Low temperature ALD growth optimization of ZnO, TiO$_2$, and Al$_2$O$_3$ to be used as a buffer layer in perovskite solar cells

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ABSTRACT
Organic materials provide a very small thermal budget for any postfabrication treatment or for a subsequent layer in a device fabrication. This demand for the low-temperature process has driven the focus of this study to obtain atomic layer deposited oxide layers at a low temperature suitable for a buffer layer in perovskite solar cells. The buffer layer will assist in blocking holes, effectively extract electrons, provide better shunt protection, and act as a sputter protection layer for organic perovskites. Three different oxide layers, Al$_2$O$_3$, ZnO, and TiO$_2$, are grown at 100 °C and studied for this purpose using synchronous modulated flow draw atomic layer deposition (ALD) technology optimized in a commercial 200 mm ALD reactor from Sundew Technologies. It allows greater precursor utilization and shorter deposition cycle times that in turn reduces thermal processing time compared to traditional ALD processes. These thin films have been shown to enhance the fill factor and high charge extraction from the solar cell. Three oxides are compared on all aspects, among which ZnO (3 nm) along with Al$_2$O$_3$ (1 nm) on top of the perovskite layer have shown excellent performance improvement in the device’s power conversion efficiency.

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I. INTRODUCTION
Research in perovskite solar cells (PVSCs) has reached a stage where its lab scale power conversion efficiency (PCE) is comparable to that of a commercial silicon solar cell. The current major concern is, however, its industrial scalability and environmental stability. All types of organic and some inorganic devices face degradation over time due to exposure to moisture and harsh environment outdoors. While the PCE has reached 25%, there has been only a few reports that have passed the international standard IEC61646, which requires a module to survive 1000 h in an environment of 85 °C and 85% relative humidity.

The degradation in a PVSC usually comes from the absorber’s intrinsic instability, exposure to elevated temperature, UV exposure, and exposure to oxygen and moisture present in ambient atmosphere. Different aspects of the PVSC device have been explored to improve the stability of the device. Because the hybrid (organic-inorganic) absorber consists of a hygroscopic ammonium cation, the perovskite is highly sensitive to the moisture and usually decomposes to PbI$_2$. Stability can be widely improved by utilizing an inorganic electron transport layer (ETL) and a hole transport layer, thus sandwiching the moisture-sensitive perovskite material within them.

Several thin film oxide semiconductors such as TiO$_2$ and Al$_2$O$_3$, have been shown to work as an excellent barrier layer for moisture ingress into the device. It is a simple understanding that the thicker the barrier layer the better the encapsulation. These oxides are very resistive, and thus using a thicker layer as a part of the charge extraction layer is prohibitive. However, a properly placed very thin layer can improve the device stability significantly.

In the reported work, we are comparing three different atomic layer deposition (ALD) grown oxide layers such as Al$_2$O$_3$, TiO$_2$, and ZnO and their possible combinations to be used as a buffer layer that will not only serve as a better charge extraction but also as a good encapsulant for the perovskite absorber layer. In addition, these oxides can be a sputter protection layer that is required for semitransparent perovskite solar cells used in tandem cells.
The effectiveness of these oxide layers is primarily assessed using the current-voltage characteristics of the resulting solar cell devices.

II. FABRICATION

A. Materials

The required materials for the cell fabrication such as nickel nitrate hexahydrate, ethylene glycol, ethylenediamine, chlorobenzene, N,N-dimethylformamide, dimethylsulfoxide, and anhydrous 2-propyl alcohol were purchased from Sigma-Aldrich. PCBM was purchased from nano-C. FAI and MABr were purchased from Great Solar. CsI was purchased from Alfa Aesar. PbI$_2$ and PbBr$_2$ were purchased from TCI. ALD precursors dimethyl zinc (DMZ), titanium tetrachloride (TiCl$_4$), and trimethyl-aluminum (TMA) were purchased from STREM Chemicals.

B. Low-temperature ALD process

Sundew Technologies’ D200 ALD system was used to grow all the oxide buffer layers. All the layers were optimized to grow at 100 °C. It is the thermal budget for most of the perovskite/organic layers. The system consists of three metal precursors (TMA, DMZ, and TiCl$_4$) and two of them (DMZ and TiCl$_4$) share a same line. Since they have very different vapor pressures, a special pressure controller was used that could handle the change in vapor pressure. H$_2$O (maintained at 22 °C) was used for the source of oxygen. The system is supported by two-stage high speed vacuum pumps to support fast deposition cycles. The first stage is a root mechanical blower backed by an Edwards dry mechanical pump (iQDP40). The whole precursor delivery system with all the fast pneumatic valves (FPVs) is under elevated temperature, such that there is no precursor condensation, and the purge efficiency is enhanced. As shown in Fig. 1, A and M are the two sets of FPVs on two sides of the showerhead that allow precursor flow through the showerhead and into the reactor, and A-DC and M-DC are the draw control (DC) valves for nitrogen gas. Here, draw control is a mechanism with which the precursor is introduced in control amount with the flow of another inert gas such as nitrogen.

The system uses synchronous modulated flow draw ALD (SMFD-ALD) technology that allows greater precursor utilization and shorter deposition cycle times than traditional ALD processes. SMFD-ALD operates by effectively modulating a pressure gradient between the reaction space and the pumping system, allowing for a low flow rate and high residence time of the reactive precursor through the reaction space or high flow rate and low residence time. The SMFD-ALD deposition cycle consists of the following substages: first for metal precursor and then for nonmetal precursor in one cycle. The different stages are explained below.

1. Delay: Precursor is introduced through A and M without the flow of DC gas, i.e., nitrogen (adding precursor at short residence time).
2. Pulse: Precursor is introduced with the flow of DC gas (adding precursor at long residence time).
3. Push: Precursor is pushed outward with the flow of N$_2$ from the purge line to provide better coverage into a large wafer. The DC is still ON. The pulse is OFF.
4. Dose: Precursor is maintained in the process space at long residence time. The DC is ON. Push is OFF.
5. Purge: Nitrogen is used to purge and clear out the ALD precursor and by-products. DC including pulse and push are OFF.
6. Purge pump: Vacuuming the chamber without the flow of nitrogen.

Recipe optimization was done for all three oxides such that they form in the ALD regime and not in the CVD regime. The process optimization at 100 °C was performed in four stages.

<table>
<thead>
<tr>
<th></th>
<th>M Delay (ms)</th>
<th>M Pulse (ms)</th>
<th>M Push (ms)</th>
<th>M Dose (ms)</th>
<th>M Purge (ms)</th>
<th>A Delay (ms)</th>
<th>A Pulse (ms)</th>
<th>A Push (ms)</th>
<th>A Dose (ms)</th>
<th>A Purge (ms)</th>
<th>Total (ms/cycle)</th>
<th>Rate (Å/cycle)</th>
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<tbody>
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<td>30</td>
<td>20</td>
<td>200</td>
<td>300</td>
<td>5</td>
<td>90</td>
<td>20</td>
<td>700</td>
<td>750</td>
<td>2115</td>
<td>1.01</td>
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<td>1500</td>
<td>300</td>
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<td>1.98</td>
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<tr>
<td>TiO$_2$</td>
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<td>20</td>
<td>100</td>
<td>500</td>
<td>0</td>
<td>90</td>
<td>20</td>
<td>700</td>
<td>750</td>
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<td>0.39</td>
</tr>
</tbody>
</table>
1. High value of dose (1 s) and purge (5 s) were fixed for both M and A precursors, and pulse was varied from high to low for both M and A precursors individually such that just enough precursor gas is introduced into the chamber.

2. With the right amount of pulse value and purge fixed at a high value (5 s), dose was varied from high to low value in order to identify how long the precursor takes to completely react.

3. Finally, with the amount of precursor (pulse) and reaction time (dose) fixed, purge was varied down from 5 s to the point where all the precursor is cleared, and the deposition is still in the ALD regime (i.e., until deposition rate starts increasing due to CVD).

4. Adjustment in push is done to adjust uniformity in thickness from the center where the precursor enters and to the edge where it is purged out.

In each stage, to verify that the film is in the ALD regime, ~30 nm thick films were grown on a 6 in. wafer. The thickness of the film was measured using reflectance spectroscopy throughout the wafer.
for its consistency. Since the thickness variation was seen mainly from center outward, the comparison plot is done accordingly. Thickness profile for M-precursor optimization is shown for each thin film. Similar experiments were done to optimize for precursor A (i.e., H$_2$O). The optimized recipes for the three oxides and their corresponding growth rates are listed in Table I. The metal-organic precursor was pulsed through the M FPVs and the H$_2$O through A FPVs. Recipe for Al$_2$O$_3$ at 100 °C was adjusted starting from a recipe that was already optimized to work at higher temperature (≥150 °C). The pulse and dose time for the TMA precursor did not have to be increased significantly. The only parameter that increased significantly was the dose, and the purge time for H$_2$O probably because of the temperature being right at the boundary of its boiling point thus took longer to react and purge.

Assuming an expected deposition rate for Al$_2$O$_3$ of a 0.1 nm/cycle, 300 cycles were run to obtain an ∼30 nm thick film. Figure 2 shows the thicknesses of Al$_2$O$_3$ films as a function of pulse time while keeping dose and purge high with push at 10 ms.

With optimized values of pulse, dose, and purge, thicknesses were measured by changing the push time as shown in Fig. 3. The convergence of the thickness can be observed as the push time increased showing the significance of using push (ms) in the recipe for larger substrates. The thickness gradient is significant at a low push value, which improves with the increase of push time, and at 20 ms, the variation is less than 1 nm from the center to the edge.

An expected deposition rate for ZnO is 0.2 nm/cycle; thus, 150 cycles were run to obtain an ∼30 nm thick film. The chemistry for ZnO (DMZ + H$_2$O) is little different. It required a significantly high dose time for both precursors to react completely at low temperature. The pulse timing shown in Fig. 4 shows that ZnO is in the ALD regime. For a typical pulse time of 60 ms, the thickness variation
between the center and the edge of the wafer was less than 0.5 nm as shown in Fig. 4.

With the expected deposition rate around 0.05 nm/cycle for TiO$_2$, 600 cycles were run to obtain $\sim$30 nm thick films. The reaction for TiO$_2$ was similar to that of Al$_2$O$_3$. Pulse and dose time did not have to change much to work at low temperature. Figure 5 shows the thickness of the TiO$_2$ film as a function of the pulse time while the pulse time was fixed at 20 ms and the purge and dose were kept high. It can be clearly observed that the thickness values converged as the pulse time increased.

For all three oxides, dose and purge times were then optimized in a similar fashion with the optimized values of pulse and push times.

III. RESULTS AND DISCUSSION

Perovskite solar cell devices were fabricated with following layers: ITO/NiO$_x$/Perovskite/PCBM/[ALD oxides]/Silver. The overall process for device fabrication is reported in our previous work. 11

A. Current-voltage characteristics

Al$_2$O$_3$ is a highly resistive material or simply an insulator. Adding it to the stack of the device would mean adding series resistance to the device. But this material as a buffer layer can also be a hole blocking layer such that the carriers are collected in a proper electrode. Any hole that terminates in the cathode would be a loss.

We can observe from Fig. 6 that with just 1 nm of Al$_2$O$_3$, the fill factor (FF) and current collection ($J_{sc}$) are already improved significantly due to hole blocking. With further increase in thickness, it improves hole blocking properties but at the same time increases...
series resistance of the device and thus degrades the FF. The open circuit voltage ($V_{oc}$) decreases with the increase in thickness of the $\text{Al}_2\text{O}_3$. It can be attributed to the potential drop across highly resistive $\text{Al}_2\text{O}_3$ and its wider bandgap adding to a potential barrier.

However, the combined effect is such that the PCE of the solar cell with 1, 2, and 3 nm of $\text{Al}_2\text{O}_3$ are very close because of the significant gain in current density. Overall, the presence of $\text{Al}_2\text{O}_3$ improved the PCE significantly compared to the absence of the buffer layer altogether. To minimize the resistive behavior of $\text{Al}_2\text{O}_3$, a bilayer $\text{ZnO}$ (3 nm)/$\text{Al}_2\text{O}_3$ (1 nm) was used, which indeed improved the PCE even further, with highest efficiency reaching 17.5%.

Figure 7 shows the best IV graphs for various thicknesses of $\text{Al}_2\text{O}_3$. It is also clear from this figure how $J_{sc}$ improves and $V_{oc}$ reduces monotonically with the increase in $\text{Al}_2\text{O}_3$ layer thickness. As expected, $\text{Al}_2\text{O}_3$ as a buffer layer helped to improve the charge transport, which in turn led to the increase in charge collection or current.

Another buffer layer $\text{ZnO}$ is more of a semiconducting material than an insulator compared to $\text{Al}_2\text{O}_3$. It showed a similar trend to that of $\text{Al}_2\text{O}_3$, that is, $J_{sc}$ improved and $V_{oc}$ decreased with the increase in the thickness of $\text{ZnO}$ as shown in Fig. 8. However, the FF initially decreased and started to increase when the thickness of the layer was larger than 5 nm. It may have to do with the nonuniformity for lower thickness layers. With a thickness of 9 nm of $\text{ZnO}$, the FF was the maximum. Unlike $\text{Al}_2\text{O}_3$, the FF for the case of $\text{ZnO}$ did not decrease for a thicker film. A thicker layer may...
help to provide sputter-damage protection without sacrificing the device performance.

Figure 9 shows the best performing IV graphs for all ZnO thicknesses. As compared to the device with no buffer layer, improvement in device performance is very significant. The PCE increased with the ZnO thickness, which was mainly due to the increase in current density and the improvement in FF for thicker ZnO films. Overall, the highest efficiency was observed for the bilayer (ZnO/Al₂O₃) buffer layer.

TiO₂ is another commonly used n-type semiconductor for the ETL layer in PVSC. It is recommended by several literature studies that the rutile phase of TiO₂ is the most desirable for it to work as an effective electron extraction layer. It requires a temperature >450 °C to form this phase. Since the thermal ALD process was done at 100 °C without additional energy in the form of plasma, it formed an amorphous structure. The resulting TiO₂ buffer in the perovskite solar cell device is shown in Fig. 10. The results are also compared with a 1 nm Al₂O₃ layer and some TiO₂/Al₂O₃ bilayers.

With the increase in TiO₂ thickness, we see a similar result for current extraction as seen on other oxides due to better hole blocking, but an s-shape characteristic also develops as depicted in Fig. 11. The s-shape characteristics arise due to the imbalance of charge extraction of electron and holes, where one carrier is collected better than the other. This phenomenon can also be attributed to voltage dependent charge extraction, which is likely due to charge trapping. S-shape free devices with amorphous TiO₂ at 100 °C is shown to work in an earlier study. The precursor used in the literature was tetrakis(dimethylamino)titanium compared to titanium tetrachloride (TiCl₄) used in this work. The difference in precursor might result in different surface states leading to the undesired s-shape, but an in-depth surface analysis of the ALD film is required to confirm this assessment.

As depicted earlier, a bilayer buffer was tested by adding 1 nm of Al₂O₃ on top of both ZnO and TiO₂. This showed superior performance than any single layer buffer design. The superior performance is attributed to the combined function of both layers. ZnO and TiO₂ are n-type semiconductors with good electron conductivity and thus are better at extracting electrons, which combined with even wider bandgap Al₂O₃ acted as an energy barrier and maximized the blocking of holes toward the cathode. For the purpose of comparison, a bilayer design was added to each single layer box-whiskers plot as shown in the figures above. In each case, the bilayer design has shown improved PCE. In case of TiO₂/Al₂O₃ bilayer, the addition of 1 nm Al₂O₃ even reduced the s-shape characteristics of the IV curve, which can be seen clearly in Fig. 11. This proves that the s-shape was caused by the interface states of TiO₂ that was reduced by the addition of 1 nm of Al₂O₃.

B. Stability test of ALD-deposited Al₂O₃ layer

The ALD grown Al₂O₃ layer was coated on top of the perovskite layer coated on a bare glass substrate. Three thicknesses of the Al₂O₃ were used. Figure 12 shows the effect of water droplet on the perovskite films coated with 1, 3, and 5 nm thick Al₂O₃ layers after 30 s exposure. It shows that a bare 5 nm thick Al₂O₃ layer was significant in preventing the water droplet from decomposing the perovskite. The perovskite films with 1 and 3 nm thick Al₂O₃ layers turned yellow on the spots where the water droplets were cast showing the decomposition of the perovskites. The water droplet on the film with 5 nm Al₂O₃ stays on the film without damaging the perovskite film underneath. While more work has to be done, it shows the promise of the ALD coated buffer layers to prevent moisture ingress into the perovskites.

IV. CONCLUSION

The ZnO formation took a longer reaction time because of its slow reaction between DMZ and H₂O precursors at 100 °C. On the other hand, Al₂O₃ and TiO₂ showed a relatively faster reaction time at low temperature. All three oxides were optimized to be grown in ALD at a temperature of 100 °C and applied as a buffer layer for the perovskite solar cell device. Since the oxides are intrinsically resistive, adding a thicker film of these oxides added to the series resistance of the device. Minimal addition of these ALD oxides improved the FF by blocking the shunting path and increased the current collection by blocking the holes on the ETL.
(PCBM in this case) side. With thicker films, the current collection was further increased but the FF was reduced due to the increase in series resistance. TiO$_2$ grown with the prescribed technique led to s-shape IV characteristics, which is attributed to the interface states. This was verified when an additional Al$_2$O$_3$ layer on top of TiO$_2$ reduced the s-shape characteristics. An optimally performing buffer layer was obtained in a bilayer configuration of 3 nm of ZnO followed by 1 nm of Al$_2$O$_3$.

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