Comparative Study of Al₂O₃ and HfO₂ for Surface Passivation of Cu(In,Ga)Se₂ Thin Films: An Innovative Al₂O₃/HfO₂ Multistack Design

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In Cu(In,Ga)Se₂ (CIGS) thin-film solar cells, interface recombination is one of the most important limiting factors with respect to device performance. Herein, metal–insulator–semiconductor samples are used to investigate and compare the passivation effects of Al₂O₃ and HfO₂ at the interface with CIGS. Capacitance–voltage–frequency measurements allow to qualitatively and quantitatively assess the existence of high negative charge density ($\frac{Q_f}{C_0} \approx 10^{12} \text{ cm}^2$) and low interface-trap density ($\frac{D_{it}}{C_0} \approx 10^{11} \text{ cm}^2 \text{ eV}^{-1}$). At the rear interface of CIGS solar cells, these, respectively, induce field-effect and chemical passivation. A trade-off is highlighted between stronger field-effect for HfO₂ and lower interface-trap density for Al₂O₃. This motivates the usage of Al₂O₃ to induce chemical passivation at the front interface of CIGS solar cells but raises the issue of its processing compatibility with the buffer layer. Therefore, an innovative Al₂O₃/HfO₂ multistack design is proposed and investigated for the first time. Effective chemical passivation is similarly demonstrated for this novel design, suggesting potential decrease in recombination rate at the front interface in CIGS solar cells and increased efficiency. 300 °C annealing in N₂ environment enable to enhance passivation effectiveness by reducing $D_{it}$ while surface cleaning may reveal useful for alternative CIGS processing methods.

1. Introduction

Solar power is now widely accepted as a strong candidate in tomorrow’s cleaner energy network, replacing conventional fossil fuel-based energies and reducing the emission of greenhouse gases.[1] With laboratory efficiencies approaching 25% and the potential use of a variety of rigid or flexible substrates, Cu(In,Ga)Se₂ (CIGS) solar cells are expected to largely contribute to the development of building integrated photovoltaics.[1]

Still, active research needs to be undertaken to further increase the performance of CIGS-based cells and more particularly reduce their voltage deficit.[1] Solving this issue should inevitably consider the electrical losses due to nonradiative recombination mechanisms, especially important at the interfaces. The solution investigated here relies on applying passivation strategies similar to the ones pursued in the silicon industry, e.g., passivated emitter and rear cell (PERC).[2–5] This method consists in integrating dielectric layers at the interfaces most affected by carrier recombination so as to mitigate the impact on performance.
Passivation has already been widely investigated and used at both interfaces in CIGS solar cells to allow overall enhancements of electrical performance, and more generally efficiency, with different dielectric materials such as Al$_2$O$_3$,[6–12] HfO$_2$,[8,13–15] and GaO$_x$.[16] Indeed, such metallic oxides enable to reduce the density of interface traps ($D_{it}$), i.e., down to the order of $10^{13}$–$10^{17}$ cm$^{-2}$ eV$^{-1}$,[6–8,11,13–15] and the related recombination losses at the concerned interface. This corresponds to a reduction of $D_{it}$ by 1–2 orders of magnitude as compared with a full metal contact.[17] At the same time, the surface density of fixed charges ($Q_f$), typically of the order of $10^{12}$–$10^{13}$ cm$^{-2}$,[11,12] present at the oxide/CIGS interface produces an electrical field potentially diminishing minority carrier concentration and hence recombination, depending on the charge sign and the concerned interface.

The focus here is put on comparing the surface passivation effects of atomic layer deposited (ALD) oxide layers made of Al$_2$O$_3$ and HfO$_2$ at the interface with CIGS. We discuss their potential integration at either the rear or front interface in CIGS solar cells. The dielectric layers investigated here have thicknesses ranging from 20 to 50 nm and are thus not highly subjected to tunneling effects, as opposed to ultrathin Al$_2$O$_3$ layers used, for instance, in tunneling-based siliconization strategies for silicon solar cells.[18] This comparative study is based on capacitance–voltage (CV) measurements realized on metal–insulator–semiconductor (MIS) structures involving both Al$_2$O$_3$ and HfO$_2$ (Section 2.1 and 2.2). Such samples allow a simple analysis of the interface effects between oxide and CIGS layers before considering the influence of the buffer and window layers. In the view of integrating these materials for front passivation of complete solar cells and increase efficiency, an innovative Al$_2$O$_3$/HfO$_2$ multistack design is similarly investigated in Section 2.3, along with the influence of annealing treatments and surface cleaning.

2. Results

2.1. Field-Effect Passivation

2.1.1. Analysis Technique

To quantify $Q_f$ in the Al$_2$O$_3$ and HfO$_2$ layers, we inspect the measured CV curves in comparison with the “defect-free” case.[17–19] This allows to determine the sign and magnitude of $Q_f$ and thus assert the effectiveness of field-effect passivation depending on the interface considered, i.e., negative (respectively, positive) $Q_f$ is better suited to passivate the rear (respectively, front) interface. The reference point for that comparison is the flat-band voltage ($V_{fb}$) which marks the onset of the depletion regime.

In the ideal situation without charged defects, $V_{fb}$ equals the intrinsic potential difference ($V_{ms}$) between the metal contact work function potential ($V_m$) and the Fermi level of the CIGS

$$V_{ms} = V_m - \frac{1}{q} \left( \chi_{CIGS} + \frac{E_F^{CIGS}}{2} + \frac{kT}{q} \ln \left( \frac{N_A}{n_i} \right) \right) \quad [1]$$

in which $V_m = \phi_m/q$, with $\phi_m$ the work function of the silver contact considered equal to 4.5 eV in this work.[21] $\chi_{CIGS}$ and $E_F^{CIGS}$ are, respectively, the electronic affinity and bandgap of CIGS, equal to 4.36 and 1.18 eV[22]; $N_A$ is the density of shallow acceptor dopants in the CIGS layer to be determined with CV measurements; $n_i$ is the intrinsic density of carriers in the CIGS layer and equal to $1.4 \times 10^{10}$ cm$^{-3}$.[22] $kT/q$ is the thermal energy.

In a real case, the charged defects induce a voltage shift of the CV curves. The magnitude and direction of this shift, respectively, determine the value and sign of the density of charges present in the oxide layer, as summarized in the following expression

$$Q_f = C_{ox} \left( \frac{V_{ms} - V_{fb}}{q} \right) \quad [2]$$

With $C_{ox}$ the oxide capacitance in F cm$^{-2}$. Three different values of $C_{ox}$ are generally considered: $C_{ox,geo}$ is the geometrical capacitance determined by the dielectric permittivity and thickness of the oxide. $C_{ox,max}$ is the maximum capacitance measured in strong accumulation, i.e., at high negative bias. $C_{ox,ext}$ is an estimation based on CV measurements.[23] As the two former quantities are assumed more sensitive to frequency dispersion and carrier statistics, the latter is expected to be the most reliable estimation, especially for the low dielectric thicknesses used here.[23] Thus, only $C_{ox,ext}$ is used in the rest of this report and referred to as $C_{ox}$. The three unknown quantities in Equation (1) and (2) then are $N_A$, $C_{ox}$, and $V_{fb}$ which are all estimated using CV measurements in the following section.

2.1.2. Quantitative Results

Figure 1a shows the 10 kHz measured CV curves corresponding to two MIS samples with either an Al$_2$O$_3$ or HfO$_2$ layer, along with their extracted oxide capacitance, respectively, equal to 0.25 and 0.81 μF cm$^{-2}$. An example of graphical estimation of $C_{ox}$ for the Al$_2$O$_3$-based sample is shown in Figure S1, Supporting Information.[23] The shown CV curves result from a correction of the raw data for series parasitic elements, i.e., resistance and inductance.[24] Both MIS devices exhibit a typical p-type CV behavior with the accumulation plateau slightly below the extracted oxide capacitance at ~1.5 V. The accumulation to depletion transition is steeper for Al$_2$O$_3$ than for HfO$_2$, suggesting slightly poorer capacitive behavior for the latter device.

The extraction of $V_{fb}$ and $N_A$ is here based on the slope of the linear part of $(1/C_m)²$ versus applied voltage.[23] where $C_m$ is the measured capacitance per unit area. It results in the values shown in Figure 1b which, following Equation (2), in turn correspond to values of $Q_f$ of about $-1.4 \times 10^{12}$ and $-5.8 \times 10^{12}$ cm$^{-2}$ for Al$_2$O$_3$ and HfO$_2$, respectively. Then, it appears that both materials present negative surface charge density as already reported,[6–8,11,14–16] with a higher density for HfO$_2$ as compared with Al$_2$O$_3$ due to both higher oxide capacitance and flat-band voltage. Consequently, HfO$_2$ would most likely induce stronger field-effect passivation of the rear interface in CIGS solar cells and is our best candidate regarding this aspect.

2.2. Chemical Passivation

2.2.1. Analysis Technique

To characterize chemical passivation effects induced by Al$_2$O$_3$ and HfO$_2$ at the interface with CIGS, we need to quantify the
density of recombination centers (traps) at that very interface. As these trap levels are spread along the whole interface bandgap and cannot be distinguished due to the negligible energy spacing between them, it is more practical for experimental evaluation to consider a continuous equivalent interface-trap density distribution ($D_{it}$) with a central energy level and expressed in $\text{cm}^{-2}\text{eV}^{-1}$.

Consequently to this approximation, only the magnitude of $D_{it}$ can be experimentally determined and not the type of interface defects (acceptor or donor).\[17\]

In practice, estimating the magnitude of $D_{it}$ is based on the evolution of either the parallel capacitance ($C$) or conductance ($G$) with both voltage ($V$) and frequency ($f$).\[17,20\] The angular frequency is here denoted $\omega$ and equal to $2\pi f$. In this work, we use the conductance method (CM) because it is less affected by parasitic elements,\[6\] such as those for which the CV curves in Figure 1 were corrected. The CM relies on the fact that, for a fixed bias in the depletion regime (above $V_{fb}$), the curve drawn by the evolution of $G/\omega$ with respect to $\omega$ reaches a peak related to maximum energy losses induced by charge exchange with interface states.\[17,19,20\] The height of this parallel conductance maximum is then a direct image of $D_{it}$, through the following simplified and straightforward expression:\[20\]

$$D_{it} = \frac{2.5 \times (\frac{G}{A \omega})_{\text{max}}}{q} \text{ cm}^{-2}\text{eV}^{-1}$$

in which $(G/A \omega)_{\text{max}}$ is the height of the peak observed on the $G/\omega$ versus $\omega$ curve, normalized by the device area $A$ and expressed in $\text{F cm}^{-2}$. One approximation in the formula used here is the constant value of 2.5 used as correction factor for the peak width statistical fluctuations.\[20\]

As the CM relies on $G/\omega$ versus $\omega$ curves observed for voltages above flat-band (depletion), it is important to reflect about which part of the interface bandgap is inspected for such bias. Indeed, the occupation state of the interface defects depends on the interface Fermi level.\[17,19,20\] Then, the energy band bending induced by varying the applied bias determines the depth of the traps for which $D_{it}$ is extracted (Figure 2).

It is visible that voltages equal to, or more positive than, $V_{fb}$ allow to characterize the density of interface states closer to the midgap. In that region of the bandgap, interface defects induce higher surface recombination as compared with band edges, and are thus more detrimental.\[17\] Therefore, we decide to estimate $D_{it}$ at two different voltages: 1) $V = V_{fb}$ for typical extraction in
and HfO
can actually be etched by ammonia-based
1
For the same bias, the HfO
can
10
2
1
cm
and b)¼ multistack. This novel CIGS/Al
MIS sample
V
8,11,15,26
passivation layer from undesired etching
þ
layer to pre-
or to a resistive potential
1
The increase in
10
is then our best candidate for mitigating
at
2
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¼
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peak is
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V
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at high frequency is
2
D
Parallel conductance peaks related to interface states, observed in depletion at a) V¼ Vfb and b) V¼ Vfb þ 0.5 V, for 20 nm Al2O3 MIS sample (blue) and 30 nm HfO2 MIS sample (red). All the curves shown result from a noise-filtering of the raw data. The values of D
it
are expressed in cm2 eV1.

2.2.2. Quantitative Results

The parallel conductance peaks related to interface traps are shown in Figure 3 for the same samples as Figure 1 and the two different chosen voltages.

At V¼ Vfb, Figure 3a shows an interface defect-related maximum around 10 kHz with a magnitude close to 0.012 mF cm2 for the sample with Al2O3. This in turn corresponds to a D
it
value of about 1.8 ¥ 1011 cm2 eV1, indicating effective chemical passivation at the Al2O3/CIGS interface, as mentioned in Section 1. In particular, the drastic reduction of interface-trap density ensured by Al2O3—made of Al2O3 and typical buffer layers in full CIGS solar cells.

Indeed, we need to guarantee that the front passivation layer—made of Al2O3 in this case—is not damaged when the buffer layer is deposited on its top surface. This is especially important to consider as Al2O3 can actually be etched by ammonia-based solutions, typically involved during the chemical bath deposition (CBD) of buffer layers in CIGS cells. Then, we need a way to protect the front Al2O3 passivation layer from undesired etching during the CBD step. The solution investigated here is to take advantage of hafnium oxide compounds’ compatibility with ammonia. In particular, we use an overlying HfO2 layer to prevent the bottom Al2O3 layer and possible contact openings pattern to be damaged during CBD of buffer layers.

Our whole passivation layer then consists in two superimposed oxide layers of Al2O3 and HfO2, which we call the Al2O3/HfO2 multistack. This novel CIGS/Al2O3/HfO2 configuration has the advantage of keeping interesting chemical passivation effects at the Al2O3/CIGS interface while being compatible with solar cells production. More generally, we believe the

Figure 3. Parallel conductance peaks related to interface states, observed in depletion at a) V¼ Vfb and b) V¼ Vfb þ 0.5 V, for 20 nm Al2O3 MIS sample (blue) and 30 nm HfO2 MIS sample (red). All the curves shown result from a noise-filtering of the raw data. The values of D
it
are expressed in cm2 eV1.

depletion; 2) V¼ Vfb þ 0.5 V to assess the density of deeper traps, i.e., with a higher incidence on recombination rate and thus electrical performance.

For our experiments, we use frequencies in the [1 kHz, 1 MHz] range, as it is typically done in practice to evaluate D
it
.[20]

2.3. Multistack

2.3.1. Motivation

The promising passivation properties of both Al2O3 and HfO2 at the interface with CIGS are compared in our CV analysis of MIS samples. The negative densities of fixed charges and low interface-trap densities observed in Al2O3 and HfO2 can be used to passivate the rear interface of CIGS solar cells and enhance performance, as already reported.[9,10,13,15] Still, we suggest also investigating the potential efficiency improvements when inserting such passivation layers at the CIGS/buffer interface. More precisely, the drastic reduction of interface-trap density ensured by Al2O3, i.e., down to the order of 1010 cm2 eV1 for near-midgap states, could be taken advantage of to guarantee chemical passivation of the front interface. However, this raises the question of processing compatibility between Al2O3 and high-temperature oxidation.

The increase in G/f0 at high frequency is due to series-resistance effects.[17,20] The origin of this parasitic resistance may possibly be attributed to the presence of border traps in the aluminum oxide layer,[29] or to a resistive potential barrier at the back contact.[16] For the same bias, the HfO2 peak is scaled up by about a factor 3 as compared with Al2O3, sign of more prominent interface-trap response and density. Quantitatively speaking, the conductance peak reaches 0.037 mF cm2 for a D
it
value of 5.8 ¥ 1011 cm2 eV1. In comparison with Al2O3, this suggests weaker but still active chemical passivation effects at the HfO2/CIGS interface, given the orders of magnitude observed in similar structures.[15]

At higher bias and thus for trap states closer to midgap (Figure 3b), D
it
is ¥6 (respectively, 8) times lower for Al2O3 (respectively, HfO2) and is reduced to an order of magnitude of 1010 cm2 eV1. The same trend is typically observed when comparing the density of deeper and shallower interface states.[17]

The characterization of chemical passivation reported here tends to indicate that, over a large part of the interface bandgap, Al2O3 induces a more significant reduction of D
it
than HfO2 at the CIGS surface. Al2O3 is then our best candidate for mitigating the interface-trap density and related recombination losses at either one of the two interfaces in CIGS solar cells.
obtained results show the possibility to use an HfO$_2$-based capping layer in multistack configurations that include other materials—also suitable for interface passivation and not resistant to buffer layer processing—than Al$_2$O$_3$.

In the next section, we also investigate two possible methods to optimize our new design. First, applying a more specific cleaning procedure on the CIGS surface before depositing the oxide may improve the CIGS/Al$_2$O$_3$ interface quality. Up to this point, standard ammonium cleaning was used as surface treatment for single-stack samples.

In the following, we compare its effect on multistack devices with another cleaning procedure that is based on ammonium sulfide (AS), reportedly etching undesired secondary phases and improving electrical performance in CIGS-based devices. Second, 300 °C annealing treatments in N$_2$ environment have a demonstrated influence on the materials composition, especially with respect to charge and interface trap distribution, and grain boundary. Therefore, we aim at seeing potential improvements of our multistack devices after application of such annealing processes.

2.3.2. Field-Effect Passivation

The 10 kHz measured CV curves obtained for multistack samples are shown in Figure 4, with a bias range extended to 2 V for observing a sufficient part of the depletion regime. Regardless of CIGS precleaning, $Q_f$ is negative and of the order of $10^{12}$ cm$^{-2}$ before annealing. This result from the superposition of the negative charge densities intrinsically present in both dielectric layers of the stack. There is a slight difference between ammonium and AS cleaning with respect to the measured capacitance at −1.5 V. This might be explained by a small diminution of the effective oxide thickness due to the AS treatment applied on the CIGS surface, thus affecting the actual value of $C_{ox}$.

Annealing treatments at 300 °C influence the charge distribution in the Al$_2$O$_3$/HfO$_2$ stack, as well as the $C_{ox}$ value most likely due to structural modification of the oxide layers. More precisely, the CV curves are shifted leftward by, respectively, 0.16 and 0.3 V for the sample cleaned with ammonia and AS, respectively. This corresponds to about a 50% decrease in $Q_f$, as shown in Figure 4. Increasing the annealing temperature to 400 °C induces similar changes in $Q_f$ (Figure S2, Supporting Information) so that, after either 300 or 400 °C annealing in N$_2$, the global charge distribution in the oxide layers remains negative and of the order of $10^{12}$ cm$^{-2}$.

Regardless of annealing, surface cleaning only has a slight impact on $Q_f$, with a variation in charge density magnitude by about 10%. The ammonium and AS treatment being applied on the CIGS surface, they thus have a limited influence on the charge composition within the oxide layers.

2.3.3. Chemical Passivation

The conductance peaks at $V = V_{fb}$ are shown in Figure 5, considering the voltage shift induced by annealing. The corresponding densities of interface traps $D_{it}$ stay of the order of $10^{11}$ cm$^{-2}$ eV$^{-1}$ for multistack samples, indicating active chemical passivation as expected with the high quality of the Al$_2$O$_3$/CIGS interface. This is especially the case of ammonia precleaned sample with $D_{it} = 2.9 \times 10^{11}$ cm$^{-2}$ eV$^{-1}$ before annealing, as compared with the AS-treated device whose density of interface traps is about three times higher. Even though the AS treatment does not provide the lowest value of $D_{it}$ in our samples, it may prove interesting to improve the quality of CIGS layers processed by one-stage coevaporation or sputtering.

For both ammonium and AS cleaning, 300 °C annealing tends to improve chemical passivation by reducing the density of recombination traps at the interface by 30–40%. An opposite trend is observed in similar samples annealed at 400 °C (Figure S3, Supporting Information), for which $D_{it}$ is increased by a factor 2 after annealing.

Contrarily to the single-layered devices, the $G/\omega$ curves at $V = V_{fb} + 0.5$ V do not exhibit clear peaks in the [1 kHz, 1 MHz] range (Figure S4, Supporting Information). Still, we expect the same trend of decreasing $D_{it}$ for deeper interface states to apply to multistack samples too.

![Figure 4](https://www.pss-a.com)

**Figure 4.** CV curves measured at 10 kHz for multistack samples, respectively, precleaned with a) ammonia and b) AS. The results for nonannealed (NA) samples (respectively, 300 °C annealed samples) are represented in blue (respectively, in red). The curves are shifted leftward after the 300 °C annealing due to the modification or charges distribution within the oxide layers. The values of $Q_f$ are expressed in cm$^{-2}$. The $C_{ox}$ values are extracted from CV measurements in the same way as in Section 2.1.
3. Conclusion

Our comparative characterization of aluminum and hafnium oxide highlights their interesting and versatile surface passivation properties at the interface with CIGS ($Q_l \approx -10^{12}$ cm$^{-2}$ and $D_h \approx 10^{11}$ cm$^{-2}$ s$^{-1}$). In particular, we highlight their complementarity as possible candidates to support the development of both rear- and front-passivated CIGS solar cells.

Indeed, at the Mo/CIGS interface where negative charges create a beneficial back electrical field, either Al$_2$O$_3$ or HfO$_2$ can be used with a tradeoff between stronger field effect for HfO$_2$ and lower interface-trap density for Al$_2$O$_3$.

At the CIGS/buffer interface where positive charges would be more appropriate to reduce minority carrier concentration, Al$_2$O$_3$ is the best choice given its both lower negative $Q_l$ and $D_h$. However, Al$_2$O$_3$ alone is not compatible with the typical deposition technique of buffer layer involved in CIGS solar cells. Therefore, we propose and characterize an innovative Al$_2$O$_3$/HfO$_2$ multistack passivation design in which HfO$_2$ is used to protect the underlying Al$_2$O$_3$ layer from undesired etching during buffer processing. The very low interface-trap density expected with Al$_2$O$_3$ is attested by our CV characterization of both rear- and front-passivated CIGS solar cells.

For the Al$_2$O$_3$/HfO$_2$ multistack, ammonium surface cleaning leads to lower values of $D_h$ as compared with AS treatment. Still, the latter procedure may reveal interesting to apply on CIGS layers deposited and/or grown differently than for our samples. Regardless of CIGS cleaning, $N_2$ annealing treatments at 300 °C have the positive effect of decreasing $D_h$. Eventually, our most effective multistack design regarding chemical passivation is the one with ammonium-based CIGS cleaning and 300 °C annealing in $N_2$, for which $D_h$ is about $2.2 \times 10^{11}$ cm$^{-2}$ s$^{-1}$.

The proposed multistack structure may be further optimized with regards to the thicknesses of the two oxide layers. Moreover, the potential association of this Al$_2$O$_3$/HfO$_2$ configuration with the patterning of contact openings is presently under investigation with encouraging results.

4. Experimental Section

Samples Processing: The general layout of our samples is shown in Figure 6. The front contact consisted of a 200 nm-thick square lattice made of thermally evaporated silver with a contact area of 0.01 cm$^2$ per device. The oxide passivation stack was either single-layered (20 nm Al$_2$O$_3$ or 30 nm HfO$_2$) or multistacked (30 nm Al$_2$O$_3$/20 nm HfO$_2$). The Al$_2$O$_3$ (respectively, HfO$_2$) layers were processed by the Savannah Thermal ALD tool at 300 °C (respectively, 250 °C), with trimethylaluminum (respectively, tetraakis (ethylmethylamino) hafnium) used as precursor and H$_2$O used as reactant for a rate of 0.13 nm/cycle (respectively, 0.15 nm/cycle). The CIGS layers used for this project were produced by three-stage coevaporation with typical thickness between 1.6 and 1.8 μm. Their top surface was cleaned by default with ammonia prior to the oxide deposition, but ammonia sulfide (AS) was used instead for some multistack samples (see Section 4.3). The diffusion of Na atoms toward the CIGS during its processing was ensured by an underlying NaF-based sodium precursor layer (omitted in Figure 6). Below was placed the 300 nm-thick DC-sputtered molybdenum back electrode, resting on top of the sodium fluoride precursor layer is
the 2 – 3 mm-thick soda-lime glass (SLG) substrate. The CIGS layers presented a notch-type gallium grading, with CGL and CCI ratios, respectively, comprised within the [0.75, 0.9] and [0.3, 0.34] ranges. In this work, we carried out annealing processes with a duration of 30 min for the high-temperature plateau at either 300 or 400 °C, and under constant N₂ flow.\(^{[3,4,13,34]}\) The annealing itself was carried out inside the ATV PEO601 fast ramping furnace, with the following sequence: 1) Initialization: 2 min of hold time under N₂ flow; 2) Heating up: 10 min of heating up to, respectively, reach 300 °C or 400 °C under N₂ flow; 3) Annealing: 30 min of thermal annealing at 300 or 400 °C under N₂ flow; 4) Cooling down: 20 min of cooling down to, respectively, reach 300 or 400 °C under N₂ flow.

**CV Measurements:** These experiments were conducted on the Agilent E4980A Precision LCR meter with a four-probe configuration. CV measurements were realized at a fixed frequency of 10 kHz and over the \([-1.5, 1.5\) V\] or \([-1.5, 2\) V\] ranges for, respectively, single-stack and multistack samples, with 61 and 71 data points in linear voltage sweep. Capacitance–frequency measurements were realized at fixed bias of either \(V_{th}\) or \(V_{fb}\) and over the \([1\) kHz, 1 MHz\] range, with 41 data points in logarithmic frequency sweep. The amplitude of the AC small-signal was always equal to 50 mV.

**Cleaning Procedure:** The CIGS layers in the samples studied here were by default cleaned with ammonia,\(^{[12]}\) as commonly used in surface treatment of III/V devices. Nevertheless, one objective of this study was to compare the effects of ammonia and ammonium sulfide cleaning on the CIGS/oxide interface quality (\(D_{ox}\)) for the multistack samples.\(^{[31–33]}\) Therefore, multistack samples were processed with the exact same configuration except from the CIGS surface cleaning applied before the oxide deposition being made with either \(\text{NH}_3\cdot\text{H}_2\text{O}\) (ammonia) or \(\text{NH}_4\text{S}\) (ammonium sulfide). The two cleaning procedures used in this study are the following: 1) \(\text{NH}_3\cdot\text{H}_2\text{O}\) cleaning: 6 min dipping into 30 % \(\text{NH}_3\cdot\text{H}_2\text{O}\) solution; 3 min rinsing into deionized water (2×). 2) \(\text{NH}_4\text{S}\) cleaning: 5 min dipping into \(\text{NH}_4\text{S}\) solution with 6.5–7% sulfur concentration; 2 min rinsing into deionized water (2×).

### Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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### Conflict of Interest

The authors declare no conflict of interest.

### Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

### Keywords

\(\text{Al}_2\text{O}_3\), CIGS interface passivation, \(\text{HfO}_2\), multistacks, thin-film photovoltaics

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