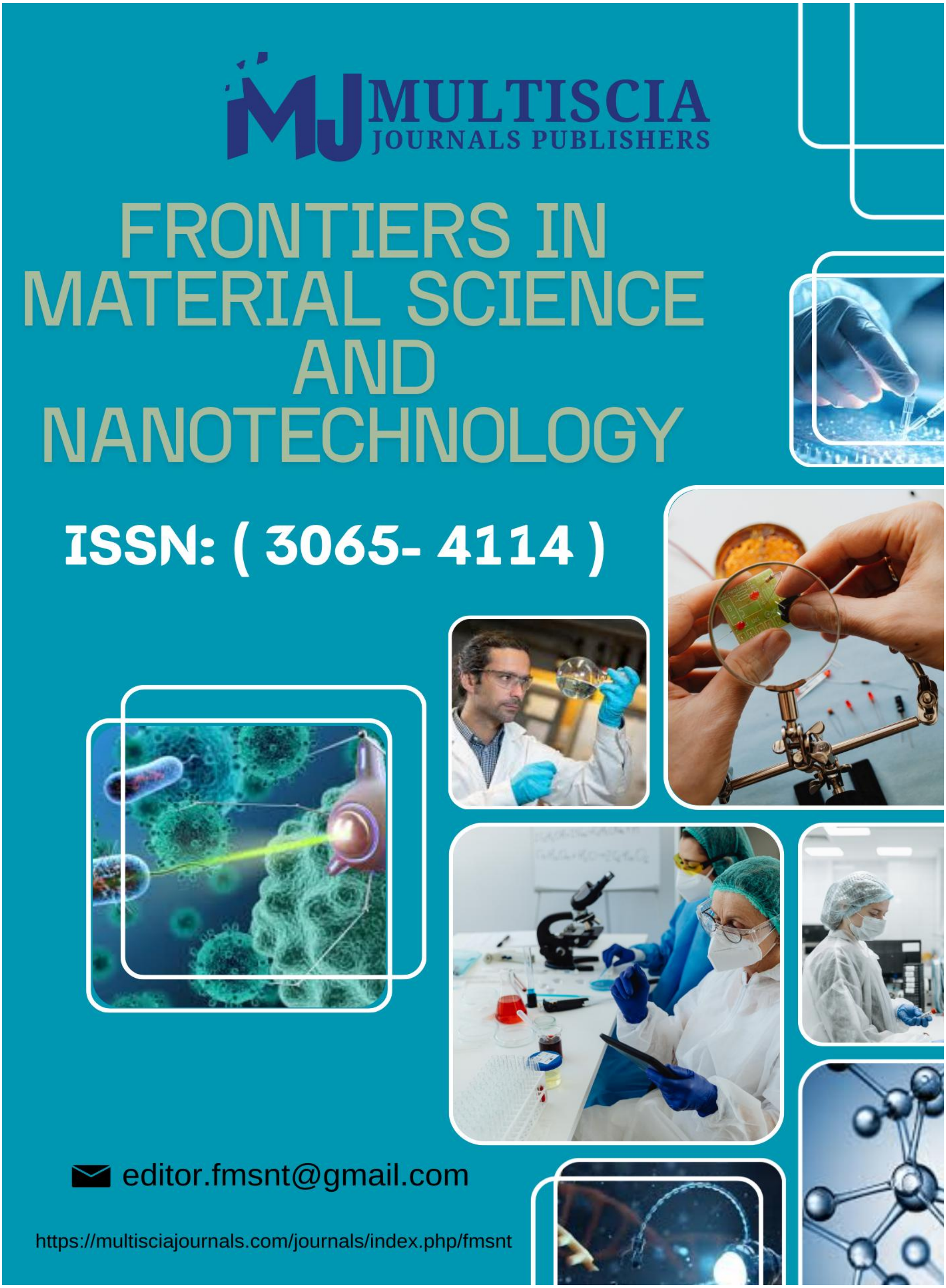

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The Three-Stage Deposition Process for Producing Cu(In,Ga)Se2 Thin Films and How Sodium Affects Their Characterization

CJSung [1], and Chen GC[2]

Department of Material Science and Nanotechnology

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Abstract

This study aims to compare Mo/SLG to Cu(In,Ga)Se2 (CIGS) thin films made using a three-stage deposition technique with a MoNa back contact and determine the effect of sodium on their properties. Unlike CIGS deposited into Na-free substrates, which have the (220/204) preferred orientation, all CIGS thin films placed onto Mo/SLG substrates have the (112) preferred orientation, according to the XRD data. Because sodium has a surfactant effect that may lower the surface free energy during development, the (220/204) orientation becomes increasingly frequent in CIGS thin films as the MoNa thickness grows. Increasing the Na concentration causes the grain size near the back contact to shrink and the Ga gradient to become greater. Raman spectroscopy shows that, in the absence of an OVC chemical, each of the CIGS thin films displays a single peak. The creation of a more stable NaInSe2 compound by replacing Cu vacancy sites with Na causes the absorber layers' Raman peaks to shift from 174 cm-1 to 171 cm-1. Solar cells deposited with CIGS on SLG/Mo have a conversion efficiency of 13.71%, whereas those on Na-free glass/Mo/MoNa(200nm)/Mo have a conversion efficiency of 14.24%.

Keywords: Cu(In,Ga)Se_2; Three-stage Deposition Process; MoNa; Back Contact

Introduction

One of the most appealing thin films for solar cells, Cu(In,Ga)Se2(CIGS) has a straight band gap, a high light absorption coefficient (1×105 cm-1), and an adjustable band gap, among other benefits [1,2]. Modern research has shown that thin films of insufficient-copper CIGS deposited using a three-stage deposition technique may reduce the energy required to create defects to less than 1eV, leading to a high conversion efficiency [3,4]. A composite defect structure with a negative formation energy value (2V − + In2+) can emerge spontaneously due to surface order vacancy compounds (OVCs). This can cause Cd ions to diffuse into the absorber layer's surface, resulting in a buried homo-junction during chemical bath deposition [5]. Also, the creation of the depth-profile gallium gradient is crucial for enhancing the open-circuit voltage and short-circuit current densities of solar devices during the three-stage deposition process [6]. Mastering the gallium gradient is crucial for creating efficient devices [7,8]. In addition, the addition of salt to non-sodium based flexible substrates like stainless steel, titanium, or polymer during the roll-to-roll manufacturing process is crucial for the advancement of high efficiency devices [9,10]. Here is a brief rundown of how the alkali metal addition was felt: Sodium inhibits gallium diffusion during the three-stage deposition process, which in turn affects the grain size in the absorber layer, the preferred orientation of the absorber layers influences Cd ion diffusion, and an increase in the electric conductivity and concentration of hole carriers in the absorber layers can improve the open-circuit voltage and fill factor of solar devices [11–19]. The evaporation-deposition of NaF fluorides is the most used method of sodium addition [14,20-22]. To avoid the substrate adhesion issue and the survival phenomena at low processing temperatures or high NaF content, CIGS solar cells produced with NaF contents lower than soda-lime glass display insufficiencies. Notably, CIGS solar cells may get efficiencies of up to 16.6% when sodium is supplied from a molybdenum target that has been doped with sodium (MoNa) [23]. Using a three-stage deposition procedure with varying thicknesses of MoNa back contacts, this research examines the surface morphology, preferred orientation of the structure, and properties of devices' absorber layers.

Experimental Procedure

CIGS absorber layers were created by plasma-enhanced chemical vapor deposition (PECVD) on soda-lime glass (SLG) and silicon wafers that were covered with around 100 nm silica. The sputtering targets, which are available for purchase, have sodium concentrations of 10%. The quantity of oxygen rose with an increase in the thickness of the MoNa because the sodium was integrated onto the Mo target material as sodiummolybdate (Na2MoO4). Two sets of back contact layers were created using 1000 nm SLG substrates and sandwiched silicon wafers with 500 nm upper and lower layers and 0, 100, and 200 nm MoNa intermediate layers. Various thicknesses of MoNa back contacts may have their resistance maintained at 40-50 μΩcm. An evaporation apparatus fitted with an X-ray fluorescence (XRF) detector was used in a three-stage deposition procedure to create the layers of the absorbers. The first step included co-evaporating In, Ga, and Se onto the substrates at a substrate temperature of 350 ˚C to create the (In,Ga)2Se3 film. In order to create a somewhat Cu-rich composition, with a Cu/(In + Ga)=1.2 ~1.22, the films were subjected to a Cu and Se flux at a substrate temperature of 550 ˚C at the conclusion of the second step. In the third step, the composition went from being Cu-rich to slightly (InGa)-rich by adding In Ga and Se flux. The absorber layers had a thickness of about 1.5 - 1.6 um and were composed of Cu / (In + Ga)= 0.80 and Ga / (In + Ga)= 0.3. An X-ray diffraction (XRD) pattern with a CuKα radiation source (λ=1.5406 Å) and field emission scanning electron microscopy (FESEM) were used to examine the absorber layers' morphology and crystal structure. The absorber layers were characterized using Raman spectroscopy, which makes use of a 488 nm laser source.To enable current collection, devices containing CIGS films were created by depositing a 50 nm CdS buffer layer, a 70 nm i-ZnO, a DC sputtered 350 nm AZO, and a 50 nm Ni/2 um Al front contact grid in a chemical bath. An AM 1.5 solar simulator was used to describe individual solar cells having a surface area of 0.5 cm2.

Results and Discussion

Figure 1 displays the XRD peaks of (112), (103), (211), (220/204), (312/116), (224), (400/008), (316/332), indicating that the structure of all absorber layers is a chalcopyrite phase. While the MoNa back contact showed a (220/204) orientation, the absorber layer placed on SLG showed a (112) preferred orientation. It was possible to quantify the absorber layers' degree of favored orientation. The computation in this work used three peaks, namely (112), (220/204) and (312/116), with the integrated intensities of the chosen peaks being proportional to the total of all peaks in the scanned range, as seen in Figure 2. The creation of Cu vacancies VCu and InCu antisite defects often results in a reduction of surface free energy, which is why the (112) preferred orientation tends to arise in Cu-poor absorber layers [11,13,14]. As the absorber layer grows, the ratio of the (006) plane to the (003) plane in (In,Ga)2Se3 films, which show up at XRD peak locations of around 27° and 46°, may be adjusted to suit the desired orientations of (112) and (220/204), according to reports [15]. It is evident, however, that the (220/204) ratio may be enhanced from

0.44-0.50 nm, with a corresponding drop in (112) orientation from 0.36 to 0.32 nm, when the thickness of the MoNa layer increases from 0 nm to 100 nm. In the literature, models have been found that explain how CIGS absorber layers develop by a three-step deposition process: vapor-liquid-solid. These models also account for the formation of a semi-liquid Cu-Se phase at temperatures over 523 ˚C. A high-quality material with big grains may be achieved via the diffusion channel provided by the Cu vacancies [24–26]. Such CIGS layers typically include sodium concentrations of around 0.1 at% [27-32]. As a result, the correct amount of sodium (Na) needed to create a surfactant effect may take some time to diffuse through the semi-liquid Cu-Se phase and reach the Na-passivated surface of a CIGS grain, which means it may not be immediately absorbed into the CIGS crystal. Instead of the (112) preferred orientation under conditions of excess Na content, which acts as a barrier that limits the inter-diffusion of In and Ga atoms, the surfactant effect is shown to promote the growth of a (220/204) preferred orientation for the formation of the lowest surface energy. The surface morphology of the absorber layers formed on the SLG is seen in Figure 3. Unlike the MoNa back contact, which has smooth and big sharp grains deposited on it, this material has facets and tiny sharp grains. In addition, the shape of the absorber layers on MoNa is noticeably different, with larger grains seen for thicker MoNa contacts. Figure 4 shows the cross-sectional scanning electron microscopy (SEM) pictures of the absorber layers, which reveal a distinct columnar structure. The columnar structure displays a consistent and big grain size from the surface to the back contact in absorber layers created on non-sodium substrates, according to observations. Layers containing Na may show a decrease in grain size along the interface of the absorber layers and back contacts. The finding that Ga has a comparatively low diffusivity is in agreement with earlier research [37]. Concurrently, chemical electronegativity makes it easy to establish bonds between Ga-O and Na-O. The bottom-aggregating Na from the rear contact inhibits the Ga diffusion [38]. This leads to the discovery of a Ga depth profile that is not uniform. Figure 5 displays the Raman spectra acquired at the surface of absorber layers that have been placed on various back contacts. It was determined that the Raman spectra belonged to the order vacancy compound (OVC) (probably with CuIn2Se2.5, CuIn3Se5, CuIn5Se8 in the spectrum) since they showed a single peak without a peak at 154 cm-1 [34]. The primary explanation for the absence of OVC peaks is because, when the copper ratio rises over 0.8, the chalcopyrite band's strength becomes stronger, and the contribution of the OVC bands becomes very insignificant [35-36]. In order from most strongly to weakestly, the absorber layers coated with SLG and with MoNa back thicknesses of 0, 100, and 200 nm exhibit Raman peaks at 171, 174, 173, and 173 cm-1, respectively. In theory, surface-level chemical change of the complex alloy is to blame for the peak shift. Reportedly, a stable compound, NaInSe2, may be formed by substituting Na into Cu sites in NaCu [33]. It could be

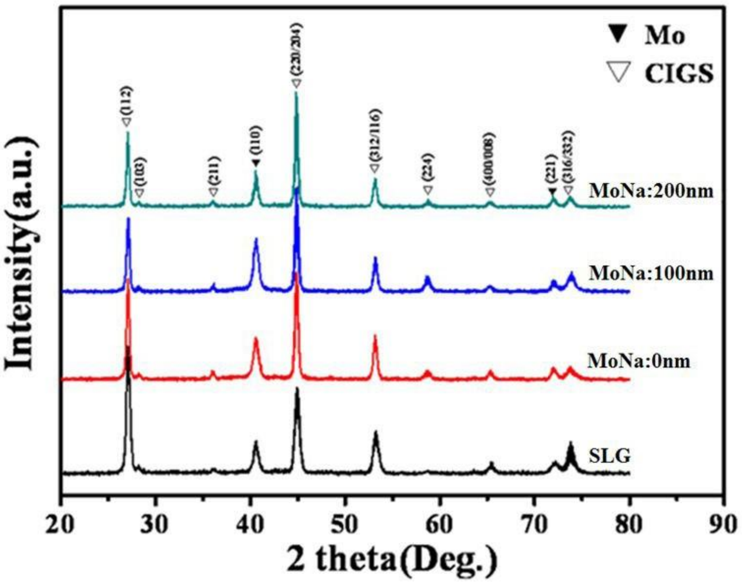

Figure 1: X-ray diffraction pattern of absorber layers with different back contact

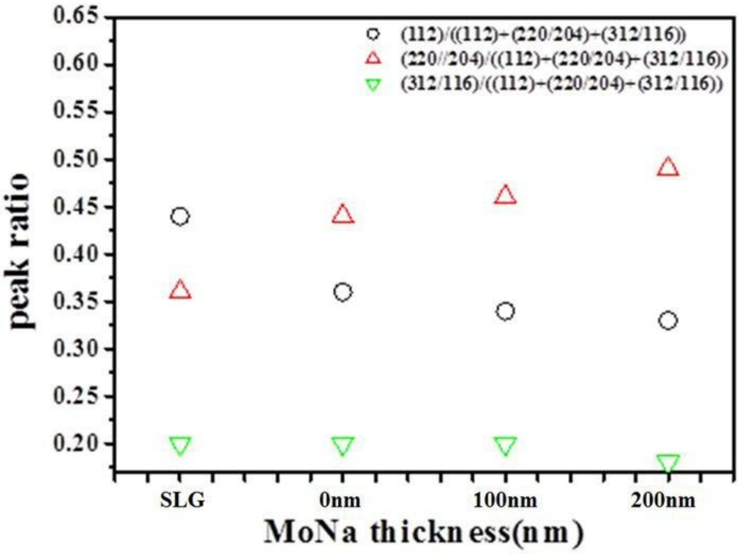

Figure 2: The peak ratio of (112), (220/204), and (312/116) of absorber layers with different back contact

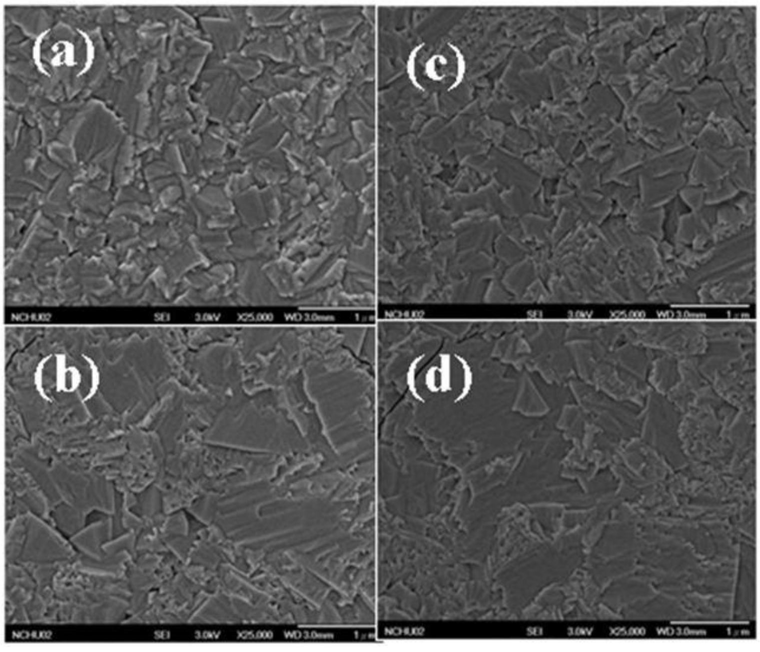

Figure 3: Plan-view SEM micrographs of CIGS film (**a**) SLG, (**b**) MoNa 0 nm, (**c**) MoNa 100 nm, (**d**) MoNa 200 nm

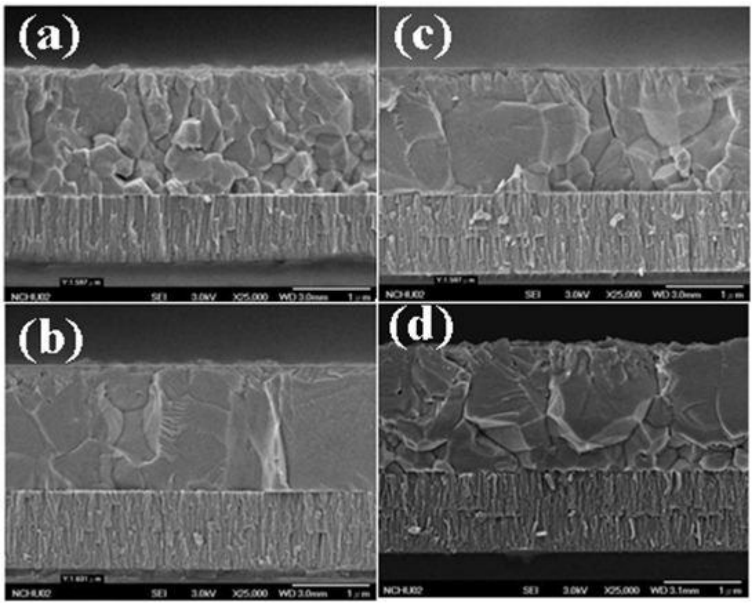

Figure 4: Cross-section SEM micrographs of CIGS film (**a**) SLG, (**b**) MoNa 0 nm, (**c**) MoNa 100 nm, (**d**) MoNa 200 nm

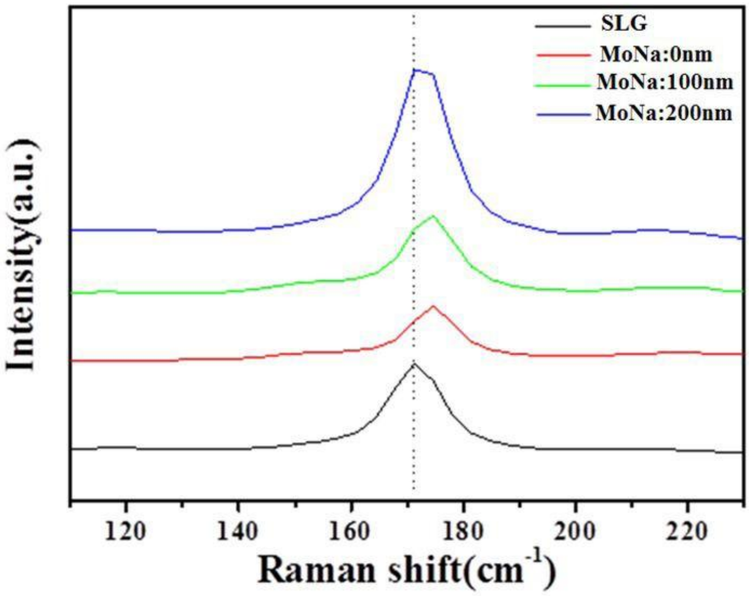

Figure 5: Raman spectra of absorber layers with different back contact

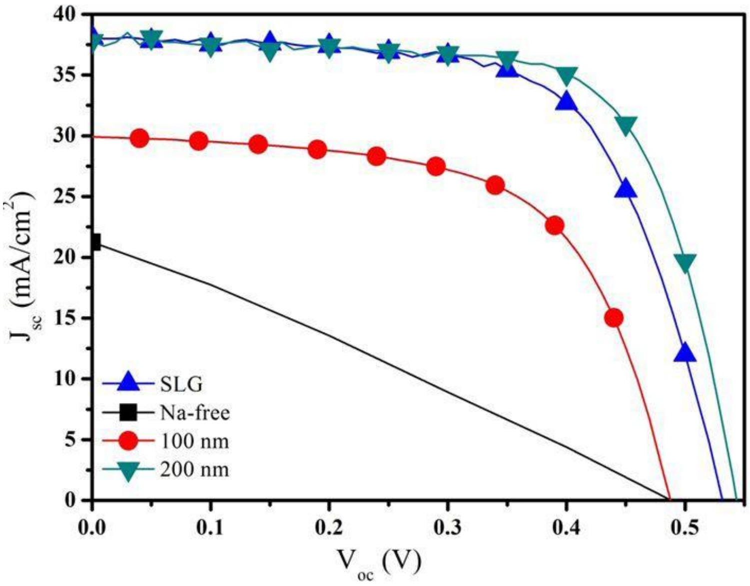

Figure 6: The I-V Characteristic of the solar cells with absorber layers deposited on SLG and different MoNa back contact thickness

demonstrated that a larger amount of Na contributing to the formation of $NaInSe_2$ at the surface can cause a Raman peak shift effect. The different absorber layers fabricated for thin film solar cells had the conventional Al-Ni/ZnO:Al/i-ZnO/CdS/CIGS/Mo/SLG structures. The efficiencies of solar cells with absorber layers deposited on SLG and MoNa backs with thickness of 0 nm, 100 nm and 200 nm are 13.71%, 2.71%, 8.98%, and 14.24%. The I-V characteristics of the solar cells with absorber layers deposited on SLG and MoNa back contacts with a thickness of 200nm are presented in detail, as shown in Figure 6. It is obvious that Na can improve the quality of the absorber layers as well as enhance the open-circuit voltage and fill factor of solar devices [11,12].

Conclusion

This research revealed that the (220/204) preferred orientation development, rather than the (112) orientation, is enhanced by selecting the appropriate Na content to provide a surfactant effect. To rephrase, an impediment to expansion is the excess Na content. It seems that the grain size is decreasing close to the back contacts, which is likely caused by the fact that Na inhibits Ga diffusion. A Raman peak shift effect occurs when additional Na is used to replace Cu, leading to the formation of more NaInSe2. Solar cells with absorber layers coated on SLG and MoNa back contact thickness of 200 nm achieve excellent conversion efficiencies of 13.71% and 14.24%, respectively.

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