Impact of Mo barrier layer on the formation of MoSe$_2$ in Cu(In,Ga)Se$_2$ solar cells

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A B S T R A C T

In this study, we investigated the impact of a Mo barrier layer (Mo$_b$) on the formation of MoSe$_2$, as it relates to the performance of Cu(In,Ga)Se$_2$ (CIGS) thin film solar cells with a structure of glass/Mo/Mo$_b$/CIGS/CdS/i-ZnO/ZnO:Al/Al. Experiments show that an increase in the thickness of Mo$_b$ led to a significant decrease in the thickness of MoSe$_2$ as well as a slight reduction in the thickness of the CIGS absorber layer following selenization. This can be attributed to the fact that the Na content in the CIGS absorber increased with an increase in the thickness of the Mo$_b$. Higher Na content in the absorber layer promoted the formation of Na$_2$Se$_x$ at grain boundaries during selenization, thereby reducing the grain boundary diffusion of Se, which retarded the growth of excess MoSe$_2$. Furthermore, the crystallinity of the absorber layer was improved when specific quantities of Na were included, which resulted in a relatively dense absorber layer of reduced thickness. Increasing the thickness of Mo$_b$ also led to a more homogeneous distribution of elemental Ga throughout the absorber layer. Under optimal conditions (i.e., Mo$_b$ = 20 nm), the thickness of MoSe$_2$ was reduced from 819 nm to 220 nm, and device efficiency was increased from 4.9% to 10.03%.

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1. Introduction

In the commercial manufacture of CIGS photovoltaic modules, absorber layers are usually produced by sputtering followed by selenization/sulfurization. During high temperature selenization (above 723 K), the surface of Mo back contact is easily transformed into MoSe$_2$, which is beneficial to the formation of an ohmic contact at the Mo/CIGS interface [1] and helps to improve adhesion to the Mo back contact [2,3]. Nonetheless, the formation of excess MoSe$_2$ can lead to the delamination of the film [4], which can have adverse effects on the Voc and FF of the resulting CIGS solar cells due to the high resistance of the MoSe$_2$ [5]. The production of high efficiency CIGS solar cells requires that the thickness of the MoSe$_2$ layer be reduced to below a particular range [6–8]. The thickness of the MoSe$_2$ layer can be influenced by residual stress in Mo contacts [9], selenization conditions [10–12], the use of a barrier layer [6,7], and sputtering conditions [8,13]. In a comparison of these factors, it has been shown that the application of a barrier layer is the most effective means by which to control the thickness of the MoSe$_2$ layer while minimizing the adverse effects on cell performance [8,11,13]. One previous study applied a TiN diffusion barrier to limit the growth of MoSe$_2$ to ~200 nm under normal processing conditions, thereby significantly improving the lifespan and performance of the resulting devices [6]. Jeon et al. [7] proposed a Mo/MoN$_x$/Mo multilayer to suppress the excessive formation of MoSe$_2$, making it possible to control the thickness of MoSe$_2$ formed after selenization annealing. However, the influence of diffusion barrier on the device performance had not shown in this study. Liu et al. [14] used a similar Ti/TiN diffusion barrier improve surface smoothness, yielding reduced Fe ion diffusion of the stainless steel substrates into the CIGS absorber layer. The influence of diffusion barrier on the formation of MoSe$_2$ had not indicated. TiN and Mo contact films differ in their physical properties, including coefficient of thermal expansion and lattice constant [15,16]. This can lead to interface mismatch at TiN/Mo resulting in the delamination of the film and a reduction in device performance. In this study, we prepared a nanoscale Mo barrier layer on the original Mo back contact in order to retard the excessive growth of MoSe$_2$. The characterization and
influence of Mo₉ barrier layer that contribute to the device performance improvement were examined thoroughly.

2. Experiment details

Mo contacts were sputtered onto soda-lime glass samples (1 cm × 1.5 cm × 1 mm) to a thickness of 500 nm, under a working pressure of 0.533 Pa and sputtering power of 200 W. A Mo₉ barrier layer was then deposited to a thickness of 10–30 nm under a working pressure of 0.667 Pa and sputtering power of 200 W. Bilayer metallic films of In/Cu₇Ga₃ precursor were deposited over the Mo contacts, beginning with elemental In, followed by Cu₇Ga₃, resulting in a Cu–Ga–In film with a total thickness of approximately 600 nm. The In precursor film was deposited using evaporation at a temperature of 1273 K under a working pressure of $2.2 \times 10^{-3}$ Pa. The Cu–Ga metal precursor film was prepared by sputtering under a working pressure of 0.399 Pa at a power of 80 W. We then initiated a two-stage annealing process involving an initial stage at 533 K for 40 min followed by a second stage annealing at...
573 K or 848 K for 40 min. Annealing of the CIGS samples was conducted in a tube furnace under an Ar (purity 99.995%) atmosphere using elemental Se. Following the selenization process, we obtained a CIGS absorber layer with a thickness of approximately 1.5–1.8 µm.

The morphology and thickness of the MoSe₂ films were characterized using a field-emission scanning electron microscope (FE-SEM, JEOL JSM-6700F). X-ray diffraction (XRD, JEOL TF-SEM JSM7000F, CuKα, λ = 1.54052 Å) and a Raman analysis (Ramboss 500i Micro-Raman System, using 532 nm excitation wavelength) were used to investigate the crystalline structure of the Mo back contact and CIGS absorber layer wherein Moₖ layers of various thicknesses were applied. Grazing incidence XRD (GIXRD) revealed a grazing incidence angle of 1° vs. regular 0°/2θ XRD. Secondary ion mass spectroscopy (SIMS, IMS-6f) was used to investigate the depth profiles of the thin film elements. Extraction voltages were set at 10 and 12.5 keV, respectively. Additionally, the current of the O₂ ions was set to 80 and 120 nA, which impacted the surface of the samples with energy of 5.5 and 8 kV, respectively. The Na and Ga intensities in the CIGS layer were determined by integrating SIMS curves obtained from absorber layers of various thicknesses.

Following the deposition of the CIGS absorber layer, we performed chemical bath deposition of CdS buffer layers. Highly resistive layers of intrinsic ZnO and conductive ZnO:Al were then deposited by sputtering. The structure of the resulting device was Glass/Mo/Moₖ/CIGS/CdS/i-ZnO/AlO/Al without an MgF₂ anti-reflection film (see Fig. 1). Device efficiency was measured at 100 mW/cm² using an AM 1.5 solar simulator.

3. Results and discussion

3.1. Characterization of Moₖ barrier layer and impact on MoSe₂ layer

Fig. 2 presents SEM images of Mo contact surfaces with Mo barrier films of various thicknesses. Images of the surface of the Mo contacts reveal that high sputtering power resulted in fish-like grains (about size of 50–90 nm) [8]. The surface of the Mo contact presents clear grain boundaries with no voids, regardless of whether a barrier film was applied. A uniform distribution of nanoscale micro-islands (about size of 5–15 nm) nucleated and grew on the surface of the Mo contact. The micro-islands gradually coarsened with an increase in the thickness of the Moₖ, resulting in indistinct fish-like grains (i.e. Moₖ ≥ 20 nm). Bauer [17] presented a thermodynamic criterion, which states that under equilibrium conditions, the growth mode is determined by the following difference in energy:

$$\Delta \sigma = \sigma_f + \sigma_i - \sigma_s$$

where $\sigma_s$ is the surface free energy of the substrate, $\sigma_i$ is the free energy at the interface, and $\sigma_f$ is the free energy of the film. In cases of metal films, the atoms are generally more bound to each other than to the substrate (i.e., $\Delta \sigma \geq 0$), such that growth progresses in Volmer–Weber (island) mode [18,19]. In addition, Liu et al. [14] indicated that the surface roughness of the substrate may impact the device performances. The AFM measurement result (no show) indicates that the RMS values are 11.8 nm and 12.0 nm from without Moₖ and with 20 nm Moₖ samples. The difference between without Moₖ and with 20 nm Moₖ samples is not significant. Therefore, the issue of the surface roughness of the substrate on the device performances can be ignored in this study.

Near-surface GIXRD scanning was applied to elucidate the influence of nanothick Moₖ on the crystalline quality of Mo contact. Fig. 3 presents GIXRD measurements from Moₖ barrier layers of various thicknesses, indicating that the preferred orientations of the Mo contact are (110) and (211). The peak intensity of Mo(110) was shown to decrease slightly with an increase in the thickness of the Moₖ barrier layer. According to previous research, a relatively sharp Mo(110) peak intensity is an indication of superior crystallinity. It has also been shown that selenization can increase the likelihood of a thicker MoSe₂ layer forming [18,20]. This can be attributed to the fact that the crystalline quality of the near-surface Mo contact degraded with an increase in the thickness of the Moₖ due to the formation of the micro-islands on the surface. Fig. 4 presents SEM images showing cross-sections of CIGS devices with Mo barrier layers of various thicknesses following selenization at first stage at 533 K for 40 min followed by a second stage annealing at 848 K for 40 min. Fig. 5 illustrates the variations in the thickness of the MoSe₂ layer as a function of Moₖ barrier layer thickness. Increasing the thickness of the Moₖ barrier layer resulted in the formation of a significantly thinner MoSe₂ layer. In fact, at Moₖ = 30 nm, the MoSe₂ layer is nearly undetectable. The mechanism by which the nanothick Moₖ layer influences the growth of MoSe₂ is discussed in the following section.

3.2. Influence of Moₖ barrier layer on the absorber layer

Table 1 presents element analysis of the CIGS absorber layer.
with Mo₉₉ barrier layers of various thicknesses following selenization at first stage at 533 K for 40 min followed by a second stage annealing at 848 K for 40 min. The Cu/(In + Ga) ratios are as follows: 0.91 (15 nm Mo₉₉ barrier layer) and 0.93 (20 nm Mo₉₉ barrier layer). The Ga/(In + Ga) ratios are 0.21 (15 nm Mo₉₉ barrier layer) and 0.26 (20 nm Mo₉₉ barrier layer). The Mo₉₉ barrier layer has considerable influence on the content and/or distribution of Ga and In in the absorber layer. Fig. 6 presents the GIXRD results and regular 0/20 XRD of the absorber layers with Mo₉₉ barrier layers of various thicknesses following selenization at first stage at 533 K for 40 min followed by a second stage annealing at 848 K for 40 min. Fig. 6 also lists FWHM values of the outermost and inner layers of the CIGS (112) absorber, which indicate that the highest crystalline quality was obtained from Mo₉₉ barrier layers of 15 nm or 20 nm. Thicker Mo₉₉ barrier layers (i.e., 30 nm) appear to be unfavorable to the formation of crystals in the outermost surface of the absorber layer. The fact that the main secondary phases in the absorber layer are Cu₂₋ₓSe and InSe means that the thickness of the Mo₉₉ layer did not have a notable effect on the amount of secondary phase. Nonlinearity in the relationship between the FWHM of the CIGS (112) and the thickness of the Mo₉₉ barrier layer may be due to the thick Mo₉₉ barrier layer impeding the diffusion of Na from the glass substrate into the absorber layer. This issue is discussed later within the context of SIMS analysis. Fig. 6(b) also reveals that the peak intensity of MoSe₂ (100) decreased with an increase in the thickness of MoSe₂ layers formed on the Cu–In–Ga precursor following selenization with various thicknesses of Mo₉₉:

(a) 0 nm; (b) 10 nm; (c) 15 nm; (d) 20 nm; (e) 30 nm.

Fig. 5. The thickness of MoSe₂ layers formed on the Cu–In–Ga precursor as a function of thicknesses of Mo₉₉.

Table 1
Composition and composition ratios of CIGS absorber layers with Mo₉₉ barrier layers of various thicknesses following selenization at first stage at 533 K for 40 min followed by a second stage annealing at 848 K for 40 min.

<table>
<thead>
<tr>
<th>Mo₉₉ thickness (nm)</th>
<th>Compositions (at %)</th>
<th>Composition ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Cu</td>
<td>Ga</td>
</tr>
<tr>
<td>0</td>
<td>23.31</td>
<td>3.64</td>
</tr>
<tr>
<td>10</td>
<td>23.01</td>
<td>8.18</td>
</tr>
<tr>
<td>15</td>
<td>23.43</td>
<td>6.76</td>
</tr>
<tr>
<td>20</td>
<td>23.28</td>
<td>5.26</td>
</tr>
<tr>
<td>30</td>
<td>24.05</td>
<td>2.04</td>
</tr>
</tbody>
</table>
thickness of the Mo$_b$ barrier layer. The SEM image in Fig. 4 helps to elucidate this observation.

Fig. 7 presents SIMS depth profile analysis of the absorber layer with Mo$_b$ barrier layers of various thicknesses, following selenization at first stage at 533 K for 40 min followed by a second stage annealing at 848 K for 40 min. Fig. 8 summarizes the results from Fig. 7 in a comparison of the distribution of Na and Ga in samples with Mo$_b$ barrier layers of various thicknesses. The thickness of the Mo$_b$ barrier layer was shown to influence the distribution of Na and Ga. It should be noted that, with a 20 nm Mo$_b$ layer, the element distribution curve of Ga is distinct from the others, indicating that the diffusion of Ga into the absorber layer was retarded. However, there is still no consensus with regard to this observation.

Fig. 9 presents an area integral of the Na and Ga distribution values in Fig. 8 with Mo$_b$ barrier layers of various thicknesses, in which the intensity of the Na and Ga in the CIGS layer was determined by integrating individual SIMS curves obtained from absorber layers of various thicknesses. The thicknesses of absorber layers are determined from Fig. 3 using Mo$_b$ barrier layers with the following thicknesses: 10 nm (2 μm), 15 nm (1.8 μm), 20 nm (1.7 μm) and 30 nm (1.5 μm). As shown in Fig. 9, the content of Na and Ga in the CIGS absorber layer increased with an increase in the thickness of the Mo$_b$ layer. About influence of Mo$_b$ on Ga: A thicker layer of Mo$_b$ may act as a barrier layer retard the migration of Ga from the absorber layer into the Mo back contact. Accordingly, this led to an increase in Ga content in the absorber layer following an increase in the thickness of the Mo$_b$ layer. About influence of Mo$_b$ on Na: an increase in the thickness of Mo$_b$ led to a significant decrease in the thickness of MoSe$_2$, which led to an overall reduction in the combined thickness of the Mo$_b$ and MoSe$_2$ layers.

It is the reduction in overall thickness that increases the probability of Na ion migration from the soda glass substrate into the CIGS absorber layer. This explains the increase in Na content in the absorber layer following an increase in the thickness of the Mo$_b$ layer. Wurz et al. discovered that the amount of Ga in the absorber layer increases with an increase in the quantity of Na [21]. These findings suggest a possible correlation between the increase in Ga and Na in the absorber layer.

As shown in Figs. 4 and 5, an increase in the thickness of the Mo$_b$ barrier layer resulted in a significant reduction in the thickness of the MoSe$_2$ layer. This can be attributed to the fact that the content of Na in the CIGS absorber increased with an increase in the thickness of the Mo$_b$ (see Fig. 9). An increase in the Na content in the absorber layer facilitated the formation of Na$_2$Se$_x$ at the grain boundaries during selenization [22], which reduced the grain boundary diffusion of Se, thereby retarding the growth of excess MoSe$_2$. On the other hand, the thickness of the CIGS absorber layer is also inversely proportional to the thickness of the Mo$_b$ barrier layers. An increase in the thickness of the Mo$_b$ barrier layer led to a reduction in the thickness of the CIGS absorber layer. This can be explained by the XRD analysis in Fig. 6(b). When the Mo$_b$ layer was less than 20 nm, the absorber layer exhibited superior crystallinity. The density of the structure in the absorber layer is inversely proportional to its thickness. Improvements in the crystalline quality of the absorber layer resulting from the application of a Mo$_b$ barrier layer can be examined from two perspectives: (1) the content of Na and (2) secondary phases in the absorber layer. As shown in the XRD analysis in Fig. 6(b), the content of Na in the absorber layer increased with an increase in the thickness of the Mo$_b$ barrier layer.
specific quantities of Na entered the absorber layer [23,24]. As shown in the GIXRD and θ/2θ XRD analysis in Fig. 6, no direct correlation was observed between the application of a MoB barrier layer and the formation of secondary phase in the absorber layer. In summary, Na content plays an important role in the crystallinity of the absorber layer. In other words, the content of Na in the CIGS absorber increased with an increase in the thickness of the MoB layer and the crystallinity of the absorber layer improved when specific quantities of Na entered the absorber layer, which resulted in a thinner absorber layer of higher density.

3.3. Device efficiency

Table 2 illustrates the strong influence that the thickness of the MoB barrier has on the thickness of MoSe2 and device efficiency. At the extremes of thickness, the MoB barrier layer has a negative influence on device efficiency. Likewise, an excessively thick layer of MoSe2 would increase resistance, thereby lowering VOC, FF, and device efficiency [5]. In contrast, an excessively thin MoSe2 layer would result in a poor Mo ohmic contact and insufficient back surface field [1]. Thus, optimizing the thickness of the MoSe2 layer is crucial to device efficiency. We also determined that the existence of a MoB barrier layer suppresses the growth of the MoSe2 layer. A MoB barrier layer of 20 nm in conjunction with a MoSe2 of 220 nm improved device efficiency from 4.9% to 10.03%, compared to the results obtained without an MoB barrier layer. Conversely, the application of a thick MoB layer (e.g., MoB = 30 nm) with the aim of limiting the growth of MoSe2 to 20 nm resulted in a reduction in device efficiency to just 3.67%.

Fig. 2 presents the uniform distribution of metallic nanoparticles of MoB (about size of 5–15 nm) on the surface of Mo contact. From an optical point of view, the incorporation of MoB metallic nanoparticles as a back reflector contributes greatly to the light-trapping effects of solar cells [25–27]. It may also affect the measured results of device efficiency.

4. Conclusions

In this work, we prepared a nanothick Mo barrier layer on the Mo contact to retard the formation of MoSe2. Our results show that the thickness of MoSe2 decreased significantly with an increase in the thickness of MoB following selenization. Under optimal conditions (i.e., MoB = 20 nm), the thickness of MoSe2 was reduced from 819 nm to 220 nm, and device efficiency was increased from 4.9% to 10.03%. This can be attributed to the fact that the content of Na in the CIGS absorber increased with an increase in the thickness of the MoB. An increase in the content of Na in the absorber layer facilitated the formation of Na2Se4 at the grain boundaries during
selenization, which reduced the grain boundary diffusion of Se, thereby retarding the excessive growth of MoSe₂. An increase in the thickness of Mob led to a slight reduction in the thickness of the absorber layer and enhanced crystallinity. The content of Na in the CIGS absorber increased with an increase in the thickness of the Mob and the crystallinity of the absorber layer improved when specific quantities of Na entered the absorber layer, which resulted in a thinner absorber layer of higher density. The content of Ga in the CIGS absorber layer increased with an increase in the thickness of the Mob layer. This is because a thicker Mob layer was able to prevent the diffusion of Ga from the absorber layer into the Mo back contact. Furthermore, metallic Mob nanoparticles were uniformly distributed on the surface of the Mo contact. The incorporation of Mob metallic nanoparticles decreased the thickness of MoSe₂ and acted as a back reflector contributing to the light-trapping ability of the solar cells, thereby enhancing the overall absorption performance of the CIGS solar cells.

Fig. 8. SIMS depth profiles of CIGS device as a function of thicknesses of Mob for: (a) Na and (b) Ga elements.

Fig. 9. Area integral of the Na and Ga distribution values in Fig. 7 with Mob barrier layers of various thicknesses, in which the intensity of the Na and Ga in the CIGS layer was determined by integrating individual SIMS curves obtained from absorber layers of various thicknesses.

### Table 2

Influence of thickness of the Mob barrier on the thickness of the MoSe₂ layer and efficiency of the resulting device.

<table>
<thead>
<tr>
<th>Mob thickness (nm)</th>
<th>MoSe₂ thickness (nm)</th>
<th>Voc (V)</th>
<th>Jsc (mA/cm²)</th>
<th>FF (%)</th>
<th>η (%)</th>
<th>Active area (cm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Without (0)</td>
<td>819</td>
<td>0.46</td>
<td>32.95</td>
<td>35.21</td>
<td>4.90</td>
<td>0.295</td>
</tr>
<tr>
<td>10</td>
<td>710</td>
<td>0.49</td>
<td>27.56</td>
<td>46.67</td>
<td>5.58</td>
<td>0.310</td>
</tr>
<tr>
<td>15</td>
<td>650</td>
<td>0.48</td>
<td>34.69</td>
<td>48.48</td>
<td>6.94</td>
<td>0.313</td>
</tr>
<tr>
<td>20</td>
<td>220</td>
<td>0.53</td>
<td>33.98</td>
<td>59.96</td>
<td>10.03</td>
<td>0.318</td>
</tr>
<tr>
<td>30</td>
<td>20</td>
<td>0.45</td>
<td>28.48</td>
<td>32.16</td>
<td>3.67</td>
<td>0.314</td>
</tr>
</tbody>
</table>

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[19] D.S. Ghosh, Ultrathin Metal Transparent Electrodes for the Optoelectronics


