

Ultrathin Cu(In,Ga)Se₂ Solar Cells with a Passivated Back Interface: A Comparative Study between Mo and In₂O₃:Sn Back Contacts

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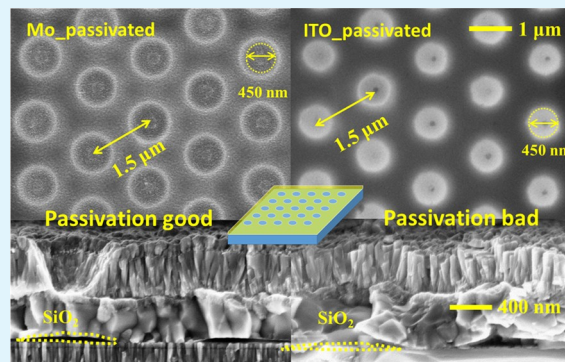
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Supporting Information

ABSTRACT: Point-contact passivation layers have been proven beneficial in most solar cells (SCs). However, the latest theoretical simulations suggested that a high back-contact recombination velocity S_b can also be beneficial in ultrathin CIGSe (Cu(In,Ga)Se₂) SCs if they have a relatively high back potential barrier height E_b . SCAPS simulations predicted that a high S_b will deteriorate the SC efficiency Eff when E_b is in the range of 0–0.17 eV (Ohmic contact). Yet, when E_b is greater than 0.17 eV (Schottky contact), a high S_b can also diminish the current limitation arising from the back Schottky diode since it has a reverse direction to the main p–n junction. Therefore, a high S_b can support the carriers in passing the Schottky barrier via recombination, thus enhancing the cell performance. This work aims to verify the simulation prediction in practical experiments. To achieve different S_b values, we fabricate SiO₂ passivation layers with point contacts of various dimensions by nanosphere lithography. The passivation effects are studied comparatively on Mo and ITO (In₂O₃:Sn) back contacts. The emphasis is on E_b , which is marginal for Mo but acts Schottky-like on ITO. We show that for Mo-based solar cells, the E_b is trivial; hence, a high S_b (without SiO₂ passivation) deteriorates the efficiency. In contrast, on ITO, the reference sample without SiO₂ shows less current limitation than the passivated ones, implying that a high S_b improves the efficiency. Comparing the differences of SiO₂ on Mo and ITO back contacts in experiments, with the contrasting behavior of S_b on Ohmic and Schottky contacts in simulation, we conclude that E_b decides about the role of S_b in ultrathin CIGSe SCs. These findings deepen the understanding of the Schottky back contact and pave the way for future optimization of bifacial semitransparent ultrathin CIGSe SCs.

KEYWORDS: ultrathin CIGSe solar cells, back interface passivation, point contact, Schottky and Ohmic contacts, back potential barrier



1. INTRODUCTION

CIGSe (Cu(In,Ga)Se₂) thin-film solar cells have demonstrated their enormous potential in the photovoltaic (PV) market with an efficiency beyond 23% on small areas.¹ Apart from the high conversion efficiency, CIGSe solar cells offer unique advantages, such as short energy payback time, compatibility with curved-surface substrates, great tolerance to a nonideal environment, etc.^{2–6} Despite great progress that has been achieved in the last decades, a lower cost-to-efficiency ratio is constantly being pursued in CIGSe solar cells, aiming at their large-scale deployment. Recently, ultrathin CIGSe solar cells, namely with a sub-500-nm absorber, have attracted extensive attention.⁷ The two major advantages of ultrathin solar cells are the reduction of rare material consumption and the resultant increase in the production throughput. These benefits can address the concern of indium scarcity and manufacturing costs simultaneously. However, ultrathin CIGSe solar cells are suffering from relatively poor performance with the highest efficiency of 15%⁸ due to the common challenges of insufficient light absorption (optical effect) and back interface recombination (electrical effect). This work emphasizes the

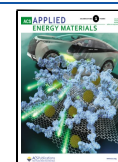
electrical recombination characteristics of ultrathin CIGSe solar cells as a central aspect to understand the cell performance and optimize the design.

Generally, back surface recombination refers to carrier annihilation at the interface of the CIGSe/back contact.⁹ Comparing to the 2 μm absorber counterparts, back recombination is particularly severe for ultrathin CIGSe solar cells. The reason is a high concentration of photogenerated carriers in the vicinity of the CIGSe/back contact interface, where also the trap density is high, naturally activating the interface recombination. To address this effect, enormous efforts have been devoted to passivating the CIGSe/Mo interface.^{10–18} For instance, inserting point contact nanostructures made of dielectric materials (e.g., SiO₂, Al₂O₃) with local

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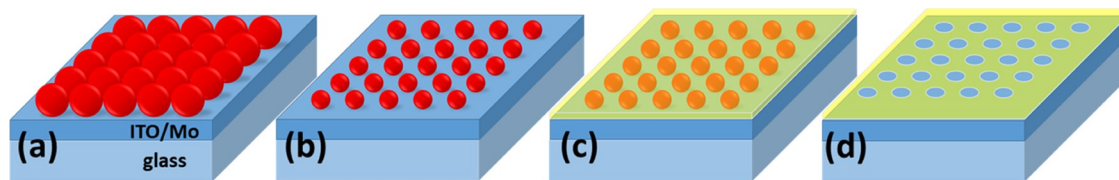


Figure 1. Fabrication steps of SiO₂ point-contact passivation layers: (a) deposition of polystyrene (PS) spheres, (b) plasma etching, (c) SiO₂ deposition, and (d) PS mask lift off.

openings between CIGSe/Mo was proved a practical and effective way. It was deduced that the point contacts contribute to back interface passivation by lowering the interface state density.¹⁹ Line contacts with SiO₂ or Al₂O₃ also showed promising results on Mo substrates.²⁰ For Al₂O₃, the formation of fixed negative charges may also contribute to field passivation effects.^{12,21} In addition, the dielectric materials have a lower refractive index than Mo over a large wavelength range and hence increase the back reflectivity of CIGSe/Mo significantly, which will further benefit the cells in terms of enhanced light absorption.^{22,23}

Alternatively, ultrathin CIGSe solar cells can also be fabricated on TCOs (transparent conductive oxides), which are inherently transparent from the visible to near-infrared wavelength range.^{24,25} In this way, the parasitic absorption loss in Mo is circumvented and the unabsorbed light after the first pass through the absorber may be further utilized.²⁶ The transparency of the back contact opens up many distinct applications such as top cells in tandem configuration, bifacial semitransparent solar cells, or photovoltaic windows.^{27,28} However, due to the work function mismatch between CIGSe and TCOs, solar cells on TCOs typically have a Schottky-like back contact, which leads to an inferior cell performance compared to the ones on Mo forming a quasi-Ohmic back contact via interfacial MoSe₂.^{29,30} Interestingly, our recent theoretical study predicts that a passivated back interface (reduced recombination velocity S_b) may harm CIGSe solar cells, which have Schottky back contacts.³¹ This poses a sharp contrast to cells on Mo, where passivation reduces the back contact recombination, increases the interface reflection, and thus enhances the efficiency.³¹ For a deeper understanding of how a passivated back interface deteriorates cells with a Schottky back contact, further research is needed, in particular on a TCO back contact. Various explorations have been conducted for solar cells on Mo already, yet most work was limited to demonstrating the beneficial effects of passivation experimentally. The relevant passivation mechanism requires further identification, especially under the fact that CIGSe/Mo is a quasi-Ohmic back contact with a relatively low back potential barrier E_b rather than an ideal Ohmic contact.

In this contribution, we first show the different experimental passivation effects of SiO₂ point contacts on Mo and ITO (In₂O₃:Sn) back contacts comparatively. To understand the controversial influences of the same SiO₂ passivation layer on different back contact materials, we fall back on the SCAPS theoretical calculations. We then present simulations for solar cells with an E_b of 0 and 0.2 eV to demonstrate the two extreme conditions of ideal Ohmic and Schottky back contacts, respectively. A varied recombination velocity S_b is used to simulate the passivation effects in practical experiments. The simulated temperature-dependent current–voltage characteristics $j_{\text{net}}V(T)$ are compared with the experimental results. To

decipher the differences in passivation effects on Mo and ITO, the decisive role of E_b is highlighted.

2. EXPERIMENTS AND SIMULATIONS

SiO₂ Point-Contact Fabrication. Nanosphere lithography is employed to prepare SiO₂ point-contact nanostructures. We use polystyrene (PS) nanospheres as a sacrificial mask, which has been demonstrated to be feasible and applicable in previous work for preparing point-contact nanostructures.⁹ Therefore, a commercially available latex solution of PS spheres, with a diameter of 1500 nm in our case, is combined in a volume ratio of 1:1 with a second solution. This latter one consists of 10 μL of H₂SO₄ (98%) mixed with 1 mL of ethanol (containing 1 vol % styrene). The complete solution is subsequently dispersed atop the surface of deionized water and forms a monolayer of closely packed PS spheres. By sucking out the water, the PS spheres are transferred onto Mo or ITO back contacts, as shown in Figure 1a. Subsequently, the PS spheres are etched by O₂ plasma treatment at an overall pressure of 0.2 mbar and a power of 240 W. The etching time is optimized at 22 min, after which the diameter of the PS spheres is reduced to 600 nm, see Figure 1b. Next, 50 nm SiO₂ is evaporated via tungsten boat heating SiO_x powder under O₂ gas flux (Figure 1c). No additional heating is used for the substrates in all of these preparation processes. Finally, the PS nanospheres are lifted off by treatment in an ultrasonic bath using toluene for 20 min. Remaining is the SiO₂ point-contact layer on a Mo or ITO back contacts (Figure 1d). More fabrication details are given in ref. 9.

Solar Cell Growth. Next, 300 nm ITO are sputtered on alkali-free (<0.3% alkali content) Corning glass 7059 substrates. The as-prepared ITO has a sheet resistance of around 20 Ω/sq , which will drop to <10 Ω/sq after the heat treatment during CIGSe coevaporation. Mo back contact with a Na diffusion barrier layer between the glass and Mo are purchased from Saint Gobain Company. For the absorber fabrication, Mo and ITO back contacts with and without a SiO₂ point-contact passivation layer are loaded into the physical vapor deposition (PVD) chamber in the same batch, and a standard three-stage coevaporation process is employed to fabricate the CIGSe absorbers.³² To maintain the conductivity of ITO, a low substrate temperature of 450 $^{\circ}\text{C}$ is adapted for the 2nd stage. After the 3rd stage, the substrate temperature is decreased to 360 $^{\circ}\text{C}$ for postdeposition treatment with 2 mg of NaF (around 3.4 nm thick). After the absorber growth, 60 nm CdS is deposited by CBD (chemical bath deposition) at 60 $^{\circ}\text{C}$ for 8 min. Subsequently, an 80 nm thick intrinsic ZnO and a 300 nm thick ZnO:Al (AZO) layer are coated by sputtering at a substrate temperature of 120 $^{\circ}\text{C}$. Following is the evaporation of 10 nm Ni/2000 nm Al grid fingers for carrier collection. Finally, the samples are mechanically scribed into 1 cm $\times$ 0.5 cm small cells for electrical characterization.

Characterization. A LEO 1530 scanning electron microscope (SEM) is employed to characterize the surface and cross-sectional morphology of the samples. X-ray fluorescence (XRF) spectroscopy is applied to determine the composition and thickness of the CIGSe absorbers. Thickness, $[\text{Cu}]/([\text{Ga}] + [\text{In}])$ and $[\text{Ga}]/([\text{Ga}] + [\text{In}])$, ratios are identified to be 450 nm, 0.80, and 0.31, respectively. To evaluate the performance, light current density–voltage ($j_{\text{net}}V$) curves are measured under standard test conditions (25 $^{\circ}\text{C}$, AM1.5, 1000 W/m²). In the $j_{\text{net}}V$ measurements, a black-painted sample holder is used to avoid reflection effects from the back. Additionally, the

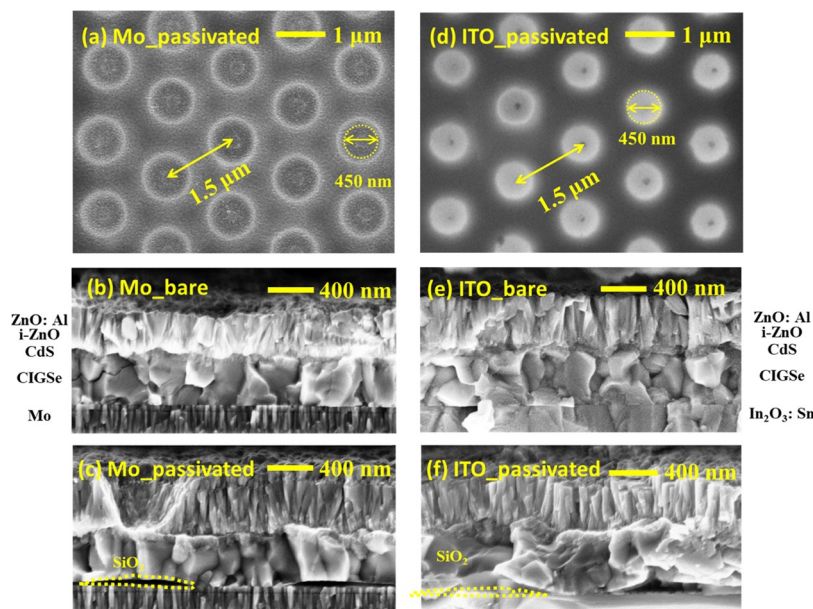


Figure 2. Top views of SiO₂ point-contact passivation layers and cross sections of ultrathin CIGSe solar cells without (_bare) and with (_passivated) point contacts: (a–c) on Mo and (d–f) on ITO.

temperature-dependent current density–voltage ($j_{\text{net}}V(T)$) measurements are performed in the range from 150 to 300 K in an enclosed liquid helium cryostat, with the temperature sensor mounted atop the sample.

SCAPS Simulation Settings. To simulate the passivation effects in the ultrathin CIGSe solar cells, SCAPS simulations are used,^{33–36} and different recombination velocities S_b are set at the back interface. The S_b for electrons and holes are set equal. According to the transport equation for recombination current density, $j_{\text{re}} = S_b \times D_p = s_p \times v_{\text{th}} \times N_t \times D_p$ (where S_b is the recombination velocity, D_p is the excess carrier density (holes here), s_p is the hole capture cross section, v_{th} is the thermal velocity, and N_t is the trap state density), it is equivalent to vary S_b and N_t in SCAPS simulation.³⁷ In the experiments, the defect density N_t is decreased at the passivated area, while it remained unchanged at the openings of the point-contact layer, so the overall quantity of the defect states Q_t at the back interface should be reduced by the SiO₂ passivation. Therefore, S_b in this contribution actually represents an effective recombination velocity, as S_b reflects the variation in Q_t at the back interface. For the settings of SCAPS simulations, based on our previous work (a simplified three-layered homojunction) in reference,³¹ the model is further elaborated to fit with the experimental results in this work. All of the simulation results presented in this work are obtained via the elaborated model, which consists of the layers back-contact/CIGSe/ODC/CdS/i-ZnO/AZO, where ODC stands for ordered defect compound, AZO for ZnO:Al, and i-ZnO for intrinsic ZnO. Detailed settings of each parameter are listed in Table S3.

3. RESULTS AND DISCUSSION

Figure 2a,d show the top views of the SiO₂ point-contact passivation layers on Mo and ITO, respectively. The holes, highlighted by the yellow dotted circles, are the openings that allow the transport of carriers toward the back contact. They follow the periodicity of the initially closely packed PS nanospheres with a hexagonal array and a pitch of 1500 nm. After SiO₂ deposition, a single point contact has a diameter of 450 nm, indicating that the ratio of the point-contact openings is 22% (78% area is covered by a SiO₂ insulator). To investigate the compatibility of the SiO₂ layers with the absorber and ITO in the solar cells, cross sections of complete devices without and with SiO₂ are shown in Figure 2b,c,e,f,

respectively. It is observed that for both Mo and ITO, the absorber exhibits similar large grains, no matter if point-contact nanostructures are present or not. The grain height is comparable to the absorber thickness despite the low substrate temperature of 450 °C during the CIGSe growth. More importantly, the absorber shows a conformal growth on the SiO₂ point-contact layers with full penetration to the back contact in the point-contact openings. The morphologies feature that good adhesive contact is formed between the absorber and the back contact.

To evaluate the passivation effects in the ultrathin CIGSe solar cells, Table 1 summarizes the PV parameters measured

Table 1. PV Parameters of Ultrathin CIGSe Solar Cells on Mo and ITO without (_bare) and with (_passivated) SiO₂ Point-Contact Passivation Layers

sample name	V_{oc} (mV)	j_{sc} (mA/cm ²)	FF (%)	Eff (%)	R_{sh} (Ω cm ²)	R_{s} (Ω cm ²)
Mo_bare	609	25.3	61.8	9.5	250	0.6
Mo_passivated	609	28.2	64.5	11.1	500	1.7
ITO_bare	596	26.6	59.9	9.5	333	3.6
ITO_passivated	574	26.9	58.0	9.0	3333	5.4

under an AM1.5 solar spectrum. On Mo, j_{sc} (short-circuit current density) exhibits a pronounced increase by nearly 3 mA/cm² after passivation (from 25.3 to 28.2 mA/cm²). Simultaneously, V_{oc} (open-circuit voltage) remained and the FF (fill factor) is enhanced moderately. As a result, the efficiency improves from 9.5 to 11.1%, corresponding to a relative enhancement of 16%. The evolution of efficiencies on Mo is broadly consistent with previous reports, and two major factors are responsible:⁹ First, the SiO₂ passivates the CIGSe/Mo interface by lowering the recombination velocity S_b and thus increases the collection efficiency of the photogenerated carriers. Second, the low refractive index of SiO₂ improves the interface reflectivity of CIGSe/Mo, redirecting the light not absorbed after the first pass back into the absorber and thus contributing around 0.9 mA/cm² photogenerated current

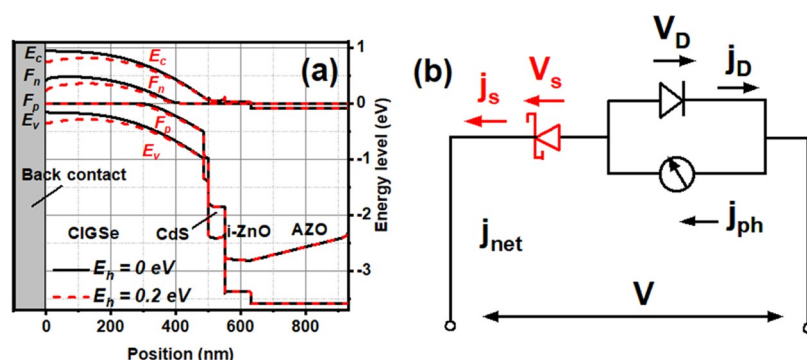


Figure 3. (a) Band diagram of the device with Ohmic contact (black line $E_h = 0$ eV) and Schottky contact (red dotted line, $E_h = 0.2$ eV) at 0 bias voltage calculated in SCAPS and (b) corresponding equivalent circuit with the additional Schottky diode marked in red.

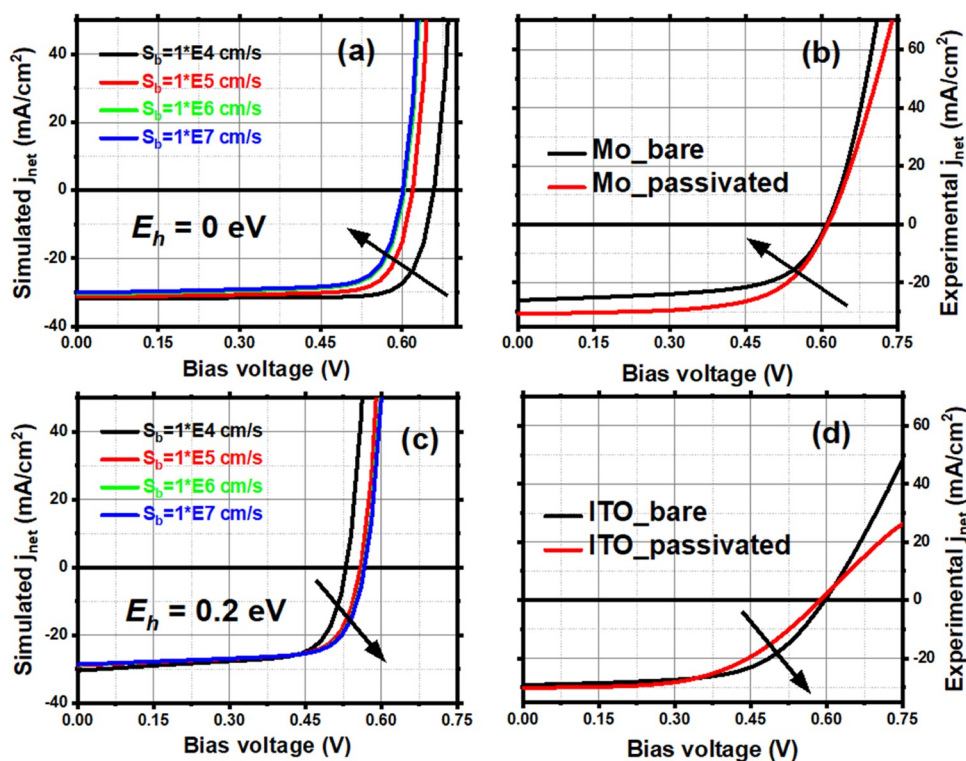


Figure 4. Simulated $j_{\text{net}}V$ curves of solar cells with (a) Ohmic ($E_h = 0$ eV) and (c) Schottky ($E_h = 0.2$ eV) contact as a function of recombination velocity S_b . Simulation details of each layer are listed in Table S3. Experimental $j_{\text{net}}V$ characteristics of ultrathin CIGSe solar cells under illumination on (b) Mo and (d) ITO. The black arrow marks the direction of increasing S_b .

density (see Supporting Information Table S1). Mo_{bare} and Mo_{passivated} exhibit overlapping Ga grading profiles toward the back contact (see Supporting Information Figure S1), indicating that SiO₂ has a marginal effect on the depth distribution of the CIGSe components. Therefore, it is inferred that the electrical passivation benefit in Mo_{passivated} is the dominant reason for its j_{sc} enhancement, being attributed to a 2 mA/cm² increase.

In contrast, the cells on the ITO substrate exhibit an inverse trend compared to Mo: ITO_{passivated} shows inferior performance than ITO_{bare}. Inserting SiO₂ passivation layers deteriorates V_{oc} and FF from 597 to 574 mV and 60 to 58%, respectively. Since the SiO₂ layer only enhances j_{sc} by 0.3 mA/cm², while the improved back reflectivity at the CIGSe/ITO interface already contributes 0.2 mA/cm² (Supporting Information Table S1), the effect of reduced back recombination on the carrier collection is marginal. Overall, on ITO,

the passivation layer leads to a drop in the cell efficiency from 9.5 to 9.0%. To confirm that the differences in Mo and ITO relate to the presence of a SiO₂ passivation layer in general rather than to the point-contact opening ratio, we have also tried 8% and 40% SiO₂ coverage on both substrates. Compared to the reference samples, the PV parameters of the passivated ones show a similar trend as those depicted in Table 1 (see Supporting Information Table S2). The SiO₂ passivation is beneficial for a back contact made from Mo, while it is detrimental for ITO. Therefore, we deduce that the reduced back-contact recombination plays a different role in Mo-based and ITO-based ultrathin CIGSe cells. Meanwhile, we notice that the FF of the ITO-based solar cells is generally lower than for the Mo-based ones, which is induced by the higher sheet resistance R_s of the devices: for the ITO layer it is around 10 Ω/sq , while it is only 0.5 Ω/sq for Mo.

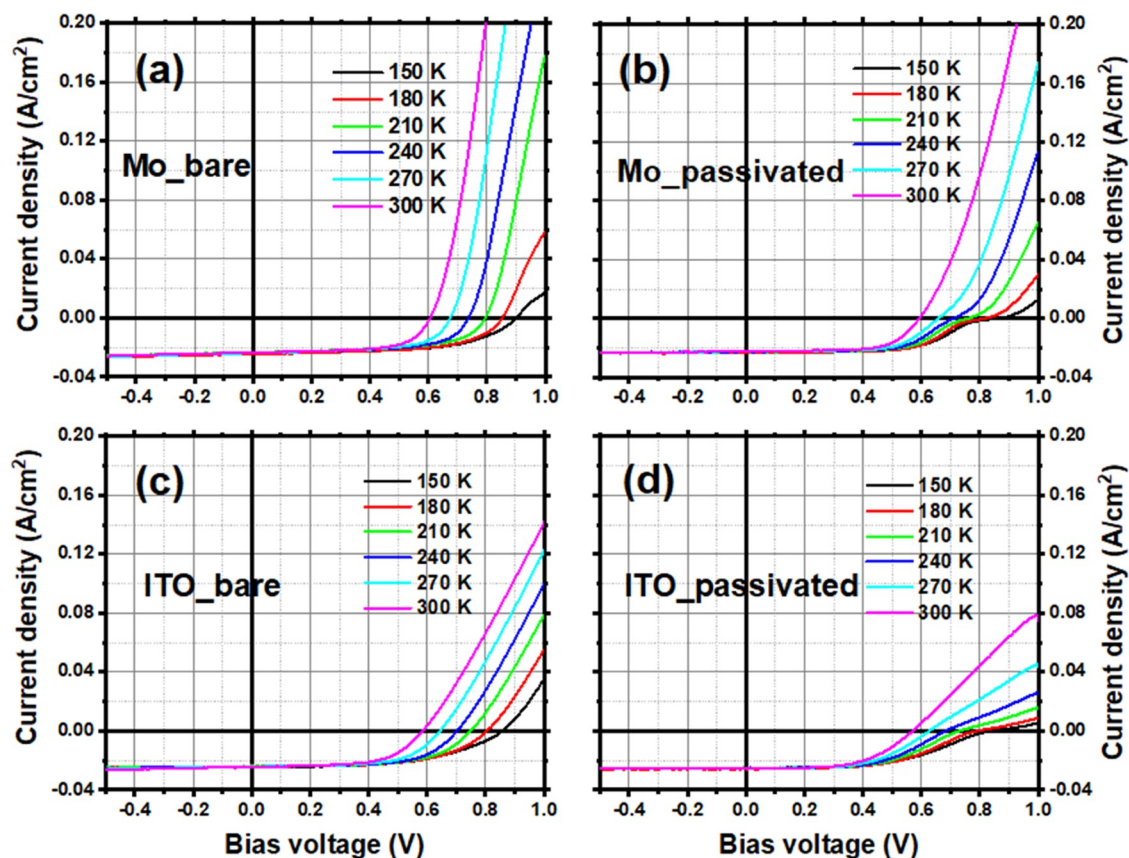


Figure 5. Temperature-dependent current–voltage properties of representative ultrathin CIGSe solar cells on Mo (a) without Mo_{bare} and (b) with SiO₂ passivation layer Mo_{passivated} and on ITO substrates (c) without ITO_{bare} and (d) with the SiO₂ passivation layer ITO_{passivated}.

In Figure 3a, the black line illustrates the band diagram of the cell with $E_h = 0$ eV. The equivalent circuit is simplified without considering shunt and serial resistances, represented as the basic circuit in black in Figure 3b. j_{ph} is the photogenerated current density in the solar cell's main p–n junction, V_D and j_D are the voltage and the current at the main diode, respectively, and j_{net} is the net current density flowing through the circuit. In addition, the red dotted line shown in Figure 3a presents the band diagram of a solar cell with $E_h = 0.2$ eV, and the equivalent circuit is shown in Figure 3b: the additional diode drawn in red simulates the Schottky back-contact diode with a reverse direction compared to the main black diode. V_s and j_s represent the voltage and the current upon the Schottky diode.

Figure 4a presents the simulated $j_{net}V$ curves as a function of S_b for the solar cell with Ohmic contact. As we expect, a higher S_b slightly deteriorates the cell performance. The reason is that increased back recombination induces a loss of photogenerated carriers during the collection process. Therefore, the back recombination not only decreases j_{sc} at zero bias but also V_{oc} and FF. Such an evolution trend is consistent with our experimental results of cells on Mo, as shown in Figure 4b. The black line corresponds to the bare solar cell without SiO₂, (Mo_{bare}) exhibiting an inferior $j_{net}V$ curve compared to Mo_{passivated} shown in red. We notice the net forward current j_{net} in the first quadrant is more restrained after passivation. The origin is an increase in R_s from 0.6 to 1.7 $\Omega\text{ cm}^2$ with the insertion of SiO₂. Generally, R_s is more likely to influence the $j_{net}V$ curve when the forward j_{net} is high in the main diode, corresponding to the first quadrant

here. In contrast, in SCAPS simulation, the $j_{net}V$ results take no R_s or R_{sh} into account. One major deviation between Figure 4a and b is the V_{oc} difference. In the simulated $j_{net}V$, the lower S_b exhibits a more significant V_{oc} enhancement than in experiments. The main reason is that the E_h of Mo-based solar cells is not 0 eV but closer to 0.1 eV, as shown in Figure S2a. We also notice that the j_{sc} enhancement of Mo_{passivated} is higher in experiments than in the simulations. This is because the optical benefit (absorption increase from the inserted low refractive index SiO₂ layer) is not being considered in SCAPS simulations. As a shortcoming in SCAPS simulations, we only put the electrical variations into the simplified simulation model. The optical increase introduced by the SiO₂ layer can be simulated by, e.g., RefDex,³⁹ as shown in Supporting Information Table S1.

In the case of a Schottky contact solar cell, however, a higher S_b improves the $j_{net}V$ characteristics, as shown in Figure 4c. The higher S_b relaxes the current limitation of the Schottky back diode, as the direction of the Schottky diode is opposite to the CdS/CIGSe main junction. In view of the carrier collection process, the Schottky back contact is a barrier for the holes to pass. With a higher S_b , the holes can annihilate at the interface supporting the flow of the current.³⁷ Correspondingly, V_{oc} and FF improve continuously for cells with a Schottky contact when S_b increases. Figure 4d plots the corresponding experimental $j_{net}V$ curves of the solar cells on ITO. In this case, the unpassivated cell (ITO_{bare}, black line) with a higher S_b exhibits a better PV performance than ITO_{passivated}. The red line of ITO_{passivated} shows a

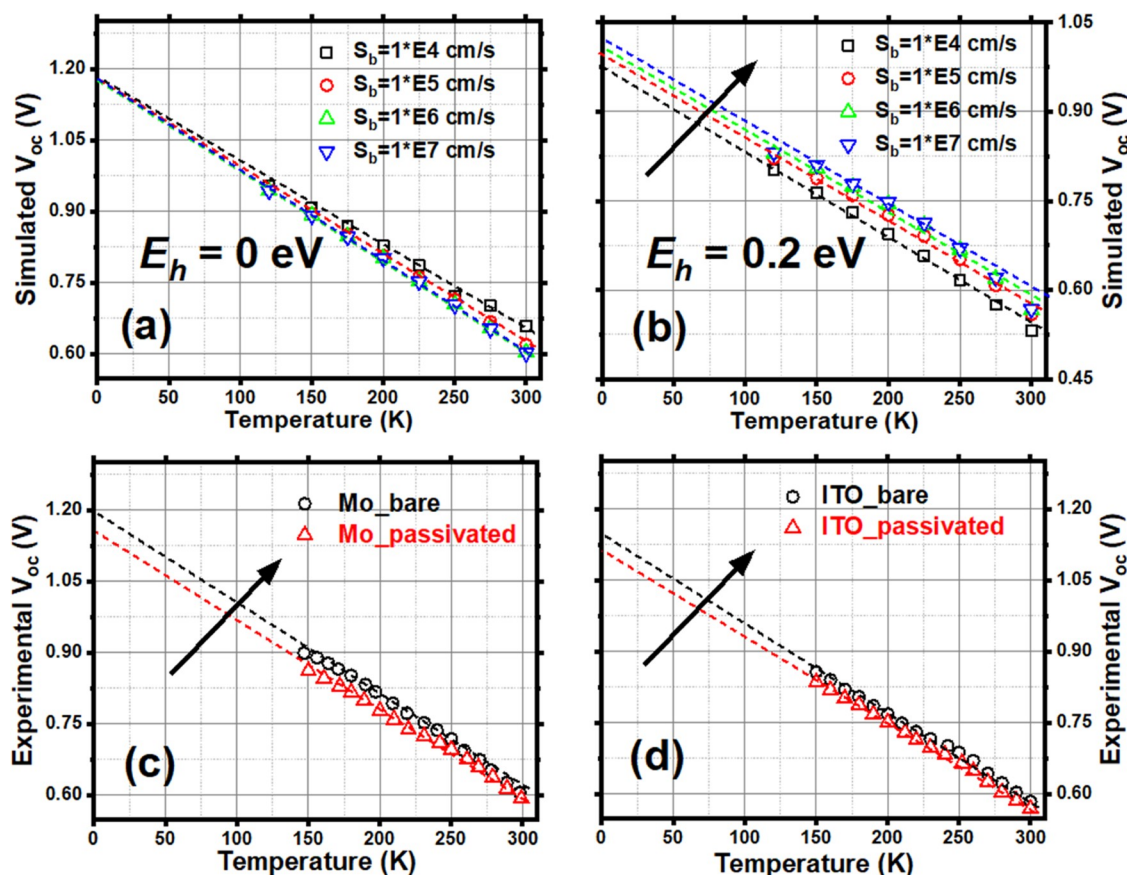


Figure 6. SCAPS-simulated temperature-dependent V_{oc} at varied S_b for (a) Ohmic ($E_h = 0$ eV) and (b) Schottky ($E_h = 0.2$ eV) back contact. Experimental temperature-dependent V_{oc} for CIGSe solar cells on (c) Mo and (d) ITO. Arrows indicate the direction of increasing S_b .

slightly suppressed j_{net} in the first quadrant for similar reasons as on Mo.

Coming back to the simulations shown in Figure 4a,c, the two E_h values of 0 and 0.2 eV are chosen as two extreme example conditions for an explicit comparison and discussion. If we vary E_h in smaller steps, there should be a turning point E_t (separation value): when E_h of the CIGSe solar cell is higher than E_t , a higher S_b will be favorable for its PV performance (here, we refer to it as the Schottky case). On the contrary, when E_h is lower than E_t , the higher S_b will be detrimental to the solar cell (we refer to it as the Ohmic case). Based on this, we simulate the solar cell characteristics with continuously varying E_h in the range from 0 to 0.5 eV, and find E_t for the ultrathin CIGSe solar cell to be 0.17 eV, as shown in Supporting Information Figure S2. Therefore, based on the Eff turning point, we define $E_h < 0.17$ eV as the Ohmic contact and $E_h > 0.17$ eV as the Schottky contact. In contrast to the simulations shown in our previous work,³¹ which were calculated based on the simplified homojunction model,³¹ the derivation of E_t shown in Table S3 used a more representative structure of the CIGSe solar cell consisting of back contact/CIGSe/ODC/CdS/i-ZnO/AZO (ODC means ordered vacancy compound).

Generally, recombination current density j_{re} and the thermal emission current density j_{th} are two independent ways to describe the carriers passing the back interface.³⁷ Recombination current density j_{re} represents the part of the current consisting of electrons and holes captured by the trap states and annihilated there. As mentioned earlier, j_{re} can be expressed as $j_{re} = S_b \times D_p = s_p \times v_{th} \times N_t \times D_p$. Therefore,

j_{re} is sensitive to the passivation as it is proportional to N_t .³⁷ Meanwhile, the thermal emission current density j_{th} describes the part of current consisting of electrons or holes surpassing the energy barrier E_h via thermal emission. j_{th} can be expressed as $j_{th} = A' \times T^2 \times \exp(-qE_h/k_B T)$, where A' is the effective Richardson constant, T is the temperature, and $q/k_B T$ is the reciprocal of the thermal energy.³⁷ Therefore, j_{th} is strongly dependent on the temperature T and barrier height E_h , while j_{re} is more likely to be affected by N_t or S_b , respectively (the thermal velocity is only weakly dependent on the temperature, resulting from $v_{th} = \sqrt{k_B T/m}$, with $k_B T$ being the thermal energy and m being the hole mass). Overall, the net current j_{net} equals the sum of the thermal emission current j_{th} and the recombination current j_{re} .

To study the influence of temperature and passivation on the $j_{net}V$ properties of the solar cells, Figure 5 shows the temperature-dependent $j_{net}V$ curves of four representative samples. For Mo_{bare} (Figure 5a), when the temperature drops to ≤ 180 K, the $j_{net}V$ curve shows a suppressed current in the first quadrant. It implies that for temperatures equal to or below 180 K, the electrons' thermal energy is not high enough to surpass the barrier, hence j_{th} decreases significantly and j_{net} appears suppressed, thus a roll-over effect shows up.⁴⁰ In comparison, for Mo_{passivated} (Figure 5b), the contribution of the recombination current is enormously reduced by the SiO₂ point-contact layer and most current originates from j_{th} . Therefore, j_{net} appears suppressed at 240 K already. In other words, because j_{re} is diminished by the SiO₂ passivation layer, j_{net} dominated by thermal emission is more easily suppressed at

relatively higher temperatures, hence the roll-over shows up earlier during the process of temperature decrease.

On the other hand, ITO_bare in Figure 5c shows no obvious roll-over in the range from 150–300 K. The roll-over only appears when the temperature is further decreased to 130 K (not shown here). It indicates a relatively high part of recombination current (compared to Mo_bare) and j_{net} does not appear suppressed even when the temperature is as low as 150 K. Nevertheless, ITO_passivated shows a roll-over at 240 K (Figure 5d), similar to Mo_passivated. This shows that j_{re} in ITO_passivated has been severely reduced by the SiO₂ alike on Mo, hence j_{net} is suppressed at 240 K. Through the comparison of the temperature when the roll-over in the j_{net}/V curve shows up, we conclude that the SiO₂ point-contact layer passivates both CIGSe/Mo and CIGSe/ITO interfaces. The contribution of j_{re} (or recombination velocity S_b) is decreased in both cases, which also explains the suppressed j_{net} in the first quadrant of Figure 4b,d.

To further demonstrate the different influences of recombination on Ohmic and Schottky contacts, we simulate $V_{\text{oc}}(T)$ curves for various S_b and extract experimental $V_{\text{oc}}(T)$ for ultrathin solar cells with and without SiO₂ passivation, as plotted in Figure 6. In the $V_{\text{oc}}(T)$ curves, the activation energy E_a can be derived from the linear extrapolation toward 0 K, as shown by the dashed lines. E_a equals the band gap E_g for an ideal Ohmic contact and $E_g - E_h$ for a Schottky back contact.⁴¹

We first look at the simulated results. Figure 6a represents the case of the Ohmic back contact. We observe an E_a of 1.18 eV, which is independent of S_b . Meanwhile, for the device with a Schottky back contact showing non-negligible E_h (Figure 6b), E_a drops below E_g (1.1 eV in our simulation), as $E_a = E_g - E_h$. From fitting the figure, E_a on the Schottky back contact is only 0.97 eV. In addition, a higher S_b leads to a larger E_a , indicating a smaller effective E_h . This indicates that a higher S_b can assist the hole transport toward the back contact, diminishing the blocking effect of E_h for the current. Overall, unlike on Ohmic contact devices, the simulations imply that a higher S_b is favorable in the cells with the Schottky back contact.

Moving forward to the experimental $V_{\text{oc}}(T)$ results shown in Figure 6c,d, we first find that E_a is lower for the passivated cells compared to the bare references on both substrates. Second, E_a is overall larger on Mo (>1.14 eV) than on ITO (<1.14 eV). It confirms two points: (1) both CIGSe/Mo and CIGSe/ITO are non-Ohmic contacts; they have nonzero E_h . (2) Ultrathin CIGSe solar cells on ITO have a higher E_h than those on Mo. More specifically, on ITO, the SiO₂ passivation layer leads to a higher E_h and thus a lower E_a , which is consistent with the theoretical demonstration that a smaller S_b means a stronger blocking effect for the solar cells with a Schottky back contact E_h . Also, the fact that SiO₂ is beneficial to Mo while detrimental to ITO was decided by the E_h value at the back contact. Besides, a notable difference between the simulation and experiment is that E_a is independent of S_b in the simulated cell with the Ohmic contact (Figure 6a), whereas it reveals a dependence in experiments on Mo (Figure 6c). The reason is a non-negligible E_h also for the CIGSe solar cells on Mo, for which the contact of CIGS/Mo is typically referred to as quasi-Ohmic instead of Ohmic contact.^{42–44}

From the $V_{\text{oc}}(T)$ comparison above, it has been revealed that the back interface passivation has a double-sided effect on the photovoltaic properties of ultrathin CIGSe solar cells. On the one hand, passivation enables lower recombination of

photogenerated carriers and hence benefits the cell performance. On the other hand, passivation aggravates the blocking of the forward current through the back Schottky diode, which deteriorates the cell with a Schottky back contact. For the solar cells on Mo, due to E_h being small and the resultant current blocking effect marginal, the favorable effect dominates over the adverse one. Therefore, in addition to optical benefits brought by the passivation layer, introducing a SiO₂ passivation layer increases the performance of the ultrathin CIGSe solar cells on Mo. In contrast, for the cells on ITO, the back potential barrier E_h and the resultant current blocking effect are not negligible. The current blocking effect dominates, and a back interface passivation tends to deteriorate the cell performance as the blocking behavior is reinforced.

Finally, on Mo substrates, regarding the absence of V_{oc} enhancement after back passivation shown in Table 1, it should be particularly interpreted. One reason is the steep Ga back grading in our samples (see supporting Figure S1). It repels photogenerated electrons away from the back contact and thus restrains the back recombination, which acts similarly to passivation. Exactly because of this, back interface passivation will bring a reduced beneficial effect on ultrathin cells with a high Ga grading. More importantly, due to the absorbers being prepared at a quite low temperature in this work (compared to the generally used 565 °C in ref 8, our 450 °C is relatively low), it is speculated that the interfacial MoSe_x was not formed well. This also decreases V_{oc} to a certain degree.^{45–47} Under the combined actions of these two factors, V_{oc} remains stable after back interface passivation for ultrathin CIGSe solar cells on Mo.

CONCLUSIONS

In this work, we comparatively study the effect of SiO₂ point-contact passivation layers in ultrathin CIGSe solar cells on Mo and ITO back contacts. The SiO₂ passivation layer improves the cell performance with a relative efficiency enhancement of 16% for the cells on Mo. In contrast, cells on ITO exhibit a reverse evolution trend, implying that the back passivation is not desirable. Two factors are responsible for the sharp contrast. Optically, the SiO₂ point-contact passivation layer improves the back reflectivity of CIGSe/Mo and leads to an increase in absorption which is negligible for the interface of CIGSe/ITO. Electrically, the passivation layer reduces the recombination of photogenerated carriers, which is beneficial for CIGSe solar cells. However, both theoretical and experimental results imply that the back passivation also aggravates the current limitation for solar cells with a Schottky back contact, as the passivation layer can suppress the hole transport to the back contact via recombination. It appears that recombination is an important method for carrier transport when E_h takes a non-negligible value. Since CIGSe solar cells on Mo have a small E_h , the electrical benefits of SiO₂ outweigh the unfavorable ones. As E_h on ITO is relatively high, the aggravated current blocking effect prevails the benefits. Consequently, back interface passivation enhances the performance for cells on Mo and deteriorates it for cells on ITO. These findings can support further understanding of the carrier transport mechanism in ultrathin CIGSe solar cells with ITO back contact.

■ ASSOCIATED CONTENT

SI Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acsam.2c00088>.

Equivalent absorption current on Mo and ITO (Table S1), PV parameters of different contact ratios (Table S2), model parameters for SCAPS simulation (Table S3), GD-OES depth distribution of the Cu and Ga ratio (Figure S1), and PV parameters of different S_b values dependent on different E_h values (Figure S2) (PDF)

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Notes

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■ REFERENCES

- (1) Nakamura, M.; Yamaguchi, K.; Kimoto, Y.; Yasaki, Y.; Kato, T.; Sugimoto, H. Cd-Free Cu(In,Ga)(Se,S)₂ Thin-Film Solar Cell with Record Efficiency of 23.35%. *IEEE J. Photovoltaics* **2019**, *9*, 1863–1867.
- (2) Abou-Ras, D.; Wagner, S.; Stanbery, B. J.; Schock, H.-W.; Scheer, R.; Stolt, L.; Siebentritt, S.; Lincot, D.; Eberspacher, C.; Kushiya, K.; Tiwari, A. N. Innovation Highway: Breakthrough Milestones and Key Developments in Chalcopyrite Photovoltaics From a Retrospective Viewpoint. *Thin Solid Films* **2017**, *633*, 2–12.
- (3) Feurer, T.; Reinhard, P.; Avancini, E.; Bissig, B.; Löckinger, J.; Fuchs, P.; Carron, R.; Weiss, T. P.; Perrenoud, J.; Stutterheim, S.; Buecheler, S.; Tiwari, A. N. Progress in Thin Film CIGS Photovoltaics

– Research and Development, Manufacturing, and Applications. *Prog. Photovoltaics Res. Appl.* **2017**, *25*, 645–667.

(4) Ramanujam, J.; Singh, U. P. Copper Indium Gallium Selenide Based Solar Cells – a review. *Energy Environ. Sci.* **2017**, *10*, 1306–1319.

(5) Wang, Y.-C.; Wu, T.-T.; Chueh, Y.-L. A Critical Review on Flexible Cu(In, Ga)Se₂ (CIGS) Solar Cells. *Mater. Chem. Phys.* **2019**, *234*, 329–344.

(6) Ochoa, M.; Buecheler, S.; Tiwari, A. N.; Carron, R. Challenges and Opportunities for An Efficiency Boost of Next Generation Cu(In,Ga)Se₂ Solar Cells: Prospects for a Paradigm Shift. *Energy Environ. Sci.* **2020**, *13*, 2047–2055.

(7) Massiot, I.; Cattoni, A.; Collin, S. Progress and Prospects for Ultrathin Solar Cells. *Nat. Energy* **2020**, *5*, 959–972.

(8) Mansfield, L. M.; Kanevce, A.; Harvey, S. P.; Bowers, K.; Beall, C.; Glynn, S.; Repins, I. L. Efficiency Increased to 15.2% for Ultra-thin Cu(In,Ga)Se₂ Solar Cells. *Prog. Photovoltaics Res. Appl.* **2018**, *26*, 949–954.

(9) Yin, G.; Song, M.; Duan, S.; Manley, P.; Greiner, D.; Kaufmann, C. A.; Schmid, M. Well-Controlled Dielectric Nanomeshes by Colloidal Nanosphere Lithography for Optoelectronic Enhancement of Ultrathin Cu(In,Ga)Se₂ Solar Cells. *ACS Appl. Mater. Interfaces* **2016**, *8*, 31646–31652.

(10) Ohm, W.; Riedel, W.; Aksünger, Ü.; Greiner, D. A. C.; Kaufmann, Ch.; Lux-Steiner, M.; Gledhill, S. In *Bifacial Cu(In,Ga)Se₂ Solar Cells with Submicron Absorber Thickness: Back-contact Passivation and Light Management*, Photovoltaic Specialist Conference (PVSC), IEEE, 2015; pp 1–5, DOI: [10.1109/PVSC.2015.7356416](https://doi.org/10.1109/PVSC.2015.7356416).

(11) Vermang, B.; Wätjen, J. T.; Fjällström, V.; Rostvall, F.; Edoff, M.; Gunnarsson, R.; Pilch, I.; Helmersson, U.; Kotipalli, R.; Henry, F.; Flandre, D. Highly Reflective Rear Surface Passivation Design for Ultra-thin Cu(In,Ga)Se₂ Solar Cells. *Thin Solid Films* **2015**, *582*, 300–303.

(12) Casper, P.; Hünig, R.; Gomard, G.; Kiowski, O.; Reitz, C.; Lemmer, U.; Powalla, M.; Hetterich, M. Optoelectrical Improvement of Ultra-thin Cu(In,Ga)Se₂ Solar Cells Through Microstructured MgF₂ and Al₂O₃ Back Contact Passivation Layer. *Phys. Status Solidi RRL* **2016**, *10*, 376–380.

(13) Bose, S.; Cunha, J. M. V.; Suresh, S.; De Wild, J.; Lopes, T. S.; Barbosa, J. R. S.; Silva, R.; Borme, J.; Fernandes, P. A.; Vermang, B.; Salomé, P. M. P. Optical Lithography Patterning of SiO₂ Layers for Interface Passivation of Thin Film Solar Cells. *Solar RRL* **2018**, *2*, No. 1800212.

(14) Cunha, J. M. V.; Fernandes, P. A.; Hultqvist, A.; Teixeira, J. P.; Bose, S.; Vermang, B.; Garud, S.; Buldu, D.; Gaspar, J.; Edoff, M.; Leitao, J. P.; Salome, P. M. P. Insulator Materials for Interface Passivation of Cu(In,Ga)Se₂ Thin Films. *IEEE J. Photovoltaics* **2018**, *8*, 1313–1319.

(15) Garud, S.; Gampa, N.; Allen, T. G.; Kotipalli, R.; Flandre, D.; Batuk, M.; Hadermann, J.; Meuris, M.; Poortmans, J.; Smets, A.; Vermang, B. Surface Passivation of CIGS Solar Cells Using Gallium Oxide. *Phys. Status Solidi A* **2018**, *215*, No. 1700826.

(16) Ledinek, D.; Donzel-Gargand, O.; Sköld, M.; Keller, J.; Edoff, M. Effect of Different Na Supply Methods on Thin Cu(In,Ga)Se₂ Solar Cells With Al₂O₃ Rear Passivation Layers. *Sol. Energy Mater. Sol. Cells* **2018**, *187*, 160–169.

(17) Lopes, T. S.; Cunha, J. M. V.; Bose, S.; Barbosa, J. R. S.; Borme, J.; Donzel-Gargand, O.; Rocha, C.; Silva, R.; Hultqvist, A.; Chen, W.-C.; Silva, A. G.; Edoff, M.; Fernandes, P. A.; Salome, P. M. P. Rear Optical Reflection and Passivation Using a Nanopatterned Metal/Dielectric Structure in Thin-Film Solar Cells. *IEEE J. Photovoltaics* **2019**, *9*, 1421–1427.

(18) Schneider, T.; Tröndle, J.; Fuhrmann, B.; Syrowatka, F.; Sprafke, A.; Scheer, R. Ultrathin CIGSe Solar Cells with Integrated Structured Back Reflector. *Solar RRL* **2020**, *4*, No. 2000295.

(19) Kotipalli, R.; Poncelet, O.; Li, G.; Zeng, Y.; Francis, L. A.; Vermang, B.; Flandre, D. Addressing the Impact of Rear Surface Passivation Mechanisms on Ultra-thin Cu(In,Ga)Se₂ Solar Cell

Performances Using SCAPS 1-D model. *Sol. Energy* **2017**, *157*, 603–613.

(20) Cunha, J. M. V.; Oliveira, K.; Lontchi, J.; Lopes, T. S.; Curado, M. A.; Barbosa, J. R. S.; Vinhais, C.; Chen, W.-C.; Borme, J.; Fonseca, H.; Gaspar, J.; Flandre, D.; Edoff, M.; Silva, A. G.; Teixeira, J. P.; Fernandes, P. A.; Salomé, P. M. P. High-Performance and Industrially Viable Nanostructured SiO_x Layers for Interface Passivation in Thin Film Solar Cells. *Solar RRL* **2021**, *5*, No. 2000534.

(21) Kotipalli, R.; Vermang, B.; Joel, J.; Rajkumar, R.; Edoff, M.; Flandre, D. Investigating the Electronic Properties of $\text{Al}_2\text{O}_3/\text{Cu}(\text{In,Ga})\text{Se}_2$ Interface. *AIP Adv.* **2015**, *5*, No. 107101.

(22) Schmid, M.; Manley, P.; Ott, A.; Song, M.; Yin, G. Nanoparticles for Light Management in Ultrathin Chalcopyrite Solar Cells. *J. Mater. Res.* **2016**, *31*, 3273–3289.

(23) Schmid, M. Review on Light Management by Nanostructures in Chalcopyrite Solar Cells. *Semicond. Sci. Technol.* **2017**, *32*, No. 043003.

(24) Kim, D.; Shin, S. S.; Lee, S. M.; Cho, J. S.; Yun, J. H.; Lee, H. S.; Park, J. H. Flexible and Semi-transparent Ultra-thin CuInSe_2 Solar Cells Prepared on Ultra-thin Glass Substrate: a Key to Flexible Bifacial Photovoltaic Applications. *Adv. Funct. Mater.* **2020**, *30*, No. 2001775.

(25) Li, Y.; Yin, G.; Gao, Y.; Köhler, T.; Lucaßen, J.; Schmid, M. Sodium Control in Ultrathin $\text{Cu}(\text{In,Ga})\text{Se}_2$ Solar Cells on Transparent Back Contact for Efficiencies Beyond 12%. *Sol. Energy Mater. Sol. Cells* **2021**, *223*, No. 110969.

(26) Gouillart, L.; Cattoni, A.; Chen, W. C.; Goffard, J.; Riekehr, L.; Keller, J.; Jubault, M.; Naghavi, N.; Edoff, M.; Collin, S. Interface Engineering of Ultrathin $\text{Cu}(\text{In,Ga})\text{Se}_2$ Solar Cells on Reflective Back Contacts. *Prog. Photovoltaics Res. Appl.* **2021**, *29*, 212–221.

(27) Shin, M. J.; Jo, J. H.; Cho, A.; Gwak, J.; Yun, J. H.; Kim, K.; Ahn, S. K.; Park, J. H.; Yoo, J.; Jeong, I.; Choi, B.-H.; Cho, J.-S. Semi-transparent Photovoltaics Using Ultra-thin $\text{Cu}(\text{In,Ga})\text{Se}_2$ Absorber Layers Prepared by Single-stage Co-evaporation. *Sol. Energy* **2019**, *181*, 276–284.

(28) Shin, M. J.; Lee, A.; Cho, A.; Kim, K.; Ahn, S. K.; Park, J. H.; Yoo, J.; Yun, J. H.; Gwak, J.; Shin, D.; Jeong, I.; Cho, J.-S. Semitransparent and Bifacial Ultrathin $\text{Cu}(\text{In,Ga})\text{Se}_2$ Solar Cells via a Single-stage Process and Light-management Strategy. *Nano Energy* **2021**, *82*, No. 105729.

(29) Saifullah, M.; Kim, D.; Cho, J.-S.; Ahn, S.; Ahn, S.; Yun, J. H.; Lee, H. S.; Park, J. H. The role of NaF Post-deposition Treatment on the Photovoltaic Characteristics of Semitransparent Ultrathin $\text{Cu}(\text{In,Ga})\text{Se}_2$ Solar Cells Prepared on Indium-tin-oxide Back Contacts: A Comparative Study. *J. Mater. Chem. A* **2019**, *7*, 21843–21853.

(30) Saifullah, M.; Rasool, S.; Ahn, S.; Kim, K.; Cho, J. S.; Yoo, J. S.; Shin, W. S.; Yun, J. H.; Park, J. H. Performance and Uniformity Improvement in Ultrathin $\text{Cu}(\text{In,Ga})\text{Se}_2$ Solar Cells with a WO_x Nano-Interlayer at the Absorber/Transparent Back-Contact Interface. *ACS Appl. Mater. Interfaces* **2019**, *11*, 655–665.

(31) Tu, Y.; Li, Y.; Klenk, R.; Yin, G.; Schmid, M. Is a Passivated Back Contact Always Beneficial for $\text{Cu}(\text{In,Ga})\text{Se}_2$ Solar Cells. *Prog. Photovoltaics Res. Appl.* **2021**, *30*, 393–400.

(32) Yin, G.; Brackmann, V.; Hoffmann, V.; Schmid, M. Enhanced Performance of Ultra-thin $\text{Cu}(\text{In,Ga})\text{Se}_2$ Solar Cells Deposited at Low Process Temperature. *Sol. Energy Mater. Sol. Cells* **2015**, *132*, 142–147.

(33) Decock, K.; Khelifi, S.; Buecheler, S.; Pianezzi, F.; Tiwari, A. N.; Burgelman, M. Defect Distributions in Thin Film Solar Cells Deduced From Admittance Measurements Under Different Bias Voltages. *J. Appl. Phys.* **2011**, *110*, No. 063722.

(34) Decock, K.; Khelifi, S.; Burgelman, M. Modelling Multivalent Defects in Thin Film Solar Cells. *Thin Solid Films* **2011**, *519*, 7481–7484.

(35) Burgelman, M.; Decock, K.; Khelifi, S.; Abass, A. Advanced Electrical Simulation of Thin Film Solar Cells. *Thin Solid Films* **2013**, *535*, 296–301.

(36) Decock, K.; Khelifi, S.; Burgelman, M. Modelling and Measurement of the Metastable Defect Distribution in Chalcopyrite-based Thin Film Solar Cells. *Thin Solid Films* **2013**, *535*, 362–365.

(37) Sze, S. M.; Ng, K. K. *Physics of Semiconductor Devices*; John Wiley & Sons: Hoboken, New Jersey, Published simultaneously in Canada, 2007; Chapter 1, p 68.

(38) Salomé, P. M. P.; Vermang, B.; Ribeiro-Andrade, R.; Teixeira, J. P.; Cunha, J. M. V.; Mendes, M. J.; Haque, S.; Borme, J.; Aguas, H.; Fortunato, E.; Martins, R.; González, J. C.; Leitão, J. P.; Fernandes, P. A.; Edoff, M.; Sadewasser, S. Passivation of Interfaces in Thin Film Solar Cells: Understanding the Effects of a Nanostructured Rear Point Contact Layer. *Adv. Mater. Interfaces* **2018**, *5*, No. 1701101.

(39) Manley, P.; Yin, G.; Schmid, M. A method for Calculating the Complex Refractive Index of Inhomogeneous Thin Films. *J. Phys. D: Appl. Phys.* **2014**, *47*, No. 205301.

(40) Rebecca, S. S-Shaped Current–Voltage Characteristics in Solar Cells: A Review. *IEEE J. Photovoltaics* **2019**, *9*, 1477–1484.

(41) Hegedus, S. S.; Shafarman, W. N. Thin-film Solar Cells: Device Measurements and Analysis. *Prog. Photovoltaics Res. Appl.* **2004**, *12*, 155–176.

(42) Chirilă, A.; Buecheler, S.; Pianezzi, F.; Bloesch, P.; Gretener, C.; Uhl, A. R.; Fella, C.; Kranz, L.; Perrenoud, J.; Seyrling, S.; Verma, R.; Nishiwaki, S.; Romanyuk, Y. E.; Bilger, G.; Tiwari, A. N. Highly Efficient $\text{Cu}(\text{In,Ga})\text{Se}_2$ Solar Cells Grown on Flexible Polymer Films. *Nat. Mater.* **2011**, *10*, 857–861.

(43) Hsiao, K. J.; Liu, J. D.; Hsieh, H. H.; Jiang, T. S. Electrical Impact of MoSe_2 on CIGS Thin-film Solar Cells. *Phys. Chem. Chem. Phys.* **2013**, *15*, 18174–18178.

(44) Zhang, X.; Kobayashi, M.; Yamada, A. Comparison of $\text{Ag}(\text{In,Ga})\text{Se}_2/\text{Mo}$ and $\text{Cu}(\text{In,Ga})\text{Se}_2/\text{Mo}$ Interfaces in Solar Cells. *ACS Appl. Mater. Interfaces* **2017**, *9*, 16215–16220.

(45) Abou-Ras, D.; Kostorz, G.; Bremaud, D.; Kälén, M.; Kurdesau, F. V.; Tiwari, A. N.; Döbeli, M. Formation and Characterisation of MoSe_2 for $\text{Cu}(\text{In,Ga})\text{Se}_2$ Based Solar Cells. *Thin Solid Films* **2005**, *480–481*, 433–438.

(46) Kohara, N.; Nishiwaki, S.; Hashimoto, Y.; Negami, T.; Wada, T. Electrical Properties of the $\text{Cu}(\text{In,Ga})\text{Se}_2/\text{MoSe}_2/\text{Mo}$ Structure. *Sol. Energy Mater. Sol. Cells* **2001**, *67*, 209–215.

(47) Hsiao, K.-J.; Liu, J.; Hsieh, H.; Jiang, T. Electrical Impact of MoSe_2 on CIGS Thin-film Solar Cells. *Phys. Chem. Chem. Phys.* **2013**, *15*, 18174–18178.