RESEARCH ARTICLE

Influence of Mo back contact porosity on co-evaporated Cu(In,Ga)Se₂ thin film properties and related solar cell

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ABSTRACT

The present study aims at investigating the influence of Ar sputtering gas pressure on the properties of molybdenum back contact (deposited on soda-lime glass) and consequences on co-evaporated Cu(In,Ga)Se₂ (CIGSe) absorber layer and related solar cell. Films 300 nm thick have been grown with argon pressure between 0.075 and 1.25 mTorr; these films have been characterized by several techniques showing that the increase of the sputtering pressure yields wider amorphous areas, containing oxygen and sodium, between the molybdenum grains, thus higher sheet resistance. The volume ratio of these amorphous areas is referenced as "porosity". The structural and morphological properties of co-evaporated CIGSe have not been reliably observed in influenced by the molybdenum porosity; the only noticeable change is the sodium content of the absorber, which increases with the porosity of the back contact. The impact of the amount of sodium on the device performance has been observed to be very important. On the one hand, as already reported, sodium is beneficial for the open-circuit voltage. On the other hand, a too high amount of sodium is detrimental for the fill factor (hindered shunt resistance), thus the cell efficiency; this latter observation is interpreted as a change in the grain boundary electrical properties. Copyright © 2011 John Wiley & Sons, Ltd.

KEYWORDS

CIGSe; molybdenum; sodium

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1. INTRODUCTION

CuIn₁₋ₓGaₓSe₂ (CIGSe)-based solar cell is the only thin film technology surpassing the 20% efficiency level [1]. Such performance is reached when the CIGSe absorber layer is grown by co-evaporation on molybdenum-coated soda-lime glass before the junction is formed with cadmium sulfide and ZnO window. These heterostructures are moreover made of polycrystalline films. It can therefore appear surprising that such device containing both hetero-interfaces (e.g., CIGSe/CdS junction) and homo-interfaces (i.e., grain boundaries (GBs)) can achieve efficiency of the level of crystalline silicon or III–V single junction cells. The recent important progress in nanoscale characterization techniques yields much better understanding of these interfaces characteristics, therefore on polycrystalline-based cell operation [2,3].

The use of molybdenum as back contact offers several advantages, such as low corrosion at high temperature in selenium atmosphere. Nevertheless, this polycrystalline layer can also be considered as a filter for the elements of the glass substrate; for instance, it allows the diffusion of sodium into the absorber, which has been demonstrated necessary for the achievement of high-efficiency devices. The longstanding issue of sodium in chalcopyrite thin film is still the seed of many debates in the CIGSe community; nevertheless, it appears that sodium influences the structural properties of CIGSe thin film through group III elements (i.e., In,Ga) distribution and relative point defects densities, which strongly impact the electrical properties of this intrinsically doped material [4–10].

From the experimental point of view, the properties of sputtered molybdenum film are strongly dependent on their deposition conditions, namely power, working gas...
pressure, substrate temperature, or the distance between the target and the substrate. The purpose of the present study is the investigation of the influence of the sputtering gas pressure during the back contact deposition on the film properties and the impact of this on co-evaporated CIGSe layers as well as related device behavior.

2. EXPERIMENTAL

2.1. Film growth and analysis

Molybdenum (Mo) thin films (thickness ~ 0.3 μm) have been grown on 30 × 30 cm² soda-lime glass (SLG, PLANILUX [Saint Gobain, France] with 14 wt% of Na₂O, 3-mm-thick) substrates by DC magnetron sputtering in dynamic deposition mode. The base pressure within the chamber was about 7.5 \(10^{-7}\) Torr before the deposition process. All of the investigated films have been deposited using 3-kW DC power. The moving substrates have been exposed four times to the deposition area; the complete film is a stack of four layers. The parameter investigated in the present study is the argon (Ar) sputtering gas pressure within the chamber during the deposition; films have been grown at 0.75, 1.5, 4.5, 7.5, and 11.25 mTorr by varying the gas flow.

CuInₓGa₁₋ₓSe₂ (thickness ~ 1.25 μm) thin films have been synthesized onto these SLG/Mo substrates by co-evaporation following the standard three-stage process. The highest temperature measured by the thermocouple during the second and third stage is 620 °C; nevertheless, the actual is likely to be lower because the 1 x 1 in.² SLG/Mo substrates did not bend. In order to take into account eventual [Ga]/[In] and/or [Cu] gradients along the substrates on the device characteristics (because of our machine design), three runs of CIGSe have been performed on sets of 1 x 1 in.² SLG/Mo substrates positioned differently on the sample holder from one run to the other. The cell open-circuit voltage \(V_{oc}\), current density \(J_{sc}\), fill factor (FF), and efficiency (Eff) presented in this paper correspond to the mean of 12 devices (four cells/Mo type/run).

The morphology of the films has been investigated by means of scanning electron microscopy (SEM), model JEOL 7600 (Tokyo, Japan). X-ray diffraction (XRD) measurements have been performed for the evaluation of the crystalline properties of the films (diffractometer: Bruker (Karlsruhe, Germany) model D8, CuKα). The composition of the CIGSe layers has been determined with the help of energy dispersive spectroscopy in a SEM (JEOL 5800) equipped with a Ge X-ray detector.

The microstructure of the Mo layers deposited at 0.75, 4.5, and 11.25 mTorr has been investigated by transmission electron microscopy (TEM); the analyses have been performed on the films cross section using a Hitachi (Japan) H-9000NAR microscope (LaB₆ filament, accelerating voltage: 300 kV, point resolution: 0.18 nm). As will be developed in the Mo thin film properties section, these TEM studies have confirmed the already reported strong influence of the sputtering pressure on intergranular properties [11]. As these intergranular channels are assumed to be the media for Na-based compounds diffusion, their volume density will be referenced to as the porosity (understood to Na) of the films. However, because of the complexity of such TEM samples preparation and investigation, we have used another technique in order to evaluate the so-called porosity of the films. This simpler method is based on the analysis of SEM images acquired in backscattered mode; after image treatment using modified Q550 Leica (Wetzlar, Germany) software (binarization and segmentation), the actual porosity is considered as the ratio of black pixels. This technique, used in the field of biomaterials for medical research (in particular in the applications of bone substitutes [12]), has been applied on all Mo layers for the determination of their so-called porosity.

The composition depth profiles of the Mo layers and completed devices have been determined by secondary ion mass spectroscopy (SIMS).

The optical reflectance has been measured with a CARY (Varian Inc., NC, USA) spectrophotometer in the wavelength range 350–2000 nm and the electrical properties (sheet resistance) of the Mo layers determined by the four-point probe method.

2.2. Solar cell fabrication and characterization

Solar cells have been prepared from the SLG/Mo/CIGSe structures; the devices have been completed by 50-nm-thick CdS layer deposited by chemical bath deposition and sputtered r-ZnO(50 nm)/ZnO:Al(350 nm) window; the resistive ZnO (i.e., r-ZnO) is sputtered from pure ZnO target. Ni/Al contact grids have finally been deposited on top of the structures before 0.5 cm² cells be mechanically designed. The performance of all devices has been evaluated through \(J(V)\) measurements performed at 25 °C under normalized AM1.5 illumination (1000 W/m²). The short-circuit current density of the cells \(J_{sc}\) has been accurately investigated through quantum efficiency measurements.

In order to further evaluate the electrical properties of the solar cells, the \(J(V)\) curves under illumination were fitted with single diode model assuming the current voltage dependence as

\[
J(V) = J_0 \left( \frac{q(V - R_s J(V))}{AT} \right) - 1 - \left( \frac{V}{R_{sh}} \right) + J_{ph}
\]

where \(J_0\) is the reverse saturation current density, \(q\) is the electron charge, \(A\) is the ideality factor, \(k\) is the Boltzmann constant, \(J_{ph}\) is the photocurrent, and \(R_s\) and \(R_{sh}\) are the series and shunt resistance, respectively. The transcendental equation is solved using the Lambert function [13]. With this calculation method, Equation 1 is rewritten in a closed form analytical expression; therefore, the \(J(V)\) curve can be fitted under Matlab environment. From the resulting fitted
diode parameters, it was possible to determine the $FF$ and $V_{oc}$ losses relative to the virtual champion cell defined by the following diode parameters: $J_0 = 10^{-10}$ A/cm², $A = 1.4$, $R_s = 0.25$ Ω cm², $R_{sh} = 10^3$ Ω cm², $J_{ph} = 37$ mA/cm² ($\eta = 21\%$); consequently, the origin of losses could be better understood.

3. RESULTS

3.1. Mo thin film properties

The properties of Mo thin film grown by DC sputtering on amorphous glass substrates are known to be influenced by several deposition parameters, namely the DC power, the target-substrate distance ($d$), and the working gas pressure ($p$). In the present study, the influence of the Ar pressure ($p$) on the Mo film properties has been investigated, whereas both the DC power and $d$ have not been intentionally varied from one deposition to another. This parameter $p$ appears to be the most frequently investigated in the literature; [14,15] nevertheless, $p$ remains a process parameter, and it would be suitable for the interest of the reader to use a material related film property as a universal parameter. The layer resistivity could have been taken as a parameter; however, in the field of CIGSe solar cell, the Mo layer not only is exclusively an electrical back contact but also acts as a filter for the elements constituting the SLG. Consequently, it can appear relevant to use a parameter related to the porosity of the Mo layer. The pressure dependence of the growing film density is known as Peening effect: [16] the kinetic energy of the species formed within the plasma during the deposition process decreases with increasing background pressure; the decrease of the Mo atoms kinetic energy hinders their mobility on the substrate and thus decreases the growing film density. Figure 1 shows the TEM images of the cross sections of the as-grown Mo films deposited with Ar sputtering pressure of 0.75, 4.5, and 11.25 mTorr. This set of images clearly illustrates that the apparent width of the intergranular zones (i.e., bright zones between the Mo grains) becomes larger with increasing sputtering pressure. The chemical composition of these intergranular areas will be discussed in the following paragraphs; however, according to literature, they can be considered to be composed of molybdenum oxide [17]. The volume density of these intergranular areas will be referenced to as the porosity of the films in the present study. As already mentioned in the Film growth and analysis section, although powerful, the TEM technique can hardly be used routinely for the evaluation of the so-called porosity. Consequently, we propose a technique based on SEM observation yielding easy and fast evaluation of such Mo film porosity (see the Film growth and analysis section). In Figure 2 are shown the SEM plan views and cross sections of the Mo films sputtered at 0.75 and 11.25 mTorr. The comparison of these images unambiguously illustrates the higher density of pore-like black areas in the case of higher Ar pressure. The cross

Figure 1. Transmission electron microscopy cross sections of Mo films deposited with Ar sputtering pressure of 11.25, 4.5, and 0.75 mTorr.
sections also corroborate the TEM observations, showing very tight columnar structure for the lowest Ar pressure, which contrasts to the elongated grain with open GB structure achieved for the highest pressure. These observations are in agreement with the roughness of the films evaluated by atomic force microscopy measurements revealing the increase of the roughness (root mean square) from 4 to 9nm when the Ar pressure is raised from 0.75 up to 11.5m Torr (not shown). The sputtering Ar pressure dependence of the so-called porosity deduced from the treatment of these plan views (see the film growth and analysis section and Ersløv et al. [8]) is plotted in Figure 3. The observed linear increase of the porosity with the Ar pressure is likely to be similar for all Mo deposition system in the investigated range; therefore, it appears relevant to use this so-called porosity as varying material parameter.

The Mo layers have been investigated by SIMS, firstly, in order to evaluate the eventual presence of contaminants; this time of flight analysis has been performed on the most porous Mo layer. On the one hand, the layer is mainly made of Mo, O, and Na although K, H, and Ca (very low) could also be detected. On the other hand, Mg, Al, Si, Fe, N, and C could not be detected. Consequently, composition depth profiles of Mo, O, and Na have been determined on all as-deposited Mo films. The only difference observed from one film to another concerns the Na and O profiles. Figures 4(a) and 4(b) respectively depict the Na and O profiles throughout the films, with porosity of 5%, 11%, and 17% (i.e., deposited at 0-75, 4-5, and 11-25 mTorr). The first information provided by these figures is that the Na and O mean contents increase when the

Figure 2. Scanning electron microscopy plane views and cross sections of the Mo layers grown for Ar sputtering pressure of 0-75 and 11.25 mTorr.

Figure 3. Evolution of the so-called “porosity” with the Ar sputtering gas pressure.
The porosity of the film is raised from 5 to 17%. It can appear surprising that even the as-deposited Mo layers contain both Na and O although the substrates were not intentionally heated during their growth. One should nevertheless keep in mind that the SLG substrate is chemically active; the Na2O can migrate into the Mo layer if the chemical potential gradient drives it. Furthermore, O is detected in the film with 5% porosity, which only contains traces of Na. This observation suggests that Mo can react either with differently bonded O atoms of the substrate or with the residual O atoms present within the chamber. The additional information that could be important is that all samples have been stored in air then treated in ammonia before their investigation by SIMS. One can therefore not exclude that the films become oxidized after deposition or that O could be bonded to Na before the layer aging (this aging may consist in Na migration towards the layer surface to form carbonates that are washed by the ammonia treatment). The second remarkable information from Figure 4 is that Na and O do not appear homogeneously distributed throughout the layers, and higher contents are observed at the position of GBs parallel to the substrate plane; one should notice that, as mentioned in the Experimental section, the films are composed of four stacked Mo layers. This observation agrees with the results of Bodegard et al. [18], suggesting that Na and O are localized at the GBs, here referenced to as intergranular areas because of their width. Therefore, valleys profiles correspond to the contributions of Na and O at the intergranular areas perpendicular to the substrate, whereas the peaks correspond to the combination of both intergranular areas perpendicular and parallel to the substrate.

From these SIMS profiles, although no causality could be established, the correlation between the level of Na and O contents and the porosity (or vice versa) is clear. All of the Mo films have been further investigated by XRD. Neither the crystalline structure nor the preferential orientation of the grains appear affected by the porosity of the films, which corroborates that the increase of Na and O contents mainly affects the amorphous intergranular areas characteristics.

Figure 5 shows the wavelength dependence of the optical reflectance of the films, with porosities of 5%, 11%, and 17%. Reflectance (coating side) has been measured on the as-grown SLG/Mo structures and after these structures have been heated up to 600 °C for 30 min under vacuum exposed or not to Se flux (performed in the CIGSe deposition chamber). All of the as-grown films show similar reflectance, which does not appear changed after the samples are heated under vacuum. In contrast, the annealing under Se flux differently affects the reflectance depending on the porosity of the Mo layer: the higher the porosity, the lower the reflectance in the wavelength range 600–1200 nm. Such a decrease can be correlated to the formation of MoSe2 at the surface of the Mo layer. As already reported, the formation of the MoSe2 on top of the Mo layer is strongly dependent on the availability of Na: [19,20] the higher the amount of Na, the thicker the MoSe2 layer [7,21]. The higher ability of porous films to be selenized corroborates their higher Na content or ability to diffuse Na.

Figure 6 shows the evolution of the sheet resistance and electrical resistivity of the films relative to their porosity; it can be recalled that the resistivity of bulk Mo is 5-4 μΩ cm. The lateral resistivity of the films increases with the porosity. According to the results of SIMS and XRD, such an evolution is most probably assignable to changes in intergranular oxide width.

In order to summarize this characterization of the Mo layers, the increase of the Ar pressure during the sputtering process leads to the increase of Mo thin film porosity (i.e., larger intergranular zones) accompanied with higher Na.
3.2. CuIn$_{1-x}$Ga$_x$Se$_2$ layers

As mentioned in the Experimental section, CIGSe layers have been co-evaporated on each kind of Mo following the standard three-stage process. These layers have been investigated through XRD measurements, and the resulting patterns (from completed cells) are presented in Figure 7. Neither the phases detected nor do the grain size and their preferential orientation appear affected by the porosity of the Mo films in the investigated range. Furthermore, the SEM pictures of the cells’ cross sections shown in Figure 8 in the case of Mo porosity of 5% and 17% do not reveal obvious changes in the morphology of the CIGSe films. Therefore, the CIGSe structural characteristics do not seem influenced by the Mo layer in the explored porosity range.

These CIGSe films have also been investigated by SIMS. Figure 9 plots the Na signal depth profiles throughout CIGSe deposited on Mo with porosity of 5%, 11%, and 17%. The Na content appears increasing with the porosity of the Mo film, which corroborates the conclusions from the reflectance measurements that the increase of the porosity favors the Na diffusion across the Mo. The eventual presence of other contaminants diffusing from SLG has been investigated through the comparison of mass scans performed on the CIGSe layers grown on Mo with 5% and 17% porosity (not shown). This study only revealed very weak higher amount of detected K and Ca in the CIGSe films grown on the most porous Mo but not more Fe. Therefore, the only difference in absorber composition considered in the Discussion section will be the Na content.
increased amount of Na when the porosity of the Mo layer increases.

3.3. Solar cell characteristic

Solar cells have been prepared from all SLG/Mo/CIGSe structures. The device parameters are plotted in Figure 10 as a function of the porosity of the Mo film (without AR coating). The values reported correspond to the average of 12 cells (four cells per CIGSe run, see the Film growth and analysis section). The $V_{oc}$ does not appear strongly affected by the porosity of the films, nevertheless showing a maximum for the Mo with porosity of 6%. Both the evolutions of $J_{sc}$ and $FF$ relative to the Mo porosity also show a maximum for 6% porosity. The $J_{sc}$ decrease is clearly due to lower quantum efficiency in the large wavelength area (Figure 11). In Figure 12 are plotted the Mo porosity dependence of the series resistance ($R_s$), the ideality factor ($A$), shunt resistance ($R_{sh}$), and the saturation current ($J_0$) extracted from the fit of the illuminated $J(V)$ curves.

Figure 8. Scanning electron microscopy cross sections of completed cells grown on Mo layers with porosity of 5% (a) and 17% (b).

Figure 9. Secondary ion mass spectroscopy signal depth profile of Na throughout the CIGSe films deposited on Mo layers with 5%, 11%, and 17% porosity.
measured at 25 °C (see the Film growth and analysis section). One should notice that these figures plot the mean value of three cells grown during different CIGSe growth process. A and $J_0$ appear almost independent of the Mo porosity if the latter is at least 6%. A much higher $R_s$ is observed for the most porous Mo layer, whereas the those measured for the lower porosities do not seem noticeably different. The changes in $A$, $J_0$, and $R_s$ therefore appear threshold-like evolutions with Mo porosity. In contradiction, $R_{sh}$ continuously decreases with the porosity of the Mo layer.

4. DISCUSSION

The characterization of the Mo layers has revealed that increasing the sputtering gas pressure during the deposition increases the porosity of the films, their Na and O contents, and/or their ability to diffuse Na. As a consequence, the resistivity of the investigated films increases. The sheet resistance of the investigated 300-nm-thick layers remains below 0.7 Ω/□ until the porosity is 15% and then is close to 1.4 Ω/□ when the porosity is 17%. Crystalline and morphological properties of the CIGSe films grown on these SLG/Mo structures by the three-stage process have not been observed remarkably affected. The only noticeable chemical characteristic evolving relative to the Mo porosity is the CIGSe layer Na content. In contradiction with this relatively weak chemical change, the device performance appears strongly dependent on the Mo layer porosity. Consequently, the purpose of the following discussion is the evaluation of the possibility to reliably interpret the cell characteristics evolution only by Mo-induced changes in absorber Na content.
CuIn$_{1-x}$Ga$_x$Se$_2$ is among the semiconductors in which the bulk cannot be extrinsically doped. As a consequence, the electrical properties of the absorber layer are ruled by the nature and the relative densities of crystal point defects. Many of them have been reviewed and are expected to behave either as donor (e.g., V$_{Se}$, In$_{Cu}$) or acceptor (e.g., V$_{Cu}$) [22]. The situation becomes much less clear when these defects interact to form complexes, which have amphoteric electrical behavior [23]. In the case of p-type Cu-poor CIGSe layers applied in devices, the formation of compensating donor-like defects must be avoided in order to reach the highest efficiencies. So far, the best experimental route yielding the decrease of compensating defects density is the addition of Na to the CIGSe. The most realistic hypothesis concerning the actual role of Na is that it avoids both the formation of In$_{Cu}$ (by formation of Na$_{Cu}$) and V$_{Se}$ (better Se capture through the formation of NaSe$_x$ on top of the growing layer). Therefore, for a given growth recipe (i.e., given temperature, Ga content, and Se/metal flux ratio), the absorber net acceptor concentration is likely to strongly depend on its Na content. Considering CIGSe film co-evaporated following the three-stage process, the expected impact of too low Na concentration (i.e., too low net acceptor density) is $V_{oc}$ hindering. Indeed, with simple qualitative approach, assuming the recombination in the neutral zone of the absorber as dominant mechanism (ideality factor of 1), the $V_{oc}$ can be described as [24]

$$V_{oc} = \frac{E_g}{q} - \frac{kT}{q} \ln \left( \frac{J_0}{J_{sc}} \right) \tag{2}$$

where $E_g$ is the absorber band gap, $q$ is the electron charge, $J_{sc}$ is the short-circuit current density and $J_0$ is the diode saturation current density. Still with the aforementioned assumptions, $J_0$ can be assumed to be

$$J_0 = \frac{qD_nN_c}{N_A L_D} \tag{3}$$

where $D_n$ is the diffusion constant for electrons, $N_{c/v}$ the effective density of states in the conduction/valence band, $L_D$ the diffusion length, and $N_A$ the acceptor density [24]. Therefore, everything else equal, $J_0$ varies as the inverse of the acceptor concentration. One should note that even if recombination in the space charge region as dominant mechanism is considered (ideality factor of 2), $J_0$ would vary as the inverse of the acceptor density square root. Combining Equations 2 and 3 suggests that the $V_{oc}$ loss due to too low doping of the absorber can be correlated to high $J_0$ values. As a conclusion, in the present work (similar Se/metal flux ratio for all sets of cells), $V_{oc}$ loss due to low $J_0$ values can be assigned to a lack of Na. One should nevertheless be cautious because for devices having similar ideality factor ($\alpha$) and short-circuit current ($J_{sc}$), $V_{oc}$ losses can also be imputed to other origins such as too low shunt resistance. The $V_{oc}$ of the cells grown on Mo with 5% porosity (i.e., Mo$_5$) is unambiguously lower than that of cells grown on Mo$_6$. This $V_{oc}$ loss can clearly be imputed to higher $J_0$ values (Figure 12); the relative impact of the other parameters, $\alpha$, $R_{sh}$, and $J_{sc}$, has been calculated much less important (not shown). Therefore, the lower $V_{oc}$ for Mo$_5$ can be assumed because of too low Na diffusion in the CIGSe layer, which perfectly agrees with the Na SIMS profile shown in Figure 9. This hypothesis is also corroborated by the $J_0$ values reached for Mo$_6$ and higher porosities. The weak losses in $V_{oc}$ of cells with Mo$_{11}$, 15, and 17 compared with Mo$_6$ can be imputed to a combination of slightly higher $J_0$ and lower $R_{sh}$. Nevertheless, in the latter case, definitive conclusions are hazardous because the changes in $V_{oc}$ are not that important. The major conclusion that can be drawn is

![Figure 12](image.png)

Figure 12. Mo porosity dependence of the series resistance ($R_s$), ideality factor ($\alpha$), shunt resistance ($R_{sh}$), and saturation current density ($J_0$). Each result is the mean value for three cells.

that Mo with 6% porosity and more is enough to ensure sufficient $N_A$ concentration in the considered absorber (thickness of 1.25 $\mu$m). The evaluation of the impact of $J_0$, $R_{sh}$, and $R_s$ on the FF losses has been performed following the procedure described in the Solar cell fabrication and characterization section; note that the contribution of $A$ in the loss has also been evaluated and appears similar for all Mo porosities. Figure 13 shows the relative contribution of those parameters on the FF loss. If one first considers the impact of $A$, it clearly appears that it is similar for all porosities except the highest (i.e., Mo_17). This result tends to show that in the present device configuration, Mo back contact sheet resistance as high as 0.6 $\Omega$ cm does not noticeably affect the cell performance; here, the eventual Mo porosity dependence of the Mo/CIGSe contact ohmic character (i.e., impact of the MoSe2 layer) will not be discussed. The contribution of $J_0$ also tends to show that too low $N_A$ concentration is likely to hinder the FF (case of Mo_5). The most remarkable influence is undoubtedly that of $R_{sh}$. One should notice that for all samples, $R_{sh}$ is not sensitive to light intensity (i.e., the photocurrent collection efficiency equals 1); therefore, the decrease of $R_{sh}$ relative to Mo porosity is most probably not due to increased voltage dependent collection [25,26] but to “real” shunt. The contribution of $R_{sh}$ continuously increases with the Mo porosity, independently of the evolution of $J_0$, which would mean that it is directly correlated to the amount of Na present in the whole absorber layer. One should keep in mind that the CIGSe films are polycrystalline and therefore made of grains and GBs. Recent studies have shown that in polycrystalline CIGSe, Na is present both within the grains and at the GBs [3]. The solubility of Na within CIGSe crystal can be estimated as a finite value for a given selenium availability during the CIGSe growth; therefore, when the amount of Na provided to the layer is above this threshold, excess alkali segregates at the crystal defects such as GBs. This vision can explain the rather insensitivity of $J_0$ (Figure 12) relative to the Mo porosity once the latter has reached a threshold value corresponding to a “sufficient” diffusion of Na within the absorber layer (i.e., sufficient $N_A$ density). Furthermore, the vision of GBs acting as sink for the additional Na atoms can also help the interpretation of the increase of the contribution of $R_{sh}$ in FF losses. Indeed, the segregation at the GBs of excess Na compared with the grain host capacity may change not only the GBs’ electrical properties but also most probably the characteristics of grain band structure at the vicinity of the GBs. It has recently been shown that deep defects at the GBs yield upward band bending inward the grains, and changes in Na content at the GBs most probably induce changes in deep level densities, thus on band configuration [2]. Therefore, the decrease in shunt resistance with increasing Na content most probably originates from the resulting changes in GBs’ properties.

It therefore appears that the addition of Na yields two contradictory evolutions for the cell performance: the effective lower density of compensating defects and the increase of shunt loss. Consequently, the control of Na availability during the absorber co-evaporation is not sufficient to reach very high efficiency. In order to combine high doping (i.e., low $J_0$) and high shunt resistance, one should also consider decreasing the density of $V_{Se}$ possibly through the increase of the Se flux during the CIGSe growth [27].

5. CONCLUSIONS

In the present work, the influence of the porosity of Mo back contact on the performance of solar cells based on co-evaporated CIGSe absorber has been investigated. The major conclusion is that it seems the amount of Na available during the CIGSe deposition presents an optimal value. The electrical characteristics of the devices

Figure 13. Contribution of series resistance ($R_s$), shunt resistance ($R_{sh}$), and saturation current density ($J_0$) on FF loss relative to a champion device (see the Solar cell fabrication and characterization section).
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of low
proof that a lack of Na yields lower performance because
layer. On the one hand, the present study brings additional
of the amount of Na present within the absorber
fabricated on Mo with different porosity can effectively be
correlated to the amount of Na present within the absorber
layer and that the optimization of the back
contact cannot be universal; it should be carried out after
defining not only the glass substrate properties but also
all of the CIGSe growth parameters, particularly those
that were not highly considered so far, namely the
substrate temperature, thickness of the absorber, and
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