INTRODUCTION

Cu(In,Ga)Se₂ (CIGS) thin film solar cells have achieved great success in laboratory in the past few decades and are now entering the large-scale commercial production stage.¹ In the laboratory, researchers at Stuttgart’s Center for Solar Energy and Hydrogen Research (ZSW) and Solar Frontier have obtained a conversion efficiency of 22.6% and 22.9%, respectively.²,³ CIGS is considered as the most promising thin film solar cell technology by many researchers due to its numerous advantages such as high conversion efficiency, low cost, and low toxicity.⁴-⁶ However, there still remain many fundamental issues to be addressed even after many decades of study on CIGS solar cells.

One question is that how the alkali atoms in the soda lime glass (SLG) get incorporated into the CIGS absorption layer. Alkali element plays a vital role in the development of CIGS solar cells as well as other solar cells like kesterite-based Cu₂ZnSn(S,Se)₄ solar cells.⁷-¹⁰ The importance of Na in the electrical performance of CIGS solar cells was first reported in 1993 by Hedstrom et al.¹¹ Since then, many researchers have investigated the effects of alkali elements in different layers of CIGS solar cells.
chalcogenide solar cell materials. The most common approach for the incorporation of alkali atoms in CIGS layer was their natural diffusion from SLG substrate which contained Na and sometimes also K. The incorporation of alkali atoms could greatly enhance both the structural and the electrical properties of CIGS absorber materials in comparison with the sodium-free glass. Tiwari and Schock had determined that alkali elements diffused from SLG through molybdenum (Mo) grain boundaries and subsequently incorporated in the CIGS films. However, excessive Na diffusion from the SLG substrate not only hindered the grain size of CIGS film but also degraded its electrical property as well as the device performances with higher defect density. In view of this result, the control of alkali atom diffusion from SLG to CIGS absorber becomes very critical although the diffusion mechanism remains elusive up to now. Very recently, some researchers have conducted an oxidation treatment to their Mo back contact films prior to CIGS deposition and believed that MoO3 on the surface of Mo back contact plays a key role by reacting with alkali cations from glass and releasing them towards CIGS film upon an alkali concentration difference. However, they have not explained how the reaction could occur between MoO3 and Na2O, which is the main form of Na in SLG.

Another important question is how Ga gradient in CIGS layer can form through a typical three-stage co-evaporation method. CIGS absorber can be viewed as a solid solution of CuInSe2 (CIS) and CuGaSe2 (CGS), with a bandgap that can be tuned from 1.0 eV (CIS) to 1.7 eV (CGS). A V-shaped Ga gradient which can increase the collection efficiency of photogenerated electrons and maintain a decent open circuit voltage of the solar cell has been widely accepted for the fabrication of high-efficiency CIGS solar cells. The realization of beneficial Ga gradient is a milestone in CIGS solar cell fabrications. However, the formation mechanism of Ga gradient is still in debate. Some researchers infer that the formation of Ga gradient during growth is the result of more favorable reaction between Cu and In than between Cu and Ga. Others favor that the Ga gradient is a result of different diffusion barriers for In and Ga atoms via Cu vacancy defects.

The study of the above two topics has contributed to the improvement of the conversion efficiency of CIGS solar cells, however, the un-addressed mechanism of these two questions may have accounted for a large portion of the non-reproducibility of CIGS solar cells observed in many laboratories, rendering the industrialization process of CIGS far behind CdTe solar cells, even though the world record conversion efficiency of CIGS is higher.

Nevertheless, it has been realized for a long time that Mo layer acts as a transport gate for alkali elements from SLG, in addition to its role for adhesion and conduction, double layered Mo back contact on SLG with a porous bottom layer and a dense top layer is often fabricated as the solution. However, there is no systematic and explicit exploration up to now on the control of alkali atom diffusion though designing Mo back contact with projected microstructures. In fact, the role of Mo back contact surface may be underestimated all the time. We speculate that the study of the structure and the surface composition of Mo back contact may hold a key to answer the previous two important questions in CIGS solar cells.

In this work, we design and fabricate a series of tri-layered Mo back contacts via sputtering deposition with the third top layer possessing various microstructure and chemical state to control the alkali element diffusion from SLG substrate to CIGS absorber layer. The effect of such top Mo layer in the back contact is manifested by the performance of the solar cells fabricated on these Mo back contacts. Atomic force microscopy (AFM) is used to characterize the surface morphology and X-ray photoelectron spectroscopy (XPS) measurements are conducted to detect the surface chemical state of the Mo back contact to search for plausible diffusion or reaction mechanisms. Secondary Ion Mass Spectrometric (SIMS) depth profiles of relevant elements in CIGS devices are systematically studied to correlate the Ga grading with the incorporated alkali element distribution.

2 | EXPERIMENTAL DETAILS

2.1 | Fabrication of CIGS solar cells

Mo back contact layers were deposited onto SLG substrates using a direct current magnetron sputtering system with a high-purity Mo target (99.99%). Normally, a double-layered Mo film consisting of 500 nm porous Mo bottom layer and 500 nm dense Mo top layer was sequentially deposited as the back contact. During sputtering no substrate heating was intentionally applied. In this work, to study the effects of the Mo surface on the performance of CIGS solar cells, while keeping the total thickness of the Mo back contact layers to be 1000 nm, a series of tri-layered Mo back contacts were fabricated. By maintaining the porous Mo bottom layer (Ar pressure 1.0 Pa) as 500 nm but reducing the original dense Mo top layer (Ar pressure 0.1 Pa) from 500 nm to 450 nm, a third Mo layer of 50 nm thick was deposited as the final top layer by varying the Ar pressure from 0.1 Pa to 1.0 Pa to tune its microstructure from dense to porous. In order to induce hydroxy group in the Mo back contact, H2O vapor of ~1 × 10−3 Pa was introduced during the growth of the third layer.

On the above prepared back contacts, the CIGS absorbers were deposited using the well-known three-stage co-evaporation process. The standard three-stage co-evaporation
process could be described as follows: In the first stage, In, Ga and Se were evaporated onto the Mo back contact at a relatively low substrate temperature of \(~ 350^\circ\text{C}\); in the second stage, Cu and Se were evaporated at a higher substrate temperature (\(\sim 550^\circ\text{C}\)) until a Cu-rich CIGS phase was just obtained; finally, in the third stage, additional In and Ga together with Se were evaporated on to the substrate, which was maintained at the same temperature as that in the second stage, to obtain an overall Cu-poor CIGS phase. The thickness of CIGS was all kept to be \(\sim 2.3 \mu\text{m}\). No postdeposition treatment of alkali including Na and K was used in this work. The solar cell devices were completed with a \(\sim 50 \text{nm CdS buffer layer via chemical bath deposition, a} \sim 50 \text{nm i-ZnO and a} \sim 350 \text{ nm Al-doped ZnO window layer via RF-sputtering. To facilitate better electron collection, Ni/Al/Ni metallic grids were deposited by electron-beam evaporation through a mechanically defined shadow mask. All the conversion efficiencies were measured on devices without an anti-reflection coating.}

2.2 | Characterizations

The surface morphology of Mo back contact was imaged by using atomic force microscopy (AFM) in the tapping mode (Sr Nano Technology Inc. NanoCute). The optical constant of Mo back contact was measured in the wavelength range from 250 nm to 1600 nm at incidence angles of 58° and 68° by a rotating-polarizer ellipsometer (J.A. Woollam Co., Inc. M-2000U).

The chemical states of the surfaces of Mo back contact were analysed by X-ray photoelectron spectroscopy (XPS) with a Thermo ESCALAB 250Xi apparatus. The X-ray was from a magnesium source of radiation (1486.6 eV) operating at 150 W. High-resolution scans were obtained in the Mo 3d and O 1s regions of the spectrum. The energy of the photoelectron of high-resolution scans was at 0.05 eV step size. The Auger electron spectroscopy (AES) measurements at different depth of Mo back contact were carried out in a UHV chamber with a base pressure less than \(1 \times 10^{-8} \text{ Pa}\) and with a primary electron-beam energy of 1.5 keV. The material removal was achieved by 1 keV Ar\(^+\) sputtering (\(\sim 5 \times 10^{-4} \text{ Pa}\)).

The grown CIGS films were characterized by time-of-flight secondary ion mass spectrometry (ToF-SIMS) (ToF SIMS V, ION-TOF GmbH, Germany) to measure their compositional depth profiles. The different depth in the film was accessed by removing the materials over a \(150 \times 150 \mu\text{m}^2\) area via sputtering with Cs\(^+\) ions of 3 keV ion energy and 30 nA ion current. An area of \(24 \times 24 \mu\text{m}^2\) in the exposed region was analysed using Bi\(^+\) ions as the primary ions with 25 keV ion energy and 1 pA ion current. Only the positive ions in the secondary ions were detected.

The performance of the fabricated CIGS solar cells was examined by current-voltage (J-V) and external quantum efficiency (EQE) measurements. The J-V curve was obtained by a Keithley 2400 source meter under standard test conditions at 25°C under 1000 W/m\(^2\) AM 1.5G illumination from an HM1 sun light simulator source (Newport, USA), whose output intensity was calibrated by the short-circuit current of a standard monocrystalline Si solar cell from Fraunhofer ISE. The EQE measurement was conducted by a QE/incident photon-to-electron conversion efficiency (IPCE) system (Enli Technology Co. Ltd., China) in a wavelength range of 300-1100 nm.
3 | RESULTS AND DISCUSSION

3.1 | Characterizations of Mo surfaces

To characterize the effect of Ar pressure on Mo surface, AFM was used to image the surface microstructure of three representative Mo back contacts with the third layer deposited at 0.1 Pa, 0.5 Pa, and 0.8 Pa. The results are shown in Figure 1A, B, and C, respectively. For the surface of Mo layer deposited at 0.1 Pa, Mo films have slender and dense needle-like grains. As the deposition Ar pressure increases, the shape of the grains remains needle-like but the size becomes relative larger and the surface becomes more porous. The optical constants, including both the refractive index (n) and extinction coefficients (k), of Mo films for these three representative samples were also measured by spectral ellipsometry and the results are displayed in Figure 1D and E. From the effective medium approximation (EMA), the optical constants of a porous Mo film can be regarded as a weighted average of those of Mo and air atmosphere. Thus, the more porous the Mo film is, the more air it contains and the smaller the optical constants. The decreased refractive index and extinction coefficient with increased Ar pressure in the visible wavelength region indeed support the picture that an increasingly porous Mo surface is formed as the Ar pressure increases, in good agreement with the results of AFM images.

Aside from the porosity of the Mo surfaces, XPS was also used to characterize the surface composition and the chemical states. Figure 2 shows a series of measured and fitted Mo 3d and O 1s XPS spectra for the third Mo layer deposited at 0.1 Pa, 0.5 Pa, and 0.8 Pa. Here, the fitting for Mo is decomposed into three components corresponding to Mo$^{6+}$ (232.6 eV), Mo$^{4+}$ (228.6 eV) and Mo (227.8 eV), respectively, according to (i) Peak position: Mo3d3/2 = Mo3d5/2 + 3.13 eV, (ii) Peak full width at half-maximum (FWHM): Mo3d3/2 = Mo3d5/2, and (iii) Peak area: Mo3d3/2 = 2/3 × Mo3d5/2 from previous work.40-42 Similarly, the O1s XPS spectra is decomposed into species associated with different Mo ions valence, namely, at a binding energy of 530.1, 530.8, and 532.1 eV corresponding to O-Mo$^{4+}$, O-Mo$^{6+}$, and OH-Mo$^{6+}$, respectively.43 The O 1s peak at 532.1 eV is a strong indication of the existence of OH group.43,44 All the fitting parameters and the relative amount of each Mo and O species are presented in Table 1. From these data, the relative amount of Mo, MoO$_2$, MoO$_3$, and Mo(OH)$_6$ for each sample can be calculated, as also shown in Table 1. The results indicate that as the Ar pressure increases, while the percentage content of Mo and MoO$_2$ varies within a small margin, MoO$_3$ decreases and Mo(OH)$_6$ increases appreciably.

As seen from Table 1, the water vapor introduced inside the sputtering chamber not only provides O$^{2-}$ for MoO$_2$ and MoO$_3$ formation but also provides OH$^-$ for Mo(OH)$_6$ formation in the sputtering deposition process. To examine whether oxidized Mo only exist at the surface, Auger electron spectroscopy (AES) measurement was carried out on a Mo back contact with its third layer prepared at 0.5 Pa Ar pressure.
Before and after degassing the sample at 150°C to remove possible adsorbents, the oxygen content has only a small change, indicating that most surface oxygen is incorporated during sputtering deposition. With further removal of the back contact materials by Ar+ sputtering, as shown in Figure 3, the AES oxygen signal persists into the bulk of the back contact, revealing a 70% decrease into the bulk and a lower content for the dense second layer but a higher content in the loose first layer. Due to the limited energy resolution of the AES, we are not able to determine the chemical states of oxygen inside the Mo back contact.

3.2 | Device performance

Figure 4 shows the $J-V$ parameters, i.e., energy conversion efficiency ($\eta$), open-circuit voltage ($V_{OC}$), short-circuit current density ($J_{SC}$), apparent series resistance ($R_s$), shunt resistance ($R_{sh}$), and fill factor ($FF$), of the fabricated CIGS solar cells with different Mo back contacts. The results indicate a strong correlation between the CIGS device performance and the preparation condition of the Mo back contacts. The $\eta$ value clearly increases as the Ar pressure for the third Mo layer deposition increases from 0.1 Pa to 0.5 Pa, and then changes the trend to decrease as the Ar pressure further increases to 1.0 Pa. The $V_{OC}$ of the devices fabricated on Mo back contact with the third layer grown at 0.5 Pa and 0.6 Pa reaches the highest value but is only slightly higher than those at lower Ar pressure by ~1% and those at higher Ar pressure by ~3%. The $J_{SC}$ value shows a similar trend with $\eta$ that first increases from ~30 mA/cm$^2$ at 0.1 Pa to ~32 mA/cm$^2$ at 0.5 and 0.6 Pa and then decreases back to ~30.5 mA/cm$^2$ at 0.8 and 1.0 Pa, contributing the largest in the change of conversion efficiency $\eta$. While there are some variations in the $R_s$ value, the $FF$ value remains almost a constant up to 0.5 Pa of Ar pressure and declines by a quite large margin afterwards as the Ar pressure continuously increases to 1.0 Pa.

3.3 | Understanding the relation between device performance and Mo surface microstructures

As described above, the major contribution to conversion efficiency change comes from the short-circuit current density $J_{SC}$. To unveil the mechanism for varied $J_{SC}$ with the Ar sputtering pressure, $EQE$ measurement of selected five samples with 0.1 Pa, 0.3 Pa, 0.5 Pa, 0.6 Pa, and 0.8 Pa was conducted and the results are shown in Figure 5A. It is demonstrated that the variation of $J_{SC}$ is mostly attributed to the different response in the infrared region, indicating that certain changes in the minimum bandgap and the detailed position-dependent energy band structure have taken place. The solar cell device with the third layer of Mo back contact prepared at 0.6 Pa displays the best infrared region response and a red-shifted band edge whereas the solar cell devices with 0.1 Pa ad 1.0 Pa show a clearly poor response in this wavelength region.

| Binding energy (eV) | Mo 3d$_{5/2}$ | Mo 3d$_{3/2}$ | O 1s | Ratio (%) |
|---------------------|---------------|---------------|------|-----------|
| Mo                  | 227.8         | 230.9         | 38.7 | 0.1 Pa    |
| MoO$_2$             | 228.6         | 231.3         | 21.8 | 0.5 Pa    |
| MoO$_2$             | 232.6         | 235.7         | 27.9 | 0.8 Pa    |
| Mo(OH)$_2$          | 227.8         | 230.9         | 33.7 |           |
| MoO$_3$             | 228.6         | 231.3         | 20.0 |           |
| MoO$_3$             | 232.6         | 235.7         | 7.7  |           |
| Mo(OH)$_2$          | 227.8         | 230.9         | 21.1 |           |
| MoO$_3$             | 232.6         | 235.7         | 11.6 |           |

TABLE 1 Fitting results of various peak positions and peak areas of Mo 3d and O 1s spectra. The relative amount of each component of Mo on the surface is also included.

FIGURE 3 Relative Auger intensities of O/Mo as a function of the depth of Mo back contact via Ar+ sputtering time.
To investigate the mechanism for the varied infrared region response, the elemental depth profile for these samples were measured using SIMS and the Ga/(Ga+In) (GGI) depth profiles are plotted in Figure 5B. The obtained GGI ratios were corrected according to composition values obtained from XRF measurements. Obviously, all samples exhibit a double-gradient GGI profile which is characteristic of the co-evaporated CIGS layers. Each GGI profile consists of a downward rear grading (from Mo back contact) and an upward front grading (towards CdS interface). However, there are some obvious differences in the GGI curves and the differences are not caused by accidental factors or measurement errors. Taking two independent runs of growing CIGS films on Mo back contact with the same conditions and procedures, the GGI depth profiles of the CIGS absorber layers are displayed in Figure 5C, revealing very small differences between them which demonstrates the reproducibility of the GGI profiles and the typical measurement uncertainties.

The differences occur mainly in terms of the GGI minimum, which ranges from 0.30 for 0.1 Pa to 0.26 for 0.5 and 0.6 Pa, and secondarily in terms of the strength of the front and back GGI gradient. For the Mo back contact with the
third layer deposited at 0.5 and 0.6 Pa, their GGI profiles exhibit the lowest minimum and both their front and rear GGI gradients are stronger than those of the others. Since the GGI value practically has no effect on the valence band of CIGS and the bandgap of CIGS is monotonic with GGI value, it implies that the position-dependent conduction band edge and the position-dependent bandgap have similar gradient as that of GGI. Thus, it can be inferred that the better infrared response for CIGS films grown on Mo back contact with the third layer prepared at 0.5 Pa and 0.6 Pa is due to their smallest minimum bandgap and their strongest conduction band edge grading.

It is surprising that the GGI profile is affected by the Mo back contact structure. In our experiment, all the CIGS absorber layers were fabricated with the same growth procedures. As pointed out above in Figure 5C, unintentional factors should not cause such noticeable observed differences in the GGI profiles. The only reasonable cause of the observed GGI profile differences must come from the differently prepared Mo back contact. There existed some reports that alkali atoms can influence the formation of Ga gradient in CIGS absorber. Rudman et al observed that co-evaporating a large amount of Na during the CIGS growth process can hinder the inter-diffusion of Ga and In and lead to changes in the GGI profile. It is likely that the amount of alkali atoms diffusing from the SLG substrate to the CIGS layers can be affected by the structure of the third layer in the tri-layered Mo back contact. In turn, these alkali elements can influence the diffusion of Ga and In atoms during the absorber layer growth and lead to different GGI depth profiles.

To confirm the conjecture that alkali atoms diffused from SLG depend on the microstructure of the Mo back contact and the diffused alkali atoms correlate with the GGI profile, SIMS profiling of Na and K elements was performed on the above mentioned five samples and the results of Na and K concentrations in the CIGS layers are shown in Figure 6A and B, respectively. Indeed, there is a remarkable difference in alkali element concentration in these CIGS samples grown on differently prepared Mo back contact, possibly arising from the different amount diffused from SLG which contains both Na and K atoms.

Figure 6 show that the distributions of alkali atoms in CIGS absorber layer. Changing the Ar pressure of depositing the third layer of the tri-layered Mo back contact remarkably affects alkali atom diffusion into CIGS absorber layer and there is an obvious difference between Na and K. Na, which has an overall higher concentration than that of K in CIGS, is mostly accumulated at the CIGS/Mo interface. As the Ar deposition pressure increases, the Na concentration first increases by ~ 3 times from 0.1 Pa to 0.5 Pa and then decreases by ~ 50% from 0.5 Pa to 0.8 Pa. The Na concentration at the CdS/CIGS interface has a similar trend of variation as that at the CIGS/Mo interface but with significantly lower intensity. In the CIGS bulk, however, Na concentration practically exhibits no change as the Ar deposition pressure varies from 0.1 Pa to 0.6 Pa but displays a significant increase at the deposition pressure of 0.8 Pa. It should be noted here that the CIGS solar cell devices with relative higher Na contents at the CIGS/Mo interface correspond to Mo back contact with the third layer deposited at 0.5 Pa and 0.6 Pa and demonstrate the lowest Rs in Figure 4D. This well agrees with the result reported by Yoon et al that Na doping can effectively reduce the barrier height of carrier transport at the back contact. In contrast, K concentration not only varies at the two interfaces but also changes within the CIGS bulk. The percentage change of K concentration at the two interfaces is much smaller than that for Na as the Ar deposition pressure increases in depositing the third layer of Mo back contact. In the CIGS bulk, the K concentration firstly increases by a factor of ~ 2 from 0.1 Pa to 0.5 Pa and then decreases by a factor more than 2 from 0.5 Pa to 0.8 Pa. Considering the variation of alkali atoms concentration in the CIGS bulk, it is more reasonable to suspect that the Ga gradient in CIGS layer is influenced by K rather than by Na.

To investigate whether K atoms influence the formation of Ga gradient, the rescaled SIMS profiles of K and Ga are displayed in Figure 7 for the above five samples. It is amazing to see that the distributions of Ga and K in CIGS bulk have a very strong correlation except at 0.8 Pa. In the opposite, no such correlation is found for Na distribution. This observation further demonstrates that the K atoms incorporated into CIGS layer may influence the formation of Ga gradient, possibly by affecting the Ga atom diffusion.
To find out why the alkali element incorporation in CIGS is related to the top layer of the Mo back contact, we observe from Table 1 that there is an obvious reduction of MoO$_3$ and an increase of Mo(OH)$_6$ with the increase of Ar pressure for the third Mo layer deposition. For the interaction of the out diffused alkali metals from glass with the Mo(OH)$_6$ in the top Mo layer, we propose the following reactions:

\[
\text{Mo(OH)}_6 + \text{Na}_2\text{O} \rightarrow \text{Na}_2\text{MoO}_4 + 3\text{H}_2\text{O} \uparrow \quad (1)
\]

\[
\text{Mo(OH)}_6 + \text{K}_2\text{O} \rightarrow \text{K}_2\text{MoO}_4 + 3\text{H}_2\text{O} \uparrow \quad (2)
\]

Both Na$_2$MoO$_4$ and K$_2$MoO$_4$ may release alkali element in ionic form into the CIGS layers. At the Mo/CIGS interface, it can be expected that the diffusion of alkali metals is also influenced by the formed molybdenum selenide interlayer; however, this is not subject of this investigation.

The influence of MoO$_3$ on the diffusion of alkali atoms into CIGS absorber layer deserves a discussion. Previously, opposite conclusions were reached by different groups. Some researchers indicated that MoO$_3$ play a key role on facilitating the incorporation of alkali ions from SLG to CIGS$^{23}$ while others believed that MoO$_3$ may only act as a barrier layer to prevent the incorporation of Na into CIGS.$^{36}$ Lin et al thought that the formation of MoO$_3$ after oxidation of Mo surface was beneficial to the incorporation of alkali from SLG while they cannot explain how the chemical reaction works between Na$_2$O and MoO$_3$.$^{23}$ Instead, they used the following reaction:

\[
\text{Na}_2\text{SiO}_3 + \text{MoO}_3 \rightarrow \text{Na}_2\text{MoO}_4 + \text{SiO}_2 \quad (3)
\]

Since the main form of sodium in SLG is Na$_2$O rather than Na$_2$SiO$_3$,$^{45}$ and SiO$_2$ should not be generated within the Mo layer as it would certainly bring negative effect to solar cells, Eq. (3) cannot be valid. In our opinion, during the growth process of CIGS absorber, water molecules produced in reaction (1) and (2) or from residual gas in the chamber can react with MoO$_3$ by the following reaction:

\[
\text{MoO}_3 + 3\text{H}_2\text{O} \rightarrow \text{Mo(OH)}_6 \quad (4)
\]

The produced Mo(OH)$_6$ by reaction (4) can further participate in reaction (1) and (2) to form a loop. With Mo(OH)$_6$ as an intermediate substance, MoO$_3$ can first be transformed to Mo(OH)$_6$ and then to MoO$_4$$^{2-}$. Combining reactions (1), (2), and (4), we can obtain the following reactions:

\[
\text{MoO}_3 + \text{Na}_2\text{OMo(OH)}_6 \rightarrow \text{Na}_2\text{MoO}_4 \quad (5)
\]

\[
\text{MoO}_3 + \text{K}_2\text{OMo(OH)}_6 \rightarrow \text{K}_2\text{MoO}_4 \quad (6)
\]

In another word, in addition to Mo(OH)$_6$, MoO$_3$ can also facilitate alkali atoms diffusion and accumulation in the presence of water molecules. Without water molecules, MoO$_3$ itself may serve as a barrier to reduce the incorporation of alkali from SLG to CIGS. That is why previous researchers hold exact opposite opinions on the role of MoO$_3$ played in the process of alkali diffusion.

We have integrated the Na and K counts in the CIGS absorbers shown in Figure 6 and the results are displayed in the form of histograms in Figure 8. The percentage amount of MoO$_3$ and Mo(OH)$_6$ on the corresponding Mo surfaces from Table 1 are also presented as the line charts in Figure 8. The total amount of MoO$_3$ and Mo(OH)$_6$ show a clear positive correlation with the total amount of alkali atoms diffused into the CIGS absorbers. With Ar pressure increasing from 0.1 Pa to 0.5 Pa, the total percentage of MoO$_3$ and Mo(OH)$_6$ on the surface of Mo back contact increases from...
39.5% to 46.3% which is beneficial to the production of Na2MoO4 and K2MoO4, in the forms of which, alkali ions can get accumulated at the interface of CIGS/Mo and then diffuse into the CIGS absorber layer. When the Ar pressure further increases to 0.8 Pa, the total percentage amount of MoO3 and Mo(OH)6 decreases to 43.1%, which results in diffuse into the CIGS absorber layer. When the Ar pressure can get accumulated at the interface of CIGS/Mo and then CIGS solar cells shown in Figure 4. The relatively high J-V differently prepared Mo surface on the and chemical states, we can now explain the mechanism of interface accordingly.

With the above characterizations of element distributions and chemical states, we can now explain the mechanism of differently prepared Mo surface on the J-V parameters of CIGS solar cells shown in Figure 4. The relatively high JSC is due to the distinct Ga grading that seems to be influenced by the incorporation of alkali especially K element. The incorporation of alkali element is mainly related with the formation of Mo(OH)6 and MoO3 on the surface of Mo back contact which has been directly controlled by the deposition pressure of the third Mo layer in its tri-layered structure. Besides, the alkali incorporation can also cause changes in Voc, Rsh, as well as FF as secondary effect.

4 CONCLUSIONS

In summary, we have observed a large effect on the conversion efficiency of CIGS solar cells fabricated on Mo back contact with different tri-layered structures. It has been found that alkali element diffusion from SLG to CIGS can be effectively adjusted by controlling the third layer of Mo back contact through Ar deposition pressure and water vapor. Combined with XPS and SIMS analysis, we have revealed that Mo(OH)6 and MoO3 formed on the surface of Mo back contact plays a key role in determining the K atom distribution and Ga gradient. It was further shown that the incorporation of larger amount of K could lead to a more pronounced Ga gradient that increases JSC. This result is also useful for other solar cells with Mo as the back contact.

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CONFLICTS OF INTEREST

There are no conflicts of interest to declare.

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