 Pa to 1.02×10^3 Pa. In addition, the CIGS crystalline quality and MoSe₂ thickness were modified by the pressure released valve (PRV) selenization process method. The crystalline qualities of the CIGS films were similarly affected by the selenization pressure at 1.02×10^3 Pa in the PRV selenization method and the MoSe₂ thicknesses were reduced from 1,219 nm to 703 nm. A higher efficiency of 5.2% was achieved with the thinner MoSe₂ obtained by using the PRV selenization method.

1. Introduction

There have been reports of the fabrication of 20.4% efficient CuIn(Ga)Se₂ (CIGS) thin film solar cells using the coevaporation method [1]. However, with this process it is still very difficult to scale up the useful area so as to achieve good solar cells. A better fabrication technique for CIGS to be used in industrial applications is sputtering using an ideally mixed Cu-In-Ga (CIG) alloy precursor followed by selenization in a rapid thermal process (RTP) system [2]. The problem is the ease with which an MoSe₂ layer forms at the interface between the CIGS and the Mo [3–5]. This occurs because of the high vapor pressure and the low melting point of Se at 221°C which is generated at the moment of rapid heating. Volobujeva et al. reported that high quality CIGS crystals could be formed with high Se pressure during the selenization process [6]. The MoSe₂ compound forms at the CIGS/Mo interface due to the diffusion of Se into the CIGS film and

the reaction with Mo above 440°C [7]. Many studies have reported that Mo has good electrical properties to serve as an ohmic contact, commensurate thermal expansion coefficient, and chemical stability during the CIGS film growth on a glass substrate [8]. The band gap of MoSe₂ is about 1.41 eV, which is higher than that of the CIGS material. A thin MoSe₂ compound forms between the CIGS/Mo interface which leads to a quasiohmic contact property [9] and an increase in the open-circuit voltaic (V_{oc}) device characteristics [10] due to the back surface field effect (BSF) [11]. The efficiency of a solar cell with a 140 nm thick MoSe₂ layer shows an enhancement of about 2.7% compared to a cell without the MoSe₂ layer [12]. However, it is found that the thicker MoSe₂ (10^1 – 10^4 Ω-cm) [13] forms high resistivity due to excessive selenization pressure. The related photovoltaic performance due to the short-circuit current density (J_{sc}) and series resistance (R_s) is affected which leads to a low efficiency in the solar cell. Some research studies have shown a decrease in the MoSe₂

thickness with increasing Mo sputtering pressure [14]. The MoSe_2 thickness can also be controlled by the Na content from the substrate [14]. However, there is a decrease in the efficiency of solar cells due to a high resistivity of Mo films produced with a high Mo sputtering pressure and the small grain size of CIGS films with excessive Na content. Palm et al. reported that CIGS films which formed on oxygen-rich Mo film had much thinner MoSe_2 layers [15]. Furthermore, Duchatelet et al. noted the formation of a thinner MoO_2 layer on the Mo surface when using the thermal oxidation method, which leads to an effective reduction of the MoSe_2 film thickness [16]. The conductivity characteristics decrease as the oxygen content in the Mo film increases [17], which leads to a reduction in the J_{sc} of the solar cell. The stability of the solar cell decreases due to the high water solubility of the MoO_2 layer. Therefore, it is more important to focus on how to control the relationship between the quality of the CIGS crystal and the thickness of the MoSe_2 . In this study, we adjusted the RTP selenization pressure to modify the quality of the CIGS crystal and the thickness of the MoSe_2 and then investigated the corresponding photovoltaic performance of CIGS solar Cells.

2. Experimental

The reaction kinetics of the CIGS/ MoSe_2 films was investigated using the Se/CIG/Mo structure. The CIG precursor was sputtered using Cu-In-Ga alloy targets (40 : 44 : 16 wt%) onto a Mo/glass substrate in a DC magnetron sputtering system. After deposition, the precursors were coated with a selenium layer using the thermal evaporation technique. The samples were then placed in a graphite box and loaded into the RTP system. The thickness of the Se and CIG precursor was controlled at $3.7 \mu\text{m}$ and $1.3 \mu\text{m}$, respectively. The samples were then selenized at 250°C for 180 sec and 550°C for 180 sec [18] under various selenization pressures (P_{Se} : 48 Pa, 1.02×10^3 Pa, and 1.45×10^4 Pa). In order to reduce the MoSe_2 thickness, the Se/CIG sample was selenized in a quartz lid with a pressure release valve (PRV), as shown in Figure 1. The crystalline structure and morphology of the CIGS films were analyzed by X-ray diffraction (XRD) and field emission scanning electron microscopy (FESEM). The elemental compositions were analyzed using energy dispersive X-ray spectrometry (EDS). The contact resistivity (ρ) of the CIGS/ MoSe_2 /Mo was determined using the three-point method [19]. Finally, CIGS solar cells were fabricated by the deposition of Al grid ($1 \mu\text{m}$)/AZO (800 nm)/i-ZnO (50 nm)/CdS (50 nm) using the standard process. The photovoltaic performance of the CIGS solar cells was measured under standard AM 1.5, 100 mW/cm^2 illumination. The effective area of the solar cell without electrode was about 1.25 cm^2 .

3. Results and Discussion

Figure 2 shows the EDS analysis of CIGS films fabricated under various selenization pressures. The ratios for the Se/CIG composition of the surface and bulk material were

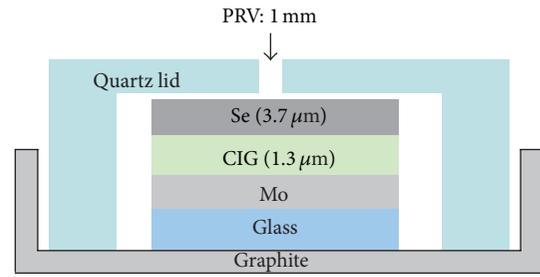


FIGURE 1: Schematic diagram of the selenization equipment with the pressure release valve design.

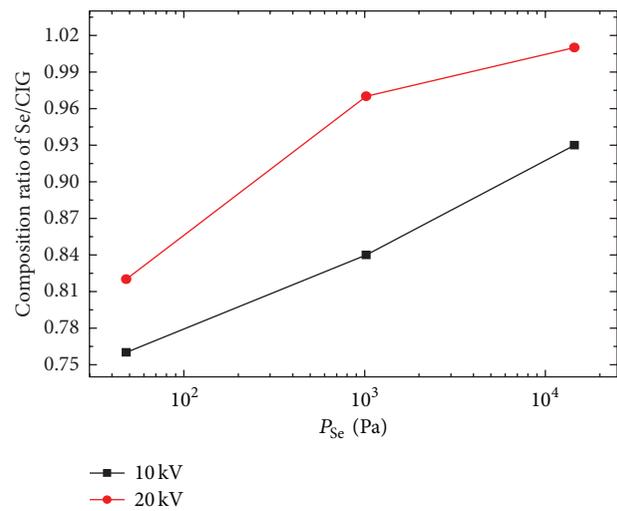


FIGURE 2: Composition ratio of Se/CIG with various selenization pressures.

calculated by EDS measurement applying acceleration voltages of 10 kV and 20 kV, respectively. Obviously, there was an increase in the Se concentration of the CIGS films due to an increase of the selenization pressure. The bulk CIGS appeared to be a Se-poor type with a selenization pressure below 10^3 Pa. The CIGS surface also appeared to be Se-poor due to a substantial amount of Se loss during the selenization process without the supply of Se. The reason is that the melt and vapor points of a Se thin film are lower than the melt and vapor points of a Se bulk. The Se layer is easy to be vaporized immediately during the rapid thermal process which affects the Se vapor to be kept in the unsealed box with difficulty. Figure 3(a) shows the XRD analysis from the Joint Committee on Powder Diffraction Standards (JCPDS) database, where each CIGS film appears to have a chalcopyrite structure (JCPDS number 35-1102). The crystalline intensity of the CIGS phases increased when the selenization pressures were increased as shown in Figure 3(b). There was a reduction in the metallic-Mo phases (JCPDS number 42-1120) due to an increase in the MoSe_2 compounds (JCPDS number 29-0914) with the high selenization pressure. A lower intensity of the MoSe_2 phase was also obtained in the PRV selenization system. Figure 4 shows the FESEM pictures of CIGS films produced with various selenization

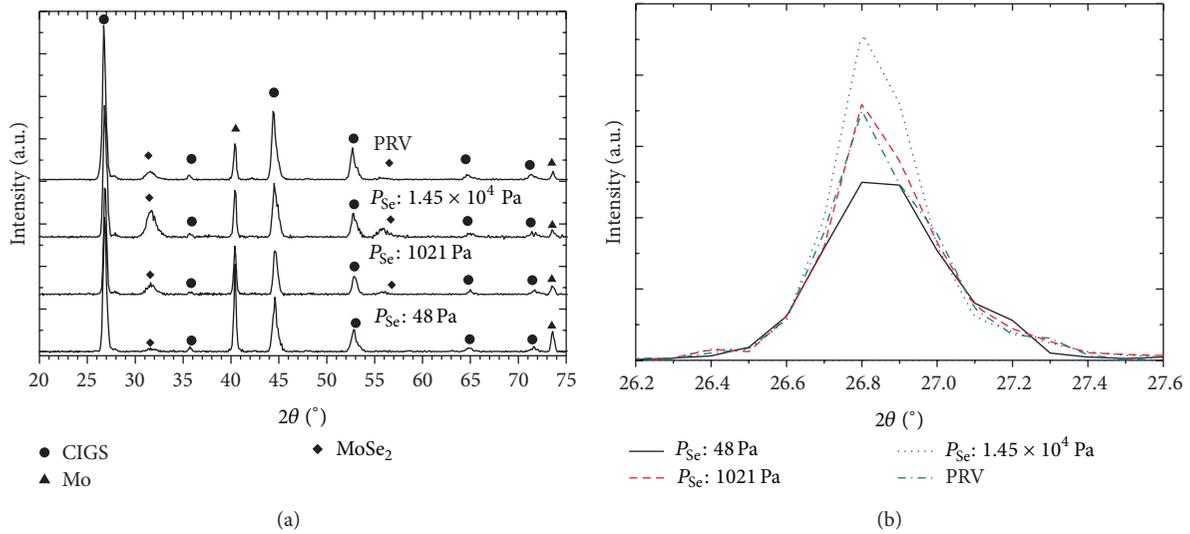


FIGURE 3: XRD patterns with various selenization pressures: (a) CIGS/MoSe₂/Mo films and (b) (112) peak of CIGS films.

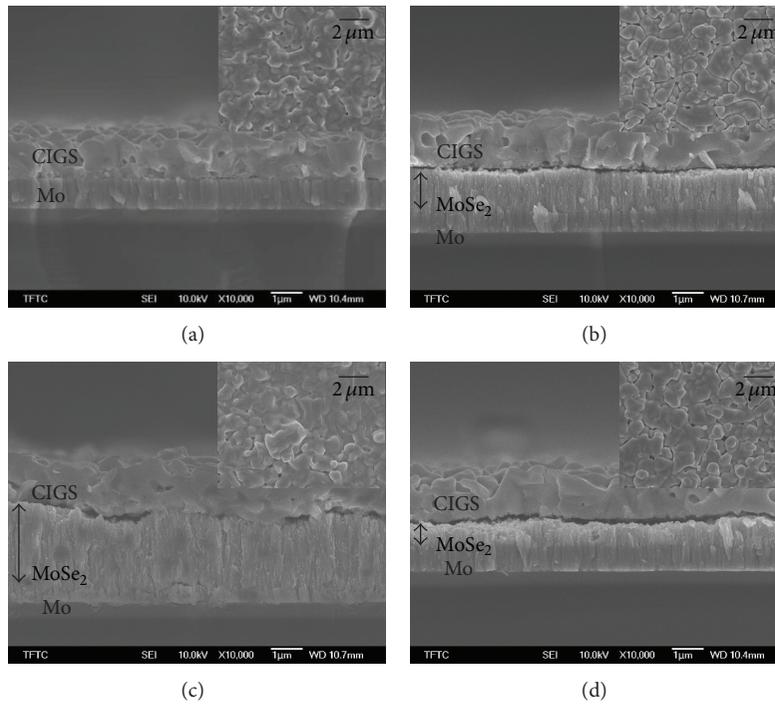


FIGURE 4: FESEM patterns of CIGS films with various selenization pressures: (a) 48 Pa, (b) 1.02×10^3 Pa, (c) 1.45×10^4 Pa, and (d) PRV.

pressures. The CIGS films were about $1.5 \mu\text{m}$ thick. Films shown in Figures 4(a), 4(b), and 4(d) were observed to have a rough surface and nonuniform grains when the selenization pressures were below 10^3 Pa or when using PRV selenization method. In this case, the pressure release valve caused a Se vapor turbulence flux phenomenon in the quartz lid during the selenization process. As can be seen in Figure 4(c), the CIGS film exhibited smooth, uniform, large crystals with sizes of about $2\text{-}3 \mu\text{m}$ at high selenization pressures of 1.45×10^4 Pa. Before the selenization process, the thickness of

the metallic-Mo film was about $1 \mu\text{m}$. During the selenization process, the Se vapor permeated into the bottom of the CIGS film and reacted with the metallic-Mo. With the increase of the selenization pressure, the thickness of the grown MoSe₂ film was between 50 nm to 2,109 nm which is similar to the previous reports [3, 4]. However, a peeling-off phenomenon at the CIGS/MoSe₂ interface was observed which was caused by excessive stress and expansion of the overly thick MoSe₂ layer that occurred at high selenization pressures, as shown in Figure 4(c). The MoSe₂ thickness could be reduced to 703 nm

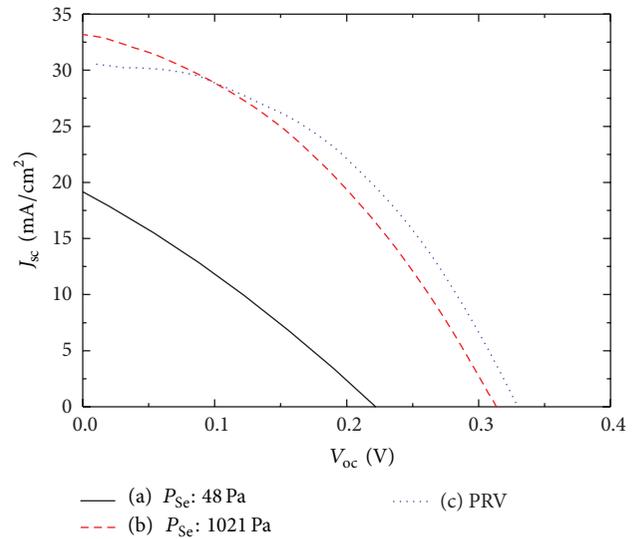
TABLE 1: Crystalline and electrical properties of CIGS/MoSe₂ films with various selenization pressures.

No.	Selenization		CIGS		CIGS/MoSe ₂ /Mo	
	P_{Se} (Pa)	FWHM (112) ori.	Grain size (112) ori.	MoSe ₂ (nm)	ρ ($\Omega\text{-cm}^2$)	
a	48	0.40	20.41	50	0.013	
b	1.02×10^3	0.35	23.32	1,219	0.032	
c	1.45×10^4	0.31	26.33	2,109	0.046	
d	PRV	0.36	22.67	703	0.022	

TABLE 2: Photovoltaic performance of CIGS solar cells with various selenization pressures.

No.	Selenization press. (Pa)	V_{oc} (V)	J_{sc} (mA/cm ²)	FF (%)	η (%)	R_s ($\Omega\text{-cm}^2$)
a	48	0.22	19.2	28.5	1.43	9.01
b	1.02×10^3	0.31	33.2	37.8	4.62	3.82
c	PRV	0.33	30.6	43.8	5.20	3.54

by using the PRV selenization method. The results showed that the diffusion rate of Se was much faster than the reaction kinetics rate of CIGS under a high selenization pressure. The diffusion rate of Se can be controlled by the selenization pressure. The MoSe₂ thicknesses, CIGS crystalline qualities, and contact resistivity of CIGS/MoSe₂/Mo films produced under various selenization pressures are summarized in Table 1. The CIGS crystalline quality and grain size with the (112) orientation were calculated using Scherrer equation from the XRD measurement. The results showed that the grain size of (112) orientation was increased with the increase of the selenization pressure. The results showed that high crystalline quality CIGS films could be achieved under high selenization pressures. The crystalline qualities of CIGS films were similar by selenization pressure at 1.02×10^3 Pa and by the PRV selenization method because the Se vapor was lost from the PRV during the selenization process. There was a decrease in the CIGS/MoSe₂/Mo contact resistivity from $0.046 \Omega\text{-cm}^2$ to $0.013 \Omega\text{-cm}^2$ which was due to the decrease in the MoSe₂ thickness from 2,109 nm to 50 nm. The photovoltaic performance of CIGS solar cells produced under various selenization pressures is shown in Figure 5 and Table 2. The CIGS films produced under a high selenization pressure at 1.45×10^4 Pa could not be fabricated into a solar cell due to the peeling-off phenomenon at the CIGS/MoSe₂ interface. When the selenization pressure increased from 48 Pa to 1.02×10^3 Pa, the J_{sc} improved from 19.2 mA/cm² to 33.2 mA/cm² and the R_s decreased from $9.01 \Omega\text{-cm}^2$ to $3.82 \Omega\text{-cm}^2$. This was due to the improvement in the CIGS crystalline quality, even the MoSe₂ thickness increased from 50 nm to 1,219 nm. When the selenization pressure was 1.02×10^3 Pa or the process was using the PRV selenization method, the CIGS films produced cells with a V_{oc} performance of 0.31 V and 0.33 V, respectively. This is related to the BSF effect where the voltage drops with the resistance characteristics due to the MoSe₂ thickness. The J_{sc} was reduced from 33.2 mA/cm² to 30.6 mA/cm², which caused the nonuniform grains on the CIGS surface during the PRV selenization process shown in Figure 4. Making a comparison to Table 1, the results show that J_{sc} and R_s are related to the crystalline quality of CIGS films and have more influence than the MoSe₂

FIGURE 5: Photovoltaic performance of CIGS solar cells with various selenization pressures: (a) 48 Pa, (b) 1.02×10^3 Pa, and (c) PRV.

thickness in the solar cells. The efficiency of CIGS solar cells was increased from 1.43% to 4.62% with increasing only the selenization pressure. There are many factors like defect density, surface roughness, element concentration distribution, stoichiometry, and electrical properties that could also affect the cell efficiency. However, one of the important reasons is the properties of the MoSe₂. A higher efficiency of 5.2% was obtained with higher CIGS crystalline quality and thinner MoSe₂ layer by using the PRV selenization method.

4. Conclusions

The formation of CIGS/MoSe₂/Mo structures under various selenization pressures in the rapid thermal annealing selenization process was investigated. When the selenization pressures increased from 48 Pa to 1.45×10^4 Pa, the CIGS crystalline qualities were also improved and the thickness of the metallic-Mo was reduced due to an increase in the MoSe₂

thickness. The CIGS/MoSe₂/Mo contact resistivity decreased from 0.046 Ω·cm² to 0.013 Ω·cm² due to a decrease of the MoSe₂ film thickness from 2,109 nm to 50 nm. However, the excess selenization pressure at 1.45 × 10⁴ Pa led to the peeling-off phenomenon at the CIGS/MoSe₂ interface due to the excessive stress and expansion with a too thick MoSe₂. There was an increase in the efficiency of CIGS solar cells from 1.43% to 4.62% and the J_{sc} was improved from 19.2 mA/cm² to 33.2 mA/cm² due to an increase of the CIGS crystalline quality when the selenization pressure was increased from 48 Pa to 1.02 × 10³ Pa. The thickness of the MoSe₂ also increased from 50 nm to 1,219 nm. The results showed that the J_{sc} is related to the crystalline quality of CIGS films with a more significant influence than the MoSe₂ thickness on these solar cells. In addition, the crystalline qualities of CIGS films were similarly affected by the selenization pressure at 1.02 × 10³ Pa and by using the PRV selenization method. There was a reduction in the MoSe₂ thicknesses from 1,219 nm to 703 nm. A higher efficiency of 5.2% was achieved with a thinner MoSe₂ film by using the PRV selenization method.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

Acknowledgments

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