Advanced Applications of Atomic Layer Deposition in Perovskite-Based Solar Cells

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Perovskite solar cells (PSCs) have shown remarkable photovoltaics progress with a record-eminent power conversion efficiency (PCE) of 25.2%. Therefore, the PSCs are potential candidates to replace traditional crystalline silicon-based solar cells. However, the PCE and stability of PSCs need to be improved for successful commercialization. Recently, the atomic layer deposition (ALD) technology is successfully applied to fabricate the encapsulation layer, which overcomes the long-standing issues of perovskite-based solar cells based on others’ pioneering work on ALD in PSCs several years ago. The organic–inorganic alternating encapsulation structure that the team researched has exhibited a water vapor transmittance rate of $1.3 \times 10^{-3}$ g m$^{-2}$ day$^{-1}$, which is the lowest value among the reported thin-film encapsulation layers of PSCs. Herein, the properties of ALD and how it is used in PSCs, such as device architecture, surface modification, passivation, and encapsulation, which result in higher PCEs and excellent stability, are discussed. In addition, the potential significance of applying ALD in the manufacture of tandem and flexible PSCs and the synthesis of high-quality perovskite materials is also analyzed.

1. Introduction

Perovskite solar cells (PSCs) render tremendous potential in photovoltaics (P.V.s) because of their superior power conversion efficiency (PCE),[1] low processing temperature ($<150 \ ^\circ\text{C}$)[2] and cost-effective fabrication.[3] For the first time in 2009, the organic–inorganic hybrid perovskites were used as the sensitizers in dye-sensitized solar cells by Kojima, which led to a water vapor transmittance rate of $1.3 \times 10^{-3}$ g m$^{-2}$ day$^{-1}$, which is the lowest value among the reported thin-film encapsulation layers of PSCs. Herein, the properties of ALD and how it is used in PSCs, such as device architecture, surface modification, passivation, and encapsulation, which result in higher PCEs and excellent stability, are discussed. In addition, the potential significance of applying ALD in the manufacture of tandem and flexible PSCs and the synthesis of high-quality perovskite materials is also analyzed.

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Several issues need to be addressed in the application of PSCs. 
a) Unfavorable interfacial charge recombination reduces the PCE of the device. 
b) The energy level misalignment between the cathode and the ETL creates a significant energy barrier that affects the effective conduction of charge in the PSC. 
c) The nonuniform film deposited by spin coating. 
d) The high molecular polarity of the water molecule makes the CH$_3$NH$_3$PbI$_3$ film unstable. Hydration forms a weak hydrogen bond between the lead halide and the organic cation (MA$^+$). MA$^+$ rapidly diffuses and separates from the PbI$_6$ octahedron, completely degrading the material by irreversibly converting the material to PbI$_2$ and M.A.(F.A.)I precursors.$^{[1]}

Figure 2. Growth mechanism of ALD-Al$_2$O$_3$ thin films.
2. Advanced Applications of ALD in PSCs

Recently, ALD is widely used to improve the efficiency and stability of PSCs. ALD can be used to prepare a continuous, dense, and almost pinhole-free film as a barrier or encapsulation layer to impede material and moisture diffusion through the device and prevent unfavorable charge recombination between interfaces. Moreover, the nondestructive nature of ALD processing renders no harm to the as-fabricated devices. In addition, high-quality, compact, and functional ALD layers promote carrier extraction efficiency, which increases the device efficiency. The utilization of ALD in the fabrication of PSCs rendered encouraging results in recent years, as shown in the efficiency roadmap in Figure 3. It is worth mentioning that ALD technology is applicable in different PSCs architectures, such as planar, inverted, and mesoporous structure, which resulted in a high PCE of 20.00%, 18.30%, and 16.20%, respectively. Therefore, PSCs’ efficiency and stability can be enhanced by advanced processing techniques, such as ALD. This section presents a brief review of ALD utilization in PSCs from scientific and technological viewpoints. The ALD applicability in PSCs has been discussed in terms of the device architecture, surface modification, surface passivation, and stability, as shown in Table 1 and schematically shown in Figure 4.

2.1. Primary Device Architectures

2.1.1. Indium-Free Transparent Electrode Material

In recent years, the manufacturing of highly efficient and translucent PSCs is being pursued using transparent electrodes, including metal nanowires\(^{[15]}\) or ultrathin metal layers, instead of conventional indium-tin-oxide (ITO).\(^{[16]}\) However, the metal is deposited as a bottom electrode before the perovskite layer, which perovskite precursors can easily corrode.\(^{[17]}\) Therefore, Hu et al.\(^{[18]}\) have designed a non-indium translucent bottom electrode using SnO\(_x\)/Ag/SnO\(_x\) architecture. They have utilized low-temperature ALD to deposit SnO\(_x\) and obtained a highly compact pinhole-free SnO\(_x\) layer, which effectively protected the ultrathin metal layer from the perovskite precursors. One should note that the solution-processed SnO\(_x\) layer cannot render the same features. More importantly, the ALD-processed SnO\(_x\) can also be used as the electron extraction layer, which alleviates unfavorable factors, including ultraviolet light erosion and light-induced shunting, and results in a stable PCE of 15.3% with a high \(V_{oc}\) of 1.17 V.

2.1.2. Compact Electron Transport Layer

Titanium dioxide (TiO\(_2\)) exhibits high transparency in the visible light range, and it has excellent electronic properties and chemical stability. Also, TiO\(_2\) can passivate devices to prevent moisture. Therefore, TiO\(_2\) is widely used as a compact electron transport layer (ETL) in PSCs. However, preparing a compact TiO\(_2\) layer requires a high temperature (500 °C) sintering step, limiting its compatibility with low-thermal-budget substrates. Therefore, alternative low-temperature routes, such as chemical bath deposition of nanocrystals,\(^{[19]}\) oxygen plasma,\(^{[20]}\) and magnetron sputtering,\(^{[21]}\) have been explored for perovskite-based solar cells. However, most of the studied methods are not compatible with inverted device designs. In contrast, ALD can deposit high-quality layers at low-temperatures, which implies that ALD...
Table 1. The utilization of ALD in PSCs in device architecture, surface modification, surface passivation, and device encapsulation.

| Material | Precursor | Oxidant  | Deposition temperature | Application | Architecture | Active area | Efficiency | Stability | Ref. |
|----------|-----------|----------|------------------------|-------------|--------------|-------------|------------|-----------|------|
| Al₂O₃    | TMA       | H₂O      | 95 °C                  | Encapsulation layer | FTO/c-TiO₂/m-TiO₂/(HC(NH₂)₂ PbI₂)₃.85 (CH₃NH₃PbBr₃)₃.15 / PTAA / Au/ALD-Al₂O₃ | N/A     | N/A       | PCE decreased by less than 4% after 7500 h exposure at room temperature | [79] |
| Al₂O₃    | TMA       | H₂O      | 60 °C                  | Encapsulation layer | FTO/b-TiO₂/m-TiO₂/ MAPbI₃/Spiro-OMeTAD/Au/ALD-Al₂O₃ | 0.16 cm² | 17.40%    | PCE decreased by less than 25% after 2250 h under environmental conditions | [80] |
| Al₂O₃    | TMA       | H₂O      | 60 °C                  | Encapsulation layer | ITO/NiO/MAPbI₃/ PC₈₅BM/ALD-TiO₂/Ag/ ALD-Al₂O₃ | N/A     | 18.30%    | Retain 97% of the initial PCE after 1000 h of storage under environmental conditions | [24] |
| Al₂O₃    | TMA       | H₂O      | 100 °C                 | Encapsulation layer | ITO/PEDOT:PPS/ MAPbI₃/PC₈₅BM/ALD-ZnO/AgNWs/ALD-Al₂O₃ | 0.12 cm² | 16.50%    | Oxygen transmittance was 1.9 × 10⁻⁴ cm² m⁻² day⁻¹, water vapor transmittance was 9.0 × 10⁻⁴ g m⁻² day⁻¹ | [52] |
| Al₂O₃    | TMA       | H₂O      | Room temperature      | Passivation layer over perovskite | ITO/TiO₂/PCBM/ CH₃NH₃PbI₃/ALD-Al₂O₃/Spiro-OMeTAD/Au | 0.16 cm² | N/A       | PCE increased from 9.4% to 10.8% after 355 days | [81] |
| Al₂O₃    | TMA       | H₂O      | N/A                   | Passivation layer over perovskite | ITO(c-TiO₂)/PCBM/ CH₃NH₃PbI₃/ALD-Al₂O₃/Spiro-OMeTAD/Au | 0.09 cm² | 18.00%    | PCE retained 60–70% of its initial PCE after 70 days of humidity exposure | [3b][3] |
| Al₂O₃    | TMA       | H₂O      | Room temperature      | Passivation layer over perovskite | FTO/TiO₂/ CH₃NH₃PbI₃/ALD-Al₂O₃/Spiro-OMeTAD/Au | 0.0965 cm² | N/A       | PCE significantly enhanced compared with the uncovered device after aging at the same time (from 6.1% to 12.4%) | [38] |
| Al₂O₃    | TMA       | H₂O      | 200 °C                | Compact layer | FTO/ALD-Al₂O₃/m-TiO₂/Perovskite/Spiro-OMeTAD/Au | 0.125 cm² | 16.20%    | N/A       | | [45] |
| Al₂O₃    | TMA       | H₂O      | N/A                   | To enable the nucleation of ZnO | CH₃NH₃PbI₃/PCBM/ ALD-Al₂O₃/ALD-ZnO | N/A     | N/A       | The sample remained dark red after 2 weeks in the environment | [82] |
| Al₂O₃    | AIP       | AA       | 100 °C                | Passivation layer over perovskite | Nonhydrolytic ALD-Al₂O₃/MAPbI₃ ,Cl | N/A     | N/A       | Relative humidity (R.H.) stability was improved by at least a factor of 10 | [37] |
| Al₂O₃    | TMA       | H₂O      | 100 °C                | Electron blocking layer | FTO/c-TiO₂/m-TiO₂/ CH₃NH₃PbI₃/ALD-Al₂O₃/Au | 0.08 cm² | 11.10%    | N/A       | | [83] |
| Al₂O₃    | TMA       | H₂O      | 95 °C                  | Encapsulation layer | FTO/c-TiO₂/m-TiO₂/(FAPbI₃)₁₀.₈₅ (MAPbBr₃)₃.₁₅/Spiro-OMeTAD/Au/PDM/Al₂O₃ | 0.075 cm² | N/A       | PCE decreased by less than 5% after exposure to 45 °C–65% R.H. for 300 h | | [84] |
| TiO₂     | TDMAT     | H₂O      | 60 °C                  | ETL          | ITO/NiO/MAPbI₃/ PCBM/ALD-TiO₂/Ag/ ALD-Al₂O₃ | N/A     | 18.30%    | 97% of the initial PCE was retained after 1000 h of storage under environmental conditions | [24] |
| TiO₂     | TDMAT     | H₂O      | 120 °C                 | Compact layer | FTO/ALD-TiO₂/ MAPbI₃ ,Cl/Spiro-OMeTAD/Au | 0.16 cm² | 11.47%    | N/A       | | [22] |
| TiO₂     | TTIP      | H₂O      | 120 °C                 | Compact layer | FTO/ALD-TiO₂/ MAPbI₃ ,Cl/Spiro-OMeTAD/Au | 0.16 cm² | 11.47%    | N/A       | | [22] |
Table 1. Continued.

| Material | Precursor | Oxidant | Deposition temperature | Application | Architecture | Active area | Efficiency | Stability | Ref. |
|----------|-----------|---------|-------------------------|-------------|--------------|-------------|------------|-----------|------|
| TiO₂     | TDMAT     | H₂O     | 200 °C                  | Compact layer | FTO/ALD-TiO₂/m-TiO₂/ perovskite/Spiro-OMeTAD/Au | 0.09 cm² | 12.56%    | N/A       | [41] |
| TiO₂/IrO₃ | TDMAT/ (EtCpIr(CHD)) | H₂O/O₂ | 170 °C                  | HTL | ITO/ALD-TiO₂/IrO₂/ C₆₀/FAO.₃₁ Pb₈₂ Br₀.₃₁ C₉₀/BCP/Ag | 0.12 cm² | 15.80%    | N/A       | [32] |
| TiO₂     | TTIP      | O₂ plasma | 130 °C                 | ETL | ITO/ALD-TiO₂/ CH₃NH₃PbI₃/Spiro-OMeTAD/Au | 0.09 cm² | 14.80%    | N/A       | [23] |
| TiO₂     | FTIP      | H₂O     | 150 °C                  | Compact layer | FTO/ALD-TiO₂/m-TiO₂/ CH₃NH₃PbI₃/C | N/A | 7.82%     | Maintain over 96% of its initial PCE after stored in ambient air for 651 h | [85] |
| TiO₂     | TiCl₄     | H₂O     | 300 °C                  | Compact layer | FTO/ALD-TiO₂/m-TiO₂/ CH₃NH₃PbI₃/Spiro-OMeTAD/Au | 0.1 cm² | 11.50%    | N/A       | [86] |
| TiO₂     | TiCl₄     | H₂O     | 300 °C                  | Compact layer | FTO/ALD-TiO₂/m-TiO₂/ CH₃NH₃PbI₃/Spiro-OMeTAD/Au | 0.09 cm² | 15.00%    | N/A       | [87] |
| TiO₂     | Ti(CpMe) (NMe₂)₃ | O₂ plasma | 150 °C                 | Compact layer | ITO/ALD-TiO₂/m-TiO₂/ MAPb₁₋ₓClₓ/SpiroOMeTAD/Au | 0.2 cm² | 9.20%     | N/A       | [88] |
| TiO₂     | Ti(CpMe) (NMe₂)₃ | O₂ plasma | 150 °C                 | Compact layer | ITO/ALD-TiO₂/m-TiO₂/ MAPb₁₋ₓClₓ/SpiroOMeTAD/Au | 0.12 cm² | 8.40%     | N/A       | [89] |
| TiO₂     | Ti(CpMe) (NMe₂)₃ | O₂ plasma | 150 °C                 | Compact layer | ITO/ALD-TiO₂/m-TiO₂/ MAPb₁₋ₓClₓ/SpiroOMeTAD/Au | 0.2 cm² | 8.40%     | N/A       | [89] |
| TiO₂     | Ti(CpMe) (NMe₂)₃ | O₂ plasma | 150 °C                 | Composite electrode | AgNWs/ZnO/ALD-TiO₂/ MAO₁ FAO.₃₁ C₆₀/₃₁ Pb₈₂ Br₀.₃₁ C₉₀/BCP/Ag | 0.0725 cm² | 17.11%    | N/A       | [63] |
| TiO₂     | Cs₂H₂N₂Ti | H₂O     | 150 °C                  | Passivation layer | FTO/SnO₂/ALD-TiO₂/ CsPbBr₃/Carbon | 0.09 cm² | 9.31%     | N/A       | [90] |
| TiO₂     | TiCl₄     | H₂O     | 200 °C                  | Passivation layer | FTO/ALD-TiO₂/ TiO₂/ TiO₂ N.R.S. | 0.1 cm² | 20.28%    | N/A       | [91] |
| TiO₂     | Cs₂H₂N₂Ti | H₂O     | 150 °C                  | ETL | ITO/ALD-TiO₂/SnO₂/ PCE₁,BM/ MAO₁ FAO.₃₁ Pb₈₂ Clₓ/Spiro-OMeTAD/Au | 0.07 cm² | 19.45%    | N/A       | [92] |
| SnO₂     | TDMASn    | H₂O     | 100 °C                  | ETL | ITO/NI/O/FAO.₃₁ C₆₀/₃₁ Pb₈₂ Br₀.₃₁ C₉₀/BCP/ALD-SnO₂/IITO | 0.39 cm² | 8.20%     | N/A       | [93] |
| SnO₂     | TDMASn    | O₂ | 100/120 °C | ETL | FTO/ALD-SnO₂/ (FAPbI)₂.₃₁ (MAPbBr)₂.₁₃/P3TA/Ag | 0.16 cm² | 0.16%     | N/A       | [28] |
| SnO₂     | TDMASn    | O₂ | 100 °C | ETL | FTO/ALD-SnO₂/ CH₃NH₃PbI₃/PCBM/ AZO/ALD-SnO₂/Au | 0.1 cm² | 18.30%    | N/A       | [94] |
| SnO₂     | TDMASn    | H₂O | 80 °C | ETL | ITO/PEDOT: PSS/ CH₃NH₃PbI₃/PCBM/ AZO/ALD-SnO₂/Au | N/A | N/A | Show stable characteristics more than 1000 h in the ambient air, more than 1000 h under 60 °C | [77] |
can be utilized to deposit TiO$_2$ as a compact ETL in PSCs with low-thermal-budget substrates and inverted structures.

Kim et al.\cite{22} have treated an amorphous ALD-TiO$_2$ layer by UV–O$_3$ and demonstrated that the resulting device can achieve the same efficiency as high-temperature synthesized TiO$_2$ films. Thus, any high-temperature induced damage to the sensitive substrate can be avoided by using ALD. In addition, the adhesion between the ETL and perovskite can be enhanced by fluorinating the surface of TiO$_2$, which renders a more favorable band arrangement and enhances its electron extraction ability.\cite{23}

In the inverted structure, nanoscale ALD oxide a-TiO$_2$, deposited on [6,6]-phenyl-C61-butyric acid methyl ester (PCBM), can be used as a highly efficient ETL to reduce the series resistance while preventing the short-circuiting of the device.\cite{25}

Recently, Li et al.\cite{24} have utilized a low-temperature ALD process to incorporate pinhole-free metal oxides, such as Al$_2$O$_3$ and TiO$_2$, into inverted PSCs (ITO/NiO/CH$_3$NH$_3$PbI$_3$/PC$_6$BM/Ag), where ALD-TiO$_2$, deposited on PC$_6$BM, worked as a composite ETL and ALD-Al$_2$O$_3$ served as an encapsulation layer. The ALD-TiO$_2$ layer partially filled the pinholes in the PC$_6$BM layer and enhanced the perovskite layer’s resistance to water vapors. The elemental composition of the interface and the chemical state between ALD-TiO$_2$ and perovskite layer, measured by X-ray photoelectron spectroscopy (XPS), exhibit that the predeposition of excess Ti precursor during the ALD process does not damage the perovskite layer. Moreover, the device delivered a maximum PCE of 18.3% and maintained 97% of the initial PCE after 1000 h of storage under ambient conditions.

Furthermore, it has been reported that SnO$_2$ exhibits higher electron mobility than TiO$_2$ and demonstrate excellent hole blocking ability, which implies that the SnO$_2$ can be used as an ETL in planar PSCs. However, the high-temperature heat treatment of solution-processed SnO$_2$ film degrades the device efficiency due to the charge recombination caused by the removal

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**Table 1. Continued.**

| Material\textsuperscript{a} | Precursor | Oxidant | Deposition temperature | Application | Architecture | Active area | Efficiency | Stability | Ref. |
|-----------------------------|-----------|---------|------------------------|-------------|--------------|-------------|-----------|----------|------|
| SnO$_2$ \textsuperscript{b} | TDMASn    | O$_3$/H$_2$O | 100/80 °C | Electron extraction layer/ composite electrode | ALD-SnO$_2$ (H$_2$O)/Ag/ ALD-SnO$_2$(H$_2$O)/SnO$_2$(O$_2$)/MAPbI$_3$/ Spiro-OMeTAD/MoO$_3$/Ag | N/A | 11.00% | N/A | [95] |
| ZnO \textsuperscript{c}   | DEZ       | H$_2$O   | 25/60/80 °C | Passivation layer | Perovskite/PCBM/ALD-Al$_2$O$_3$/ALD-ZnO | N/A | N/A | The sample remained dark red after 2 weeks in the environment | [82] |
| ZnO \textsuperscript{c}   | DEZ       | H$_2$O   | 70 °C | Compact layer | FTO/ALD-ZnO/m-Al$_2$O$_3$/CH$_3$NH$_3$PbI$_3$/Spiro-OMeTAD/Ag | 0.04 cm$^2$ | 13.10% | N/A | [43] |
| ZnO \textsuperscript{c}   | DEZ       | H$_2$O   | 95 °C | Buffer layer | TCO/ITO nanoparticles/ Perovskite/PCBM/ZnO nanoparticles/ALD-ZnO/ITO | 0.09 cm$^2$ | 14.70% | Constant for 15 h of continuous illumination | [96] |
| ZnO \textsuperscript{c}   | DEZ       | H$_2$O   | 80 °C | Energy level modification | ITO/PEDOT:PSS/ MAPbI$_3$/PC$_6$BM/ALD-ZnO/AgNWs/ALD-Al$_2$O$_3$ | 0.12 cm$^2$ | 16.50% | Oxygen transmittance was 1.9 × 10$^{-5}$ cm$^2$ m$^{-2}$ day$^{-1}$, water vapor transmittance was 9.0 × 10$^{-4}$ g m$^{-2}$ day$^{-1}$ | [52] |
| Hf:ZnO \textsuperscript{d} | DEZn/ TDMAHf | H$_2$O | 90 °C | Composite electrode | AgNW/Hf:ZnO/ MAPbI$_3$/Spiro-OMeTAD/Au | 0.09 cm$^2$ | 14.46% | Water vapor transmittance was 5.1 × 10$^{-6}$ g m$^{-2}$ day$^{-1}$ | [97] |
| NiO \textsuperscript{e}   | Ni (diam-b) | O$_3$ | 200 °C | HTL | ITO/ALD-NiO/MAPbI$_3$/PCBM/Ag | 0.24 cm$^2$ | 16.40% | N/A | [31] |
| VO$_2$ \textsuperscript{f} | VTIP      | H$_2$O   | 80 °C | Buffer layer | ITO/SnO$_2$/C$_6$O$_{17}$F$_{33}$ Pb(Br$_{0.1}$/I$_{0.9}$)/Spiro-ITTO/ ALD-VO$_2$/ITO | 0.39 cm$^2$ | N/A | Maintain efficiency after being stored at 85 °C for 1000 h in N$_2$ environment | [98] |
| VO$_2$ \textsuperscript{g} | V(dma)$_4$ | H$_2$O | 150 °C | HTL | FTO/ALD-VO$_2$/MAPbI$_3$/PCBM/BCP/Ag | 0.1 cm$^2$ | 11.53% | N/A | [99] |
| PbS \textsuperscript{h}   | Pb(tmhd)$_2$ | H$_2$S | 150 °C | Perovskite layer | N/A | N/A | N/A | N/A | [100] |
| PbI$_2$ \textsuperscript{i} | Pb(bta)$_2$ | SnI$_4$ | 90 °C | Perovskite layer | N/A | N/A | N/A | N/A | [67] |

\textsuperscript{a}The table summarizes the materials used in recent years and the device enhancements achieved. The choice of oxidant needs to be determined by combining the substrate material’s properties, the target requirements of the device, and the conditions of the ALD equipment.

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of self-passivation SnOCl\(_2\).\(^{[25]}\) Therefore, ALD-SnO\(_2\), deposited at a low temperature, become a viable choice for improving the hole blocking ability of ETL. Brinkmann et al. have created a double-layer electron extraction intermediate layer composed of aluminum-doped zinc oxide and tin oxide. The SnO\(_2\) grown by the ALD does form a dense gas permeation barrier, which can effectively prevent water from entering the perovskite layer. More importantly, it can prevent the escape of decomposition products of the perovskite.\(^{[26]}\) On this basis, Zhao et al. added the ALD-SnO\(_2\) layer to the translucent PSC, which effectively protected the perovskite and ultrathin silver electrodes from the adverse effects of moisture.\(^{[27]}\) Lee et al.\(^{[28]}\) also have fabricated ALD-SnO\(_2\) film as ETL in PSCs, at low temperatures and demonstrated that the residual precursor (TDMASn) the ALD-SnO\(_2\) surface acts as an excellent self-passivation material. One should note that the surface passivation of SnO\(_2\) can reduce the charge recombination at the perovskite/ETL interface, resulting in PCE exceeding 20%.

### 2.1.3. Hole Transport Layer

The hole transport layer (HTL) is one of the critical components in planar PSCs. The correct choice of materials and preparation methods of the HTL can effectively improve device efficiency. Even though the commonly used organic/polymer hole-transporting materials, such as Spiro-OMeTAD and poly(triarylamine), render excellent device properties, their instability and high cost necessitate the exploration of novel HTL materials. To date, some research groups have studied nickel oxide (NiO) as a stable and viable HTL alternative due to its wide bandgap (>3.50 eV), p-type semiconducting behavior, high optical transmittance, excellent chemical stability, and appropriate valence band alignment with various photoactive layers.\(^{[29]}\) NiO films can be prepared by multiple methods, such as spray pyrolysis, spin coating, sputtering, and electrodeposition.\(^{[30]}\) However, most of these methods result in a minimum film thickness of \(\approx 15\)–\(20\) nm. In contrast, NiO only exhibits high conductivity when the film thickness is equivalent to the space charge region’s characteristic length. The film has high conformation. Simultaneously, the hydroxylated substance (NiOOH) produced on NiO surface, prepared under ambient conditions, reduces the hole transport efficiency from the perovskite layer to the NiO layer. As mentioned earlier, ALD renders high-quality, conformal, and pinhole-free coatings with excellent control over thicknesses. Therefore, Seo et al.\(^{[31]}\) have utilized ALD to deposit high-performance ultrathin undoped NiO films as HTLs in PSCs. It has been reported that the NiO thickness of \(\approx 1\)–\(2\) nm, which is equivalent to the Debye length, significantly increases the practical work function (W.F.) and hole concentration in ultrathin NiO film, resulting in improved P.V. performance. Moreover, the postdeposition annealing treatment reduces the hydroxylated NiOOH on the surface of NiO, which results in a NiO film with better interfacial properties. Apart from NiO, Tan et al.\(^{[32]}\) have synthesized a novel HTL by alloying TiO\(_2\) with IrO\(_2\) in a supercycle ALD process, which resulted in a high efficiency of 15.8% and \(V_{\text{oc}}\) of more than 1 V.

### 2.2. Barrier Layers against Moisture and Material Diffusion

#### 2.2.1. Perovskite Passivation

The instability of perovskites is a decisive issue, hindering the rapid development and commercialization of perovskite-based solar cell technology. The high molecular polarity of the water molecule makes CH\(_3\)NH\(_3\)PbI\(_3\) films unstable, which results in rapid decomposition of the perovskites in the presence of moisture and leads to the observed device instability. This phenomenon is that hydration converts the chemical action into a weak hydrogen bond between the lead halide and the organic cation (for example, MA\(^+\)). MA\(^+\) diffuses rapidly and separates from the PbI\(_6\) octahedron, completely degrading the material by reversibly converting the material to PbI\(_2\) and M.A. (F.A.) precursors.\(^{[33]}\) To solve this problem, a hydrophobic polymer (PDPPDBTE) can be used instead of Spiro-OMeTAD as HTL.
to improve PSCs' stability; however, the efficiency can only reach 9.2%.[34] It has been reported that the solar cells with a carbon layer as an electrode and without HTL remain stable for more than 1000 h under ambient conditions, which can be ascribed to the excellent water-resistance of the carbon layer.[35] However, the devices with carbon electrode are not as efficient as Spiro-OMeTAD-based devices.

Recently, several studies have been conducted to enhance the stability of PSCs under ambient conditions. For instance, interface defects have been passivated using aluminum oxide (Al₂O₃).[36] In addition, because Al₂O₃ has a very low water vapor transmission rate (WVTR), it is added to PSCs to prevent the perovskite layer from being etched by moisture. Dong et al.[7b] have used ultrathin and compact ALD-Al₂O₃ layer to isolate the CH₃NH₃PbI₃ layer from moisture and prevent the degradation of the perovskite structure, which led to the enhanced stability of the device. However, introducing a strong oxidant, O₂, decomposes CH₃NH₃PbI₃ during ALD processing. Therefore, the device structure was modified to fluorine-doped tin oxide (FTO)/TiO₂/CH₃NH₃PbI₃/Spiro-OMeTAD/ALD-Al₂O₃/Ag, which retained 90% of its initial PCE after 24 days of storage under ambient conditions. The ultrathin ALD-Al₂O₃ film effectively protected the perovskite layer. It served as a tunneling barrier that does not affect carriers' transmission because it is sufficiently thin. Controlling the number of ALD cycles can effectively delay the decline in efficiency due to degradation. Koushik et al.[3b] have demonstrated that a device with 10 ALD cycles of Al₂O₃ retained ≈60–70% of its initial PCE after 70 days of humidity exposure. Furthermore, Kim et al.[37] have developed a novel nonhydrolyzed (nh) ALD-Al₂O₃ process to avoid O₂- and H₂O-induced degradation, which resulted in direct growth of ultrathin oxide barrier films on perovskites and avoided the deposition-induced damage. Moreover, the research has shown that ALD-Al₂O₃ passivated perovskite-based device renders a significantly higher PCE than the bare perovskite-based device after aging, without illumination, under the same conditions. One should note that the ALD precursor is only chemically active on the perovskite surface and passivates it at room temperature without affecting the film itself.[38]

2.2.2. Compact Layer between Transparent Conductive Oxide and Perovskite

In mesoscopic PSCs, the porosity of mesoporous TiO₂ film facilitates the undesirable physical contact between the perovskite layer and transparent conductive oxide (TCO), which leads to charge recombination and decreases PCE. Therefore, a compact layer needs to be added between the TCO and perovskite layer. Simultaneously, the layer can prevent the holes in the perovskite or HTL from reaching the anode. Several methods, such as spin coating,[39] sputtering,[40] and spray pyrolysis, have been used to prepare compact layers. However, the spin coating cannot produce high-quality films, and thermal methods are not compatible with commonly used substrates. Therefore, ALD is a desirable choice due to its unique processing advantages, such as low-temperature, excellent thickness control, and conformality.

Wu et al.[41] have utilized ALD to prepare TiO₂ barrier layer and compared it with spray pyrolysis and spin coating. The results reveal that the density of nanoscale pinholes in the ALD-TiO₂ compact layer is much lower than the spray-pyrolyzed TiO₂ and spin-coated TiO₂. And, the PSCs with the ALD-TiO₂ barrier achieved a maximum PCE of 12.36% among these three methods. One should note that the pinhole density significantly influences the shunt resistance and interfacial charge recombination inside the device. Recently, Giacomo et al.[42] have developed an efficient low-temperature mesoporous PSC by depositing a compact layer of TiO₂ at 150 °C and treating the spin-coated mesoporous TiO₂ with U.V. irradiation, which resulted in a PCE of 15.9% under standard test conditions (STC: 1000 W m⁻², 25°C, AM 1.5 spectrum) and PCE of 24–25.4% under a compact fluorescent lamp. In addition, the energy level of ZnO is comparable to TiO₂ and it does not require high-temperature sintering. Therefore, the as-deposited ALD-ZnO layer can effectively suppress charge recombination, making it a viable alternative to TiO₂. Therefore, Dong et al.[43] have deposited a compact layer of ALD-ZnO on FTO at 70 °C. The resulting device (FTO/ALD-ZnO/mesoporous Al₂O₃/CH₃NH₃PbI₃/Spiro-OMeTAD/Ag) exhibited a significantly enhanced PCE of 13.1% because the ALD-ZnO layer is more compact than the solution-based ZnO layer, and the contact between the FTO and the perovskite is better avoided, thereby effectively suppressing charge recombination in the PSC. It is worth noting that the compact ALD-ZnO layer promotes the one-step synthesis of CH₃NH₃PbI₃ in precursors with chloride ions, which can be ascribed to a higher number of oxygen vacancies in ALD-ZnO than the solution-processed-ZnO, resulting in enhanced reactivity.[44]

Zhang et al.[45] have effectively prevented the electron recombination at the perovskite/FTO interface by depositing ALD-Al₂O₃ under-layers on FTO resulted in excellent electron transport capability due to tunneling. One should note that the thickness of Al₂O₃ significantly influenced the electron transfer resistance in PSCs and, in turn, determined the electronic recombination rate. Therefore, 50 cycles of ALD-Al₂O₃ compact layer (≈5 nm) resulted in the highest PCE of 16.2%. In contrast, the devices have attained an efficiency of 11.0% without under-layers.

2.2.3. Passivation Layer over Scaffold Nanostructure

One of the significant problems of perovskite-based solar cells is the optimization of mesoporous TiO₂ (mp-TiO₂), which blocks the rapid flow of electrons and results in inferior cell efficiency. Therefore, it has been reported that PSCs with 1D nanostructures, such as rutile 1D TiO₂ and 1D ZnO, render a high PCE of 9.4% and 11%, respectively.[46]

Recently, Mali et al.[47] have deposited ultrathin ALD TiO₂ passivation layers, with different thicknesses, on 1D TiO₂ nanorods (N.R.s) and demonstrated that the PCE can be increased to 13.45% with a passivation layer of 4 nm. The same device has exhibited a JSC of 19.78 mA cm⁻², VOC of 0.945 V, and fill factor (F.F.) of 72. And, it has been reported that the deposition of ultrathin ALD-TiO₂ layers promotes a low recombination rate. Moreover, the presence of the ALD-TiO₂ layer on top of a spin-coated mesoporous nanoparticulate TiO₂ film effectively prevents the reaction between FTO and hole conductor. It reduces the surface defects of the mesoporous film. For instance,
Chandiran et al. have demonstrated that a 2 nm ALD-TiO2 passivation layer can increase the device efficiency to 11.5%. [48]

2.2.4. Energy Level Modification

The efficient conduction of charge in PSCs requires compatible interaction between the various structural layers. Therefore, the optimal energy level alignments of the selected interlayers with the perovskite absorber layer are required to prevent and minimize the energy barriers of different interfaces, which is highly desirable for efficient carrier extraction. [49]

To minimize the influence of ambient oxidation on the device, more stable metals, such as silver (Ag, \(\approx 4.7\) eV) and gold (Au, \(\approx 5.1\) eV), are typically used as the cathode. However, the electron extraction capability of these metals is reduced due to a large discrepancy between the lowest unoccupied molecular orbital (LUMO) level of PCBM (\(\approx 4.2\) eV) and the high W.F. of these metals. Therefore, an additional cathode buffer layer (CBL) is inserted between the cathode and PCBM layer to solve these issues. [50] Among various CBL materials, n-type metal oxide semiconductors (such as TiOx or ZnO) are widely used due to their low cost, high charge carrier mobility, and excellent stability. [51] However, the formation of these CBLs usually requires annealing at higher temperatures (\(\geq 400^\circ\)C) to ensure higher film quality, limiting their development in reverse PSCs, flexible solar cells, and high-performance multijunction tandem solar cells. Based on the unique features of ALD, such as low deposition temperature, excellent film conformability, high uniformity on large-area substrates, and precise thickness control, we can exactly overcome the above challenges. Chang et al. [52] have deposited ALD-ZnO as the CBL, and demonstrated a significantly enhanced PCE of 16.5% due to fine adjustment of the electrode W.F., excellent electron transport capability (16.1 cm² V⁻¹ s⁻¹), and compactness of the ALD-ZnO film.

2.3. ALD-Assisted Device Encapsulation

It should be noted that the commercialization and future development of PSCs are mainly hindered by their widely reported operational instability, particularly in the presence of moisture or at high temperatures. [53,54] Apart from compositional engineering of the perovskite film [55] and replacement of functional layers with durable alternatives, [56] a well-developed encapsulation process is a promising route to mitigate the instability of PSCs.

At present, various encapsulation methods are being used to protect PSCs from the external environment, such as the utilization of a flexible barrier sealant thermoplastic polymer film with integrated adhesive, [57] ethylene vinyl acetate (EVA) encapsulation film, glass–glass encapsulation film, and a UV-curable epoxy resin as a sealant. [58] However, alternative encapsulation methods should be explored due to poor performance, low mechanical stability, and different approaches. As mentioned earlier, ALD is a promising method to produce continuous, compact, and pinhole-free films, which can act as a barrier against moisture and improve PSCs’ stability. A comparison of the structure and characteristics between the cover encapsulation and the thin film encapsulation is shown in Figure 5.

Choi et al. [59] have utilized ALD-Al2O3, deposited at a low temperature (95°C), as a sealant for PSCs and demonstrated a WVTR of \(1.84 \times 10^{-2}\) g m⁻² d⁻¹ at 45°C–100% R.H. Furthermore, Lv et al. [24] have designed a novel stacked ALD Al2O3 encapsulation layer (Al2O3 (10 nm)/Al2O3 with intermediates of Al precursor (20 nm)/Al2O3 (30 nm)) and demonstrated a PCE retention of 97% after 1000 h of storage under ambient conditions due to the presence of composite encapsulation layer. Moreover, the device with a composite encapsulation layer retained 95% of the initial efficiency after being immersed in deionized water for 2 h. Thus, it is shown that incorporating a water vapor barrier layer based on low-temperature ALD metal oxides into the PSCs can effectively extend the lifetime of the devices.

However, an encapsulation structure having excellent gas barrier properties often needs to be prepared under an environment of high temperature and full of harmful precursors. Currently, many researchers have developed low-temperature ALD technology for preparing the excellent permeable barrier. However, it is necessary to increase the number of cycles or purge time to prepare films with low WVTRs at low temperatures. A longer

![Figure 5. Comparison between cover encapsulation and thin-film encapsulation.](image-url)
deposition time is unfavorable for the commercialization of PSCs. And, when using the same ALD recipe to deposit thin films, high-temperature deposited films tend to have higher quality than a low-temperature deposition. PSCs exposed to such harsh environments for long deposition can cause damage. To solve this problem, our team developed an organic–inorganic alternating encapsulation structure (alucone/Al₂O₃) that can be prepared at 50°C. The encapsulation layer reduces the damage of PSCs by plasma-enhanced ALD through the use of a thin layer of alucone induced by ethylene glycol. Simultaneously, the PEALD Al₂O₃ layer on alucone can avoid molecules of water from penetrating the PSCs, reaching an ultralow WVTR of 1.3 × 10⁻⁵ g m⁻² day⁻¹, which is currently the lowest value of the thin-film encapsulation method for PSCs. This achievement is also attributed to Park’s team’s previous work on the Al₂O₃/alucone barrier. Since the preparation temperature is lower than the ideal growth temperature of alucone, many methyl groups remain in alucone. However, such methyl groups can effectively consume oxygen in the plasma, which is harmful to PSCs. With the help of this encapsulation layer, our PSCs can survive for more than 2000 h at a relative humidity of 80% and a temperature of 30°C and retain 96% of their initial performance.

3. Future Research Focus

ALD technology is widely used to enhance PSCs’ PCE and stability due to its precise control thickness, conformal properties, and high-quality thin film deposition. It has been proven that the structure layers, interface passivation layers, and encapsulation layers of perovskite devices can be prepared by ALD technology. In addition, other practical advantages may become the focus of future research.

3.1. Compatibility with Flexible Devices

Perovskite materials have incredibly high efficiency, also their mechanical flexibility and solution processability provide great potential for large-scale production. To achieve high-performance flexible PSCs, three key issues must be addressed. The first is to find new types of flexible transparent electrodes that can replace fragile ITO or FTO electrodes; second, the device needs to be prepared at low temperature to match the thermal limit of the plastic substrate; finally, it is necessary to minimize charge recombination losses through interface engineering. The compact, high-quality ALD film that can be deposited at low temperatures can solve these problems.

Recently, Jin et al. have developed a flexible composite electrode (AgNWs/ZnO/ALD-TiO₂) with good electrical conductivity, transparency, and excellent mechanical properties. The ALD-TiO₂ thin layer can sufficiently passivate the charge recombination defects on the ZnO surface and effectively prevent the decomposition of the perovskite absorption layer. The optimal PCE of this flexible PSC on plastic substrates can reach 17.11%, comparable to rigid devices (PCE = 18.26%). And, after 2000 bending cycles with six times the radius, it still maintained 77% of its initial PCE.

3.2. Assisted Preparation of High-Quality Perovskite Materials

ALD-based thin films are deposited by the reaction of organometallic precursors and oxidants. It can deposit many different materials using the ALD process, including oxides, chalcogenides, phosphides, and metals. In the past, a small amount of research has focused on ALD deposition methods for metal halides, such as metal fluorides, copper chloride, and copper bromide. ALD technology can deposit dense, high-quality thin films, making it possible to synthesize high-purity and high-crystallinity perovskite thin films. Currently, there is no method for directly preparing perovskite materials by ALD. However, people have tried to deposit a seed layer to form PbI₂, converted into a CH₃NH₃PbI₃ film.

Popov et al. synthesized PbI₂ films using Pb(btsa)₂ as the lead precursor and SnI₄ as the iodine precursor. The process can work at lower deposition temperatures (<90°C), making the method compatible with substrates that are not resistant to high temperatures. Due to ALD technology, the prepared PbI₂ film has excellent characteristics such as high film quality, uniformity, and scalability.

3.3. Application in Tandem PSCs

At present, the most efficient tandem solar cell uses epitaxially grown III–V semiconductors to achieve a 1-sun PCE of over 38%. Its expensive preparation methods have hindered its commercialization. However, metal halide perovskites are inexpensive. By stacking two layers of perovskite with complementary bandgaps, higher PCE can be achieved. Therefore, all-perovskite tandem solar cells have become candidates for achieving efficient and low-cost solar cells.

However, tandem solar cells still face challenges including the following: 1) the problem of the composite layer of two perovskite materials; 2) the insufficient voltage generated by wide-bandgap perovskite; 3) the limitation of stability; 4) eliminating process-induced degradation of the bottom cell; and 5) matching the individual photocurrents of the subcells. We believe that the benefits of ALD can provide solutions to each of these issues. Axel F. et al. developed a method to improve the composite of two perovskite materials by introducing a nucleation layer.
3.4. Spatial ALD

Traditional ALD has commercial limitations due to its slow deposition speed and time consuming. Recently, people have overcome the limitations of classic batch-based ALD (B-ALD) by introducing spatial ALD (S-ALD). It can operate S-ALD continuously at atmospheric pressure,[74] thus bringing the deposition rate closer to industrial requirements.[75] Riedl’s team outlined the S-ALD concepts reported in the past few decades.[76]

Hoffmann et al.[77] recently deposited a dense electron extraction layer SnO$_x$ in a PSC using atmospheric pressure S-ALD technology. The S-ALD deposition process and the architecture of the device used in this work are shown in Figure 8. The preparation of the thin layer not only achieves continuous deposition but also does not reduce its excellent electrical properties and barrier properties compared to traditional ALD-SnO$_2$.

However, highly active and high vapor pressure precursors are usually preferred, so people often use highly active DEZ precursors to deposit ZnO instead of SnO$_2$. Using DEZ precursors can reduce the exposure time and precursor transport requirements in the ALD process, thereby achieving a faster film deposition rate. Najafi et al.[78] developed a thin layer of ZnO based on S-ALD as an effective buffer layer before sputtering the ITO electrode. They obtained a translucent PSC with 14.7% stable PCE.

4. Conclusion

ALD technology has become an important method to enhance the PCE and stability of PSCs due to its low-temperature deposition and excellent control of thickness, conformality, and high-quality thin films. Using ALD technology can prepare dense structure layers, interface passivation layers, encapsulation layers of perovskite devices and, to a certain extent, solve the challenges of preparing flexible, tandem PSCs and synthesizing high-quality perovskite materials, which have received much attention recently.

However, the successful and effective application of ALD technology in PSC still faces some challenges. For example, the ALD process consumes much more time than traditional coating methods such as sputtering. Although the development of space ALD has dramatically increased the deposition rate of thin films, further improvements are needed to improve industrial-scale productivity. Moreover, high-efficiency PSCs manufactured by ALD technology have only been tested on small-scale samples so far. In contrast, larger laboratory-scale micromodules have
not yet been proven. It should be noted that using ALD technology to deposit various thin films in a large-area PSC and accurately control the thickness is still a hard task. Finally, ALD technology must be combined with other processing steps to build efficient production lines. All in all, the use of ALD technology in PSC is a step toward the next generation of P.V. devices.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords

atomic layer deposition, flexible and tandem, perovskite solar cells, power conversion efficiency, stability

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