

Mini Review

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# Influences of deposition conditions on atomic layer deposition films for enhanced performance in perovskite solar cells

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## Abstract

Atomic layer deposition (ALD) is a key technology for fabricating functional layers in perovskite solar cells, as it can deposit pinhole-free films with atomic-level thickness and tunable composition on high-aspect-ratio surfaces. Various deposition conditions have significant effects on the growth, physical, and chemical properties of ALD films, which, in turn, critically influences the performance of associated devices. Here, we review the reaction mechanisms underlying ALD and summarize how variables, such as precursors, deposition temperatures, and



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substrates, impinge upon the quality of ALD films and the related devices. We emphasize the role of substrate in determining the nucleation and growth behavior of ALD films, which has been overlooked in previous reviews. Finally, we highlight the potential application of ALD in efficient perovskite solar cells in terms of carrier transport, encapsulated, and buffer layers, especially for tandem cells.

**Keywords:** Atomic layer deposition, substrate, perovskite solar cells, tandem solar cells

## INTRODUCTION

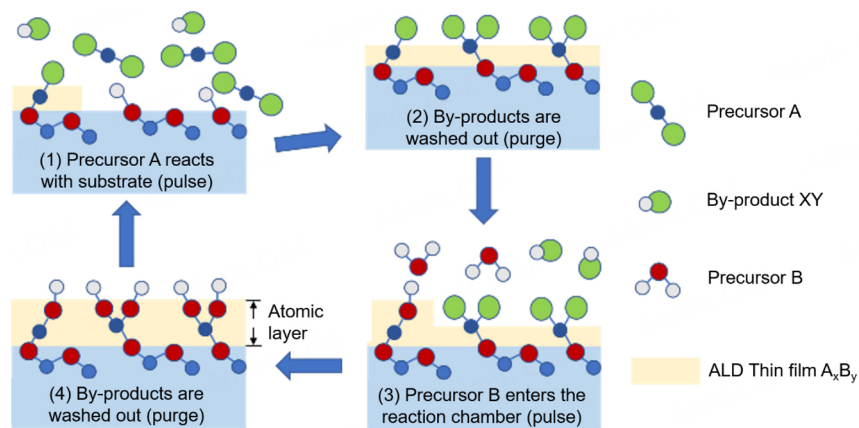
In recent years, atomic layer deposition (ALD)<sup>[1]</sup> has aroused much attention in the semiconductor fields such as corrosion<sup>[2]</sup>, catalysis<sup>[3]</sup> and solar cells<sup>[4-8]</sup>. As for solar cells, perovskite solar cells (PSCs) have been widely investigated owing to their advantages such as tunable bandgap<sup>[9]</sup>, high absorption coefficient<sup>[10]</sup> and versatile fabrication methods<sup>[11]</sup>. For the fabrication of carrier transport, sputtering buffer, and encapsulated layers of PSCs, ALD<sup>[12]</sup> is a unique technology for growth conformal film growth based on self-limiting surface reactions, as compared with other methods such as spin-coating, thermal evaporation, and magnetron sputtering<sup>[13]</sup>. As shown in [Table 1](#), compared to other film deposition techniques such as physical (PVD)<sup>[14]</sup> and chemical vapor deposition (CVD)<sup>[6,15]</sup>, ALD provides the distinctive capability to form monolayer films. This facilitates precise control over film thickness and composition, ensuring exceptional uniformity and conformality at the angstrom level. As illustrated in [Figure 1](#), an ideal ALD process consists of the following four steps: Step 1: The precursor of the first reactant A is pulsed into the reaction chamber and adsorbed on the substrate surface; Step 2: After the surface adsorption is saturated, the surplus precursor and by-products are purged out of the reaction chamber with inert gas; Step 3: The precursor of the second reactant B is pulsed into the reaction chamber and undergoes reaction with precursor A on the surface to grow the  $A_xB_y$  film; and Step 4: After the reaction is complete, the surplus precursor and by-products are purged out of the reaction chamber with inert gas. Based on the above steps, a conformal, pinhole-free film is cyclically deposited layer-by-layer.

The physical and chemical properties of ALD films are strongly influenced by three main factors: precursors, deposition temperatures, and substrates. Metal and oxygen sources are commonly used as precursors to fabricate metal oxide films in PSCs<sup>[16]</sup>. The reaction precursors should effectively react with the surface groups of the material<sup>[17-20]</sup>. Secondly, they must have sufficient chemical stability and cannot decompose due to physical factors (temperature, pressure, *etc.*) or corrode the underlying material. Deposition temperature is another key factor influencing the quality of ALD films and the performance of devices. Too high deposition temperatures may lead to decomposition of perovskite and deterioration of device performance<sup>[21]</sup>. As for substrates, the sufficient adsorption of the precursor molecules on the high-aspect-ratio surface is the prerequisite for achieving an ideal ALD film<sup>[12]</sup>, which we also demonstrated in our previous research on the application of ALD for PSCs and tandem solar cells<sup>[22]</sup>. Therefore, the surface properties of the substrate significantly influence the film quality of ALD, which cannot be ignored.

Previous review articles have examined the benefits of ALD in the realm of PSCs. Brinkmann *et al.* have investigated functional layers prepared by ALD for PSCs<sup>[16]</sup>. Very recently, Zhang *et al.* have discussed ALD-prepared buffer and encapsulation layers for enhancing the stability of PSCs<sup>[23]</sup>. To fabricate high-quality ALD films in PSCs and their related tandem solar cells, a comprehensive review of the selection of reaction precursors, deposition temperatures, and substrates is necessary. In this mini review, we explore the ALD reaction mechanisms and the effects of different reaction conditions, such as precursors and temperatures, especially the deposition substrates, on the film properties. Additional studies on ALD substrates in the semiconductor field are also summarized, which may have potential impacts and applications on the PSCs.

**Table 1. Comparison of PVD, CVD, and ALD**

Film deposition techniques	Deposition principle	Deposition pattern	Uniformity	Conformality	Expansibility	Degree of vacuum	Film thickness
PVD	Physical vapor deposition	Nucleation growth	High number of pinholes and particles exist	Low and only for flat substrate	Medium	High requirement for vacuum degree and sensitive to the change of vacuum degree	Nanometer level
CVD	Gas-phase chemical reaction	Nucleation growth	Low number of pinholes and particles exist	Medium	Low	Medium	Nanometer level
ALD	Surface saturated reaction	Layer-by-layer growth	Low number of pinholes and no particles	High	High	Low	Angstrom level

**Figure 1.** The reaction process of ALD.

## EFFECT OF ALD REACTION CONDITIONS ON FILM PROPERTIES

### Precursor

The underlying mechanism of precursor chemistry in ALD is predicated on the adsorption and subsequent reaction of precursor molecules onto the substrate surface<sup>[20]</sup>. So, ALD requires using highly reactive precursor molecules to interact selectively with the substrate surface. The chemical structure of the precursors also affects the surface chemistry and the growth rate of the film. As for PSCs, various metal oxides, such as ZnO, TiO<sub>x</sub>, Al<sub>2</sub>O<sub>3</sub>, and SnO<sub>x</sub>, are prepared by ALD as different functional layers, which respectively correspond to the metal precursors: diethyl zinc (DEZn)<sup>[24]</sup>, titanium tetrachloride (TiCl<sub>4</sub>)<sup>[25]</sup>, tetrakis(dimethylamido)titanium (TDMA-Ti)<sup>[26]</sup>, Titanium isopropoxide (TTIP)<sup>[27]</sup>, tris(dimethylamido)methylcyclopentadienyl titanium (Ti(CpMe)(NMe<sub>2</sub>)<sub>3</sub>)<sup>[28]</sup>, trimethylaluminum (TMA)<sup>[29]</sup>, and tetrakis(dimethylamido)titanium (TDMA-Sn)<sup>[30,31]</sup>. The common oxygen precursors are H<sub>2</sub>O, O plasma, O<sub>3</sub><sup>[32]</sup>, and H<sub>2</sub>O<sub>2</sub><sup>[33]</sup>, which form the Metal-O bands. The selection of precursors may cause different effects on the reactant surface due to the different properties, such as strong Lewis acidity, and thus affect the performance of devices. The choice of inappropriate metal precursors will damage the substrate. Choudhury *et al.* reported that TMA precursors could break the interaction between PbI<sub>3</sub><sup>-</sup> and CH<sub>3</sub>NH<sub>3</sub><sup>+</sup>, forming PbI<sub>3</sub>-Al(CH<sub>3</sub>)<sub>3</sub> and releasing CH<sub>3</sub>NH<sub>2</sub> and CH<sub>4</sub><sup>[29]</sup>. These results revealed that they can damage the perovskite substrate. To further demonstrate, they observed an apparent mass loss due to the absence of CH<sub>3</sub>NH<sub>3</sub><sup>+</sup> and the presence of only a PbI<sub>2</sub> peak in the X-ray diffraction (XRD) spectrum after 100 TMA pulses, which also confirms the decomposition of perovskite<sup>[29]</sup>. Hultqvist *et al.* investigated the compatibility of ALD directly deposited on the mixed halide perovskite. The Zn precursor DEZn was found

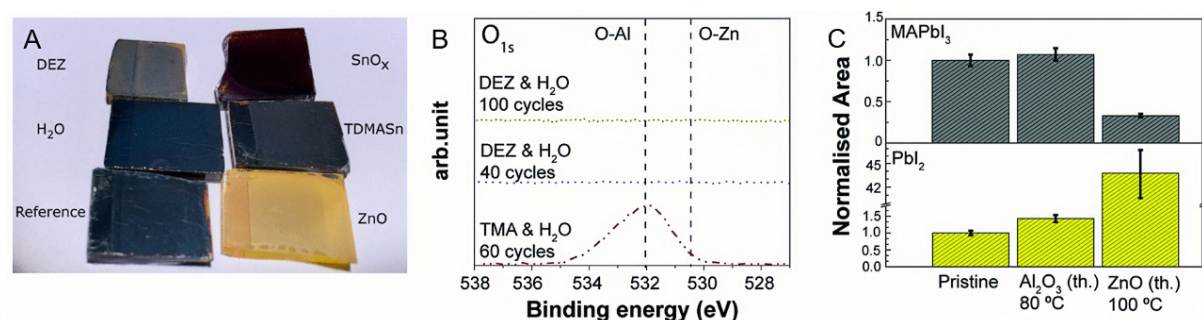
to exacerbate the degradation of the perovskite film, which converted into  $\text{PbI}_2$  without forming ZnO. Different from the case of ZnO, the Sn precursor TDMASn did not degrade the perovskite, and conformal  $\text{SnO}_x$  films could be successfully formed<sup>[34]</sup>, as shown in Figure 2A. Zardetto *et al.* compared ALD processes of  $\text{Al}_2\text{O}_3$  and ZnO. They found that the DEZn precursor failed to react with the perovskite substrate to form ZnO films and instead caused the perovskite to decompose. A loss of 80% of the  $\text{MAPbI}_3$  peak and a huge increase of the  $\text{PbI}_2$  peak were observed in XRD analysis, which indicated the degradation of perovskite. In contrast, the evident growth of  $\text{Al}_2\text{O}_3$  was observed, and the nitrogen peak intensity of perovskite did not decrease in the same situation [Figure 2B and C]<sup>[35]</sup>. Kruszyńska *et al.* used DEZn/ $\text{H}_2\text{O}$  (AZO-1) and TMA/ $\text{H}_2\text{O}$  (AZO-2) to grow aluminum-doped zinc oxide (AZO) films<sup>[36]</sup>. They found that AZO-2 enhanced the thermal stability of the perovskite layer and facilitated charge transport at the interface. The better thermal stability of AZO-2 was explained by the weak acid-base reaction between ZnO and  $\text{MAPbI}_3$ . As for the charge transport, the increased carrier concentration improved the surface conductivity and electron mobility for AZO-2<sup>[36]</sup>. It can be seen from these results that the compatibility of metal precursors and substrates is very important.

As for oxygen precursors, it is worth mentioning that the exposure levels to a single pulse of  $\text{H}_2\text{O}$  are very low in the vacuum-based ALD process<sup>[35]</sup>. Thus, water is usually chosen as the oxygen source in the ALD of metal oxides. The influence of oxygen sources has also been investigated by several studies. Hu *et al.* reported a comparative study of  $\text{SnO}_x$  films and their devices prepared by ALD using  $\text{H}_2\text{O}$ ,  $\text{O}_3$  and plasma precursors as precursors<sup>[32]</sup>. It is found that the  $\text{H}_2\text{O}$ -based devices had the largest electron extraction barriers in the conduction band (CB) between  $\text{PbI}_2$  and  $\text{MAPbI}_3$ , resulting in the poor ability of electron extraction. Additionally, the considerable gap states were found in  $\text{H}_2\text{O}$ - $\text{SnO}_x$ , which were not found in the  $\text{O}_3$ - and plasma-based  $\text{SnO}_x$  layers. These gap states caused parasitic recombination and poor electron selectivity at the interface, resulting in low efficiency and large hysteresis for the devices based on  $\text{H}_2\text{O}$ - $\text{SnO}_x$ <sup>[32]</sup>. Similarly, Zardetto *et al.* studied the impact of direct exposure of  $\text{MAPbI}_3$  to  $\text{H}_2\text{O}$  and  $\text{O}_2$  plasma. It is found that the decomposition effect was more evident when  $\text{MAPbI}_3$  was directly exposed to the  $\text{O}_2$  plasma [Figure 3A]<sup>[35]</sup>. Behrendt *et al.* compared the characteristics of  $\text{SnO}_x$  films grown with  $\text{O}_3$  and  $\text{H}_2\text{O}$  as oxygen source precursors<sup>[37]</sup>, respectively, as shown in Table 2. Compared to  $\text{H}_2\text{O}$ -based layers,  $\text{O}_3$ -based layers had a trend of lower water vapor transmission rates (WVTR) with increasing deposition temperatures, which was related to the rising layer density. They had higher values for bandgap energy ( $E_g$ ), which can be explained by particle size effects. Furthermore, the ALD  $\text{SnO}_x$  film prepared by  $\text{O}_3$  source exhibited better transmittance in the visible region, while  $\text{H}_2\text{O}$ -based layers had poor transmittance due to subgap absorption<sup>[37]</sup>, as shown in Figure 3B and C. Wang *et al.* compared ALD  $\text{Al}_2\text{O}_3$  films prepared by low temperature using  $\text{H}_2\text{O}$ ,  $\text{O}_2$  plasma and  $\text{O}_3$  as oxygen sources<sup>[38]</sup>. They proved that using  $\text{O}_2$  plasma or  $\text{O}_3$  as an oxygen precursor could make the film denser and grow at a higher rate under low temperature conditions [Figure 3D]. Compared with  $\text{H}_2\text{O}$ - and  $\text{O}_2$  plasma-based films, the  $\text{O}_3$ -based film had the minimum root mean square (RMS) value, exhibiting a smooth surface. Fourier transform infrared (FTIR) spectroscopy analysis unveiled a significant presence of OCO, C-O, and C-H bonds in the  $\text{H}_2\text{O}$ -based film, whereas the lowest concentration of these carbon species was observed in the  $\text{O}_3$ -based film. The notable abundance of carbon species in the  $\text{H}_2\text{O}$ -based film may impede the self-limiting ALD reaction, consequently resulting in the formation of a film of inferior quality<sup>[38]</sup>. Compared with the  $\text{H}_2\text{O}$  precursor, Lee *et al.* discovered that the ALD- $\text{SnO}_x$  layer fabricated using  $\text{H}_2\text{O}_2$  exhibited enhanced electron extraction ability, attributed to a decrease in oxygen vacancies, which is associated with the highly oxidizing properties of  $\text{H}_2\text{O}_2$ <sup>[39]</sup>. The surface roughness reduced from 36.43 nm for  $\text{H}_2\text{O}$ -based films to 32.02 nm for  $\text{H}_2\text{O}_2$ -based ones. The reduced roughness of  $\text{H}_2\text{O}_2$ -based films exhibited better contact with the perovskite, leading to the enhanced open circuit voltage ( $V_{oc}$ ) and fill factor (FF)<sup>[39]</sup>.

**Table 2. Properties of ALD SnO<sub>x</sub> films using O<sub>3</sub> or H<sub>2</sub>O as oxidants. Reprinted with permission from ref.<sup>[37]</sup>. Copyright 2015 Wiley**

ALD-film	T <sub>D</sub> [°C]	WVTR average [g (m <sup>2</sup> day) <sup>-1</sup> ]	Density ρ [g cm <sup>-3</sup> ]	σ [S cm <sup>-1</sup> ]	n [cm <sup>-3</sup> ]	μ [cm <sup>2</sup> Vs <sup>-1</sup> ]	Carbon content [%]	Nitrogen content [%]	[O]/[Sn]	E <sub>g</sub> [eV]	T <sub>av</sub> [%]
SnO <sub>x</sub> (O <sub>3</sub> )	100	2.2 × 10 <sup>-4</sup>	3.8	3 × 10 <sup>-5</sup>	-	-	12.8	6.7	2.6	4.23	89
	150	8.8 × 10 <sup>-6</sup>	4.8	2	2 × 10 <sup>18</sup>	5	7.3	5.4	2.3	3.88	84
	200	3.6 × 10 <sup>-6</sup>	7.0	3 × 10 <sup>2</sup>	2 × 10 <sup>20</sup>	10	1.8	1.4	2.1	3.67	80
SnO <sub>x</sub> (H <sub>2</sub> O)	100	7 × 10 <sup>-5</sup>	5.4	6 × 10 <sup>-4</sup>	1 × 10 <sup>15</sup>	4	3.6	2.1	2.2	3.80	78
	150	3 × 10 <sup>-5</sup>	5.3	3 × 10 <sup>-3</sup>	1 × 10 <sup>16</sup>	2	3.6	1.4	2.0	3.19	67
	200	3.1 × 10 <sup>-6</sup>	5.7	6 × 10 <sup>-5</sup>	-	-	1.9	0.3	1.8	3.21	69

The deposition temperature T<sub>D</sub>, the water vapor transmittance WVTR, density ρ, conductivity σ, carrier density n, carrier mobility μ, [O]/[Sn] of 200 nm SnO<sub>x</sub> and the data in % are expressed. The element content, band gap energy E<sub>g</sub>, and transmittance T<sub>av</sub> of 200 nm SnO<sub>x</sub> are measured by RBS, which indicates that the meaningful data cannot be obtained with too low content.

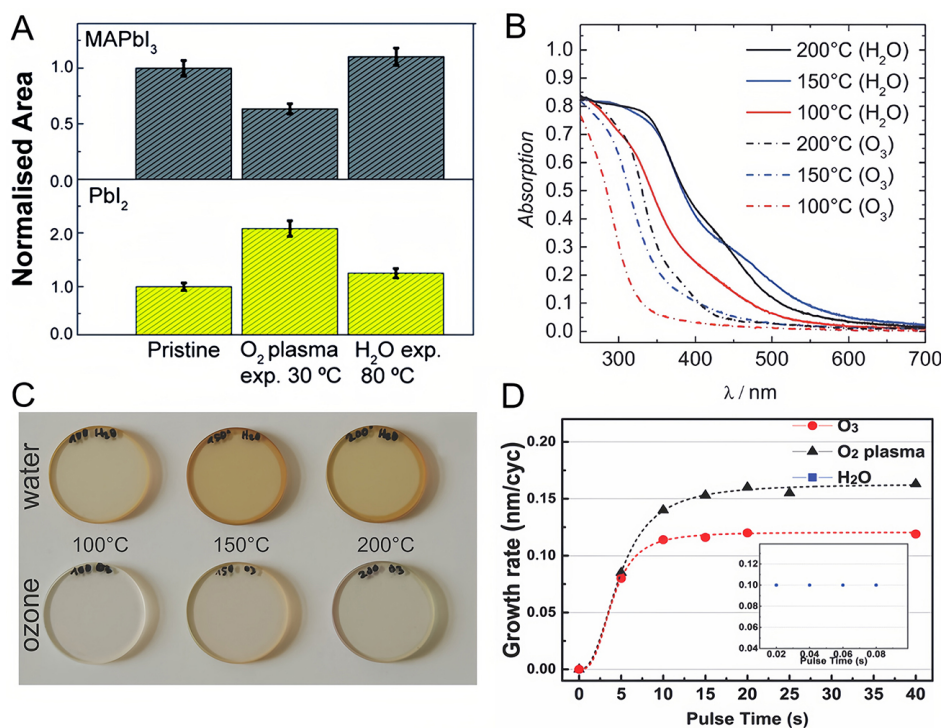


**Figure 2.** (A) Image showing perovskite films subjected to partial ALD treatments employing H<sub>2</sub>O, DEZn, or TDMASn or subjected to complete ALD processes for either ZnO or SnO<sub>x</sub>. Reprinted with permission from ref.<sup>[34]</sup>. Copyright 2017 American Chemical Society. (B) XPS pattern of O 1s spectra for three distinct perovskite samples: pristine, post thermal ALD Al<sub>2</sub>O<sub>3</sub>, and ZnO treatments. (C) Normalized areas of the MAPbI<sub>3</sub> {110} peak and PbI<sub>2</sub> {001} peak. Reprinted with permission from ref.<sup>[35]</sup>. Copyright 2017 Royal Society of Chemistry.

In summary, it is necessary to fully understand the compatibility between ALD precursors and the reactant substrate to keep a substrate from decomposition or degradation.

### Deposition temperature

The deposition temperature is a critical factor in the growth of ALD films, significantly affecting the reaction kinetics and surface chemistry of the precursor molecules<sup>[20]</sup>. Notably, the growth rate of ALD films, quantified by the growth per cycle (GPC), is significantly influenced by temperature. It remains consistent within a specific range of deposition temperatures, ensuring adequate thermal energy for the chemical reactions involved in the ALD process. Beyond this range, it increases due to the disruption in the self-limitation caused by the thermal degradation of the metal precursor<sup>[40]</sup>. However, a contrary phenomenon is occasionally observed, where the growth rate decreases with the increasing growth temperature, possibly owing to insufficient precursor reaction or the condensation of the precursors<sup>[41]</sup>. Therefore, optimal temperatures are necessary to promote the chemisorption reactions and achieve desirable growth rates. As per previous reports, ALD can occur in different temperature ranges in a limited amount of time. In typical thermal ALD processes for metal oxides, temperatures ranging from 100 to 400 °C are commonly used<sup>[42]</sup>. Spatial ALD processes and plasma-assisted methods could facilitate processing temperatures below 100 °C<sup>[43-46]</sup>. Zardetto *et al.* explored the influence of deposition temperature on the perovskite layer. Samples were kept for 4 h at 30, 80 and 100 °C during the ALD process<sup>[35]</sup>. Compared to 30 and 80 °C, the XRD peak of MAPbI<sub>3</sub> decreased by almost 40%, and that of PbI<sub>2</sub> increased



**Figure 3.** (A) Normalized areas of the MAPbI<sub>3</sub> {110} peak and PbI<sub>2</sub> {001} peak. Reprinted with permission from ref.<sup>[35]</sup>. Copyright 2017 Royal Society of Chemistry. (B) The optical absorption spectra of SnO<sub>x</sub> layers synthesized at various temperatures using either O<sub>3</sub> or H<sub>2</sub>O as oxygen source. (C) Images depicting SnO<sub>x</sub> layers fabricated at different temperatures utilizing either O<sub>3</sub> or H<sub>2</sub>O as oxygen source on quartz substrates. Reprinted with permission from ref.<sup>[37]</sup>. Copyright 2015 Wiley. (D) The growth per cycle plotted against the pulse time of oxidants, as determined from ellipsometry measurements. Reprinted with permission from ref.<sup>[38]</sup>. Copyright 2018 Wiley.

dramatically at 100 °C. The organic methylammonium component degraded into HI and CH<sub>3</sub>NH<sub>2</sub> by-products due to the thermal stress, and they further sublimated and formed PbI<sub>2</sub>. After only 1 h at 100 °C, no perovskite degradation was detected, indicating that the ALD processing time should be shortened when using a higher reaction temperature<sup>[35]</sup>. Lindahl *et al.* studied the structure and optical properties of zinc tin oxide (ZTO) films with growth temperatures between 90 and 180 °C. It is found that the growth temperature had minimal impact on the composition of the films. However, it significantly influenced the growth rate, density, and E<sub>g</sub> of ZTO films<sup>[47]</sup>. As deposition temperatures rose, the density of ZTO films increased, while the E<sub>g</sub> decreased, which was associated with the microstructural alterations of the ZTO films. Transmission electron microscopy (TEM) measurements showed that ZTO films contained small ZnO or ZnO (Sn) crystallites, and the size of these crystallites increased with rising Zn content and deposition temperature. They caused the quantum confinement effects to reduce the E<sub>g</sub> due to the increased size<sup>[47]</sup>. Chistiakova *et al.* investigated the effect of temperature for two kinds of ALD processes: non-optimized (2 s, 150 W oxygen plasma treatment step) and optimized (6 s, 300 W oxygen plasma treatment step with an additional flow of 10 sccm of Ar)<sup>[48]</sup>. They found that the resistivity of ALD SnO<sub>x</sub> layers decreased by 4-5 orders with increasing deposition temperature from 120 to 200 °C, and a slight decrease of resistivity also occurred for the non-optimized ALD process. The carbon and nitrogen contaminations on the SnO<sub>x</sub> layer decreased with increasing temperature, resulting in the augmentation of the refractive index and the decline of the optical E<sub>g</sub> due to the Burstein-Moss shift<sup>[48]</sup>. Köhnen *et al.* analyzed the relationship between optical properties and deposition temperatures in the deposition of SnO<sub>x</sub> layers. The film exhibited higher ultraviolet (UV) absorption and refractive index at higher temperatures<sup>[49]</sup>. In addition, it is found that the deposition temperature had no effect on the short circuit current density (J<sub>sc</sub>) and V<sub>oc</sub> of PSCs,

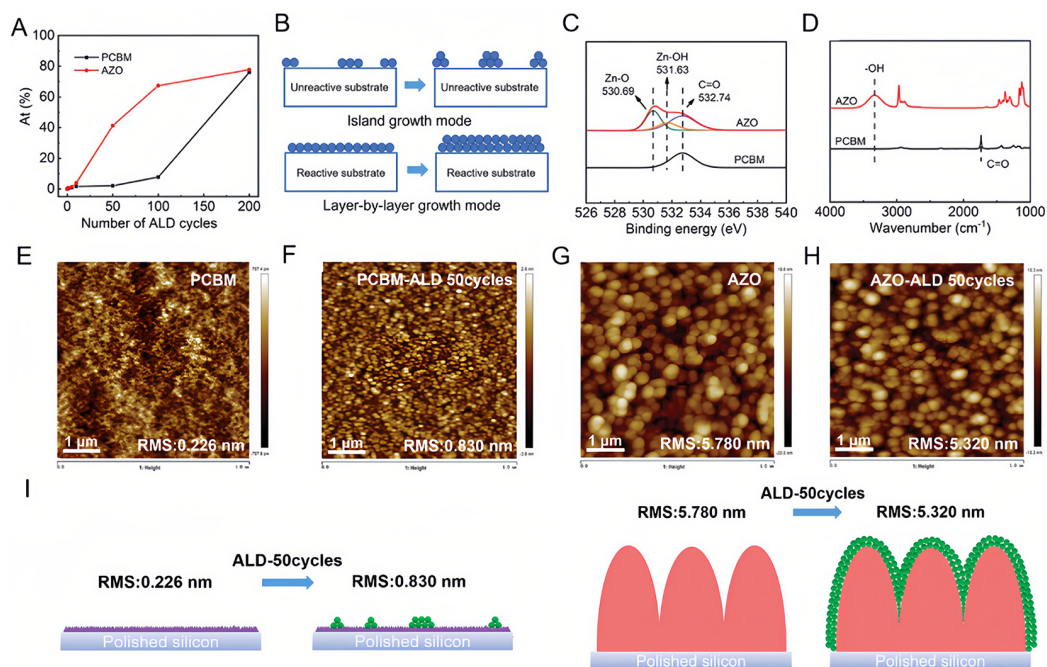
while the FF reduced with the increasing deposition temperature from 80 to 120 °C<sup>[49]</sup>. In contrast, Hultqvist *et al.* found that the PSCs with SnO<sub>x</sub> deposited at 60 °C exhibited lower V<sub>OC</sub> and FF than those with SnO<sub>x</sub> deposited at 90 °C owing to a double diode-like behavior<sup>[50]</sup>.

In summary, the deposition temperature significantly influences the optical and electrical properties of the films. For example, the atoms of amorphous materials form electronic states at the edge of the energy band, which replace the electronic states at the tail of the energy band, leading to higher optical absorption and lower optical band gap<sup>[48,51]</sup>.

## THE REACTION SUBSTRATE OF ALD

The substrate type is integral to the deposition process, as it dictates the adsorption and subsequent reactions of precursor molecules<sup>[20]</sup>. The nature of the substrate can influence the nucleation and growth of the film and its properties, such as composition, crystallinity, and morphology. Variations in the surface structure and chemical makeup of substrates can lead to differential adsorption and reaction behaviors of the precursors, which, in turn, affect the growth rate and the ultimate properties of the film. The ALD procedure relies on self-terminating surface reactions, which are closely linked to the surface functionalities on the deposition substrates. ALD substrates can be classified into two major categories<sup>[22,52]</sup>: (1) unreactive substrates lacking nucleation sites for deposition; and (2) reactive substrates with abundant reactive sites. Puurunen *et al.* proposed that the ALD process transitioned into island growth when the substrate was unresponsive to the ALD reactant, a phenomenon also known as substrate-inhibited growth<sup>[52]</sup>. Compared with island growth, layer-by-layer growth is necessary to shape an extremely pinhole-free, conformal, and smooth surface that improves PSC performances<sup>[22,52]</sup>. The deposition mode of ALD is nonstatic. For instance, Stranski-Krastanov growth illustrates a scenario where ALD initially proceeds with layer-by-layer growth but transitions to island growth due to stress effects within the film<sup>[53,54]</sup>. According to the GPC, the growth mode can be further classified into three categories<sup>[18,52]</sup>: (1) Substrate-inhibited growth, where the GPC is primitively low (island growth) and then reaches a linear growth mode; (2) Linear growth, where the GPC is constant throughout the process of ALD; and (3) Substrate-enhanced growth, wherein the GPC exhibits elevated levels initially before transitioning into linear growth. The last two cases correspond to layer-by-layer growth mode<sup>[18]</sup>.

Brinkmann *et al.* used a bistratal AZO/SnO<sub>x</sub> electron transportation layer (ETL) to create excellent resilience against moisture and heat in PSCs. They discovered that the stability of the AZO/SnO<sub>x</sub> devices was superior to that of the devices with SnO<sub>x</sub> deposited directly on the surface of [6,6']-phenyl-C61-butyric acid methyl ester (PCBM), which was attributed to the nonideal ALD growth of SnO<sub>x</sub> directly on the surface of the unreactive PCBM layer<sup>[55]</sup>. Furthermore, Yu *et al.* discovered that ZnO could not nucleate on the PCBM surface. Subsequently, they utilized TMA, a potent Lewis acid, to react with the C=O groups present in PCBM. The Al<sub>2</sub>O<sub>3</sub> could provide nucleation sites for the growth of ZnO<sup>[56]</sup>. Gong *et al.* used 2-mercaptoethanol (2-mcpEtOH) to modify the perovskite surface, allowing the S in the thiol group to bond with Pb<sup>2+</sup> of perovskite. The modified layer provided the reactant sites -OH and thiol protons (SH) for ALD. Upon exposure to water, the surface exhibited stronger chemical resistance than a bare, unmodified perovskite film<sup>[57]</sup>. Wang *et al.* improved the PCBM surface by adding 3-aminopropyl triethoxysilane (APTS) molecules, which provided nucleation sites to form dense SnO<sub>x</sub> films, improving the stability of inverted flexible PSCs<sup>[58]</sup>. As illustrated in [Figure 4](#) of our previous study, Yu *et al.* reported that the nucleation of ALD SnO<sub>x</sub> films was delayed on the unreactive substrate PCBM<sup>[22]</sup>. They activated the unreactive layer by introducing AZO with -OH groups. Through a combination of XPS and FTIR analysis, it was demonstrated that the modified PCBM layer provided adequate reactive sites for layer-by-layer growth, forming impermeable SnO<sub>x</sub> films. Additionally, a significant increase in roughness was observed in

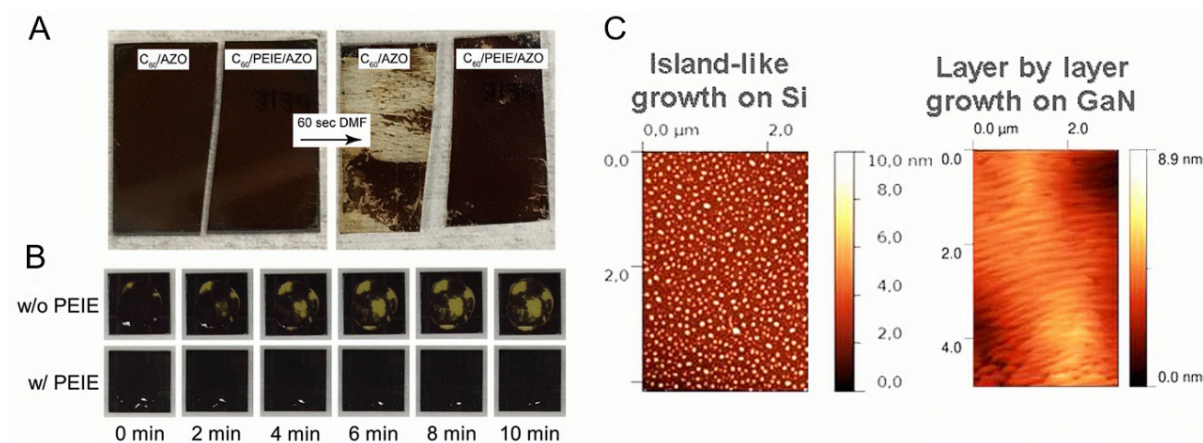


**Figure 4.** (A) Sn content (expressed as atomic percentage, At%) in relation to the number of SnO<sub>x</sub> cycles. (B) A diagram of different deposition modes. (C) XPS spectra. (D) FTIR spectra. (E-H) AFM images. (I) Diagram of two deposition modes on PCBM and AZO substrates. Reprinted with permission from ref. [22]. Copyright 2023 Wiley.

the PCBM sample by AFM, indicating non-continuous island growth on the PCBM substrate, contrasting with the layer-by-layer growth on the AZO substrate. This discrepancy in growth behaviors was attributed to the island and layer-by-layer growth modes on the unreactive and reactive substrates, respectively<sup>[22]</sup>. Similarly, Liu *et al.* observed the island growth of ALD SnO<sub>x</sub> on the unreactive substrate C<sub>60</sub>, which caused the problem of excessive dark current of the device. To address this issue, WO<sub>3</sub> was added to the surface of C<sub>60</sub>, and dense ALD films grown layer-by-layer were obtained<sup>[59]</sup>.

Polyethyleneimine ethoxylated (PEIE) is an ideal material for ALD, which has a rich density of hydroxyl groups. ALD precursors can penetrate into polymer or small-molecule substrates, leading to sub-surface formation<sup>[60]</sup>. Instead of a chemically inert C<sub>60</sub> surface, Palmstrom *et al.* used PEIE as a nucleation layer for recombination layers prepared by ALD in all-perovskite tandem cells<sup>[60]</sup>. Furthermore, metal oxides, including TiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, and SnO<sub>x</sub>, were respectively deposited on C<sub>60</sub> and PEIE substrates. The former ALD layers degraded significantly in solvents [water and dimethylformamide (DMF)], whereas the latter ALD films remained stable in solvents [Figure 5A]. The solvents-resistance property was enhanced by the more impermeable ALD film grown on the PEIE layer, which provided both hydroxyl and amine functional groups. These groups were suitable for nucleating and reacting with the precursors<sup>[60]</sup>. Besides, Li *et al.* introduced PEIE to facilitate the nucleation and crystal growth of perovskite films and provide surface reactive sites for ALD ZnO<sup>[61]</sup>. Raiford *et al.* also utilized PEIE to functionalize the surface of C<sub>60</sub> for the subsequent deposition of ALD SnO<sub>x</sub> and VO<sub>x</sub> films, which served as barrier layers to improve the stability of PSCs<sup>[62]</sup>. It is seen that the nucleation of ALD SnO<sub>x</sub> formed a more continuous and denser barrier layer after using PEIE, which exhibited excellent water vapor barrier performance and protected the perovskite film from degradation under high temperature (200 °C) and humidity conditions, as shown in Figure 5B. The unpackaged device with a Ag electrode still maintained 94% of the initial efficiency after 670 h of thermal aging at 85 °C, whereas the efficiency of similar devices without PEIE dropped to 0 at 670 h. In addition,





**Figure 5.** (A) Images of perovskite samples: before and after exposure to DMF for 60 s. Reprinted with permission from ref.<sup>[60]</sup>. Copyright 2019 Elsevier. (B) Time-lapse images of water-resistance test. Reprinted with permission from ref.<sup>[62]</sup>. Copyright 2019 Wiley. (C) AFM images of ALD ZnO films indicated the island-like growth on Si substrate and the layer-by-layer growth on GaN. Reprinted with permission from ref.<sup>[64]</sup>. Copyright 2012 American Chemical Society.

PEIE-based devices also showed better light stability<sup>[62]</sup>. Indeed, the substrate plays a significant role in determining the growth behavior of ALD films. Therefore, the substrate modification engineering is crucial for improving the quality of ALD films and the performance of PSCs. Table 3 summarizes the properties of ALD films prepared on different substrates and the stability performance of the corresponding PSCs. The modification of the substrate can form denser and smoother ALD thin films, which greatly improves the stability of the PSCs.

In addition to the perovskite field, the research on the ALD substrate is also carried out in other semiconductor fields, which have significant support for improving the performance of PSCs. Labbe *et al.* used TEM and spectroscopic ellipsometry (SE) to investigate the nucleation behavior of ALD  $\text{FeO}_x$ <sup>[53]</sup>. During the ALD process, both substrate-enhanced and substrate-inhibited growth modes were observed. They found that layer-by-layer growth did not always occur in the linear growth regime after island coalescence<sup>[53]</sup>. Moreover, several studies have indicated that the island growth mode is unfavorable for achieving high-quality ALD films. Yun *et al.* noted that during island growth, the nucleation stage of the ALD process exhibited nonideal behavior, impeding layer-by-layer growth and resulting in delayed nucleation<sup>[63]</sup>. This behavior was attributed to a deficiency in reaction sites, necessitating additional incubation cycles for nucleus formation. They further explored the nucleation and growth behavior of AlN film on Si and TiN substrates by thermal ALD. The nucleation of AlN films was delayed on the Si substrates, while they grew without any nucleation delay on TiN substrates. The substrate-inhibited growth on Si surfaces was attributed to the scarcity of reactive sites, and ammonia ( $\text{NH}_3$ ) pretreatment on Si surfaces was applied to grow uniform AlN films<sup>[63]</sup>. Baji *et al.* observed that the island growth occurred on the unreactive substrate Si, while it grew layer-by-layer on the reactive substrate GaN during the ALD deposition of ZnO. The latter had a smoother film than the former<sup>[64]</sup>, as shown in Figure 5C. Uğur *et al.* also reported that island growth of  $\text{Al}_2\text{O}_3$  occurred when the reactant materials were deposited on unreactive substrates. They observed through TEM that ALD  $\text{Al}_2\text{O}_3$  could not completely cover the hexagonal boron nitride (hBN) substrate because of an unreactive substrate<sup>[65]</sup>. Hagen *et al.* found that the ALD Cu processes varied significantly depending on the substrate materials employed. On Si and TaN surfaces, isolated island formation was observed<sup>[66]</sup>. Polymers are special substrate materials for ALD processes as well. Wilson showed that  $\text{Al}_2\text{O}_3$  films deposited by ALD on various polymer substrates, including polystyrene (PS), polypropylene (PP), poly(methyl methacrylate) (PMMA), polyethylene (PE), and poly(vinyl chloride)

**Table 3. The properties of ALD films prepared on different substrates and the stability of the corresponding PSCs**

ALD thin film	Substrate	Quality of ALD thin film	Storage condition	Stability of devices	Ref.
SnO <sub>x</sub>	PCBM	Roughness increased from 0.226 to 0.830 nm after 50 cycles of SnO <sub>x</sub> deposition	Ambient air (at 25 °C, 30%RH) for 75 h; N <sub>2</sub> atmosphere (at 25 °C) for 670 h; Heated at 85 °C in N <sub>2</sub> atmosphere for 700 h; Operated at ambient under 1 sun illumination for 32 h	Normalized PCE decreased to 0.77; Normalized PCE decreased to 0.73; Normalized PCE decreased to 0.81; Normalized PCE decreased to 0.80	[22]
	AZO	Roughness decreased from 5.780 to 5.320 nm after 50 cycles of SnO <sub>x</sub> deposition	Ambient air (at 25 °C, 30%RH) for 2,300 h; N <sub>2</sub> atmosphere (at 25 °C) for 5,100 h; Heated at 85 °C in N <sub>2</sub> atmosphere for 1,580 h; Operated at ambient under 1 sun illumination for 1,000 h	Normalized PCE decreased to 0.84; Normalized PCE decreased to 0.99; Normalized PCE decreased to 0.81; Normalized PCE decreased to 0.84	
SnO <sub>x</sub>	PCBM	Nonideal growth	Ambient air (at 22 °C, 60%RH) for 150 h	V <sub>OC</sub> and FF decreased to 0	[55]
	AZO	Impermeable	Ambient air (at 22 °C, 60%RH) for 150 h	V <sub>OC</sub> increased from 0.84 to 0.95, and FF decreased from 60% to 50%	
SnO <sub>x</sub>	PCBM	Roughness of 8.32 nm; R <sub>s</sub> of 64 Ω	Ambient air (at 25 °C, 85%RH) for 600 h	Normalized PCE decreased to 0.77	[58]
	APTS modified PCBM	Roughness of 4.29 nm; R <sub>s</sub> of 46 Ω	Ambient air (at 25 °C, 85%RH) for 600 h	Normalized PCE decreased to 0.9	
SnO <sub>x</sub>	C <sub>60</sub>	Large SnO <sub>x</sub> gains and lower atomic concentrations of Sn and C	Operated in ambient air (at 60 °C, 30%RH) under 0.77 sun illumination at 60 °C for 250 h; Heated at 85 °C in N <sub>2</sub> atmosphere for 700 h	Normalized Avg. P <sub>MAX</sub> decreased to 0.585, Normalized Avg. V <sub>OC</sub> decreased to 0.231; Normalized PCE decreased to 0	[62]
	PEIE	Small SnO <sub>x</sub> gains and higher atomic concentrations of Sn and C	Operated in ambient air (at 60 °C, 30%RH) under 0.77 sun illumination at 60 °C for 250 h; Heated at 85 °C in N <sub>2</sub> atmosphere for 670 h	Normalized Avg. P <sub>MAX</sub> decreased to 0.815, Normalized Avg. V <sub>OC</sub> decreased to 0.585; Normalized PCE decreased to 0.94	

Relative humidity RH, open circuit voltage V<sub>OC</sub>, fill factor FF, series resistance R<sub>s</sub>, power conversion efficiency PCE, average maximum power Avg. P<sub>MAX</sub>, average open circuit voltage Avg.

(PVC). TMA first diffused into the polymer and then reacts with H<sub>2</sub>O on the substrate surface to form Al<sub>2</sub>O<sub>3</sub>, leaving some TMA unreacted<sup>[67]</sup>. A similar phenomenon was found by Jur *et al.*<sup>[68]</sup>. Demelius *et al.* investigated the PE-ALD growth of ZnO on polyethylene glycol dimethacrylate (pEGDMA) and poly 2-hydroxyethyl methacrylate (pHEMA)<sup>[69]</sup>. They discovered more intense precursor diffusion in pEGDMA with fewer reactive sites. The growth process of ZnO consisted of plasma etching of the polymer substrate and ALD growth of ZnO. Besides, they found that ZnO films were formed after 3-5 cycles on pHEMA using *in-situ* SE and X-ray reflectivity (XRR), whereas a significant nucleation delay after 12-16 cycles was detected on pEGDMA. By comparing the growth modes<sup>[52]</sup>, island growth, as the dominant growth mode on pEGDMA, was found, while nucleation on pHEMA was more similar to layer-by-layer growth. These results revealed that the density of reactant sites affected the nucleation behavior for ALD substrates<sup>[69]</sup>. Weiß *et al.* compared the GPC of ALD CuO films on Si, Al<sub>2</sub>O<sub>3</sub>, and TiO<sub>2</sub> substrates at room temperature. The Si substrate had the highest GPC, but this phenomenon was not further explained<sup>[70]</sup>. Zhou *et al.* proposed a two-step interface engineering process (chemical mechanical polishing and RCA SC-2 treatment) to optimize the deposition process of ALD AlO<sub>x</sub> and avoid substrate-inhibited growth, thereby improving the ALD surface quality and wettability<sup>[71]</sup>. In addition, introducing seed layers, such as Al<sub>2</sub>O<sub>3</sub><sup>[56,72,73]</sup> and black phosphorus<sup>[74]</sup>, was often an effective way to activate unreactive substrates.

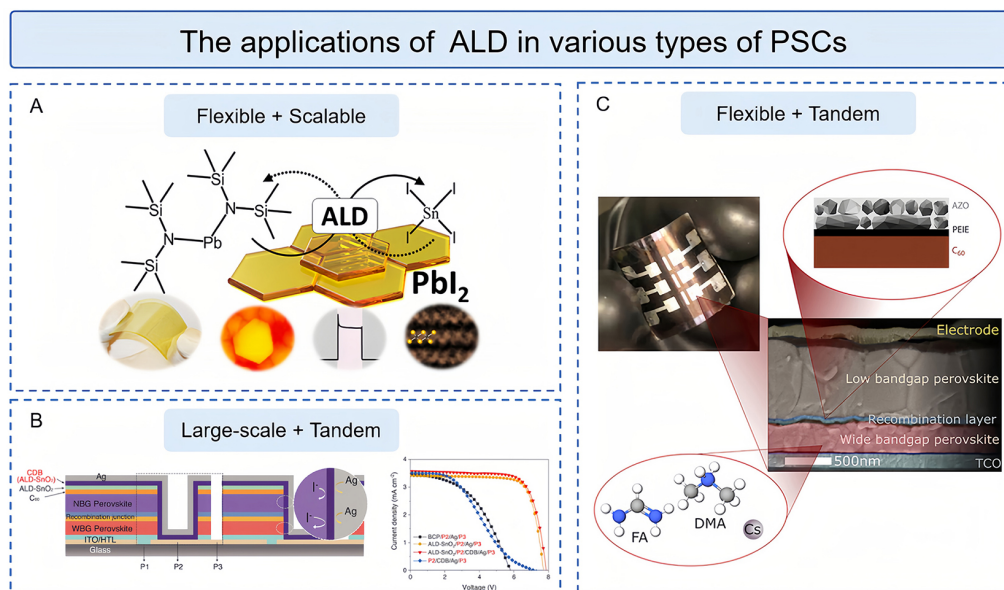
## THE APPLICATIONS OF ALD FOR ENHANCED PERFORMANCE IN PSCS

As shown in Figure 6, ALD enables the precise and conformal deposition of materials in various types of PSCs, including scalable, flexible and tandem solar cells. The efficiency of the PSCs always suffers from charge recombination loss because of defects in bulk or at interfaces<sup>[75-77]</sup>. Therefore, surface passivation strategy and interface engineering are needed to reduce the nonradiative recombination and enhance charge carrier transportation and collection. In some aspects, the ALD layer presents a viable approach to address these challenges, improving performance of various types of PSCs.

ALD enables preparation at a low temperature, making it particularly suitable for PSC fabrication. Based on the discussion of the precursor and deposition temperature section, it is known that organic-inorganic hybrid perovskites are nature-sensitive with precursors and deposition temperatures. Zhao *et al.* also found that perovskite degraded when the deposition temperature was higher than 125 °C and chose 75 °C as the best deposition temperature to grow Al<sub>2</sub>O<sub>3</sub><sup>[21]</sup>. Then, ALD Al<sub>2</sub>O<sub>3</sub> deposited at 75 °C was used to sufficiently passivate defect states at the surface of perovskite. After interface passivation via ten cycles of the ALD Al<sub>2</sub>O<sub>3</sub> layer, the efficiency of the device enhanced from 18.8% to 20.0%. The ALD Al<sub>2</sub>O<sub>3</sub>-based devices can maintain more than 95% of their initial efficiency after being stored in the N<sub>2</sub> atmosphere for 150 days<sup>[21]</sup>. ALD is also a potential technology for fabricating the flexible, compatible, and scalable films. On different substrates (polymers, metals, metal sulfides, and oxides), PbI<sub>2</sub> films were first prepared through ALD processes with the deposition temperatures below 90 °C using Pb(btsa)<sub>2</sub> and SnI<sub>4</sub> as precursors. Moreover, ALD Al<sub>2</sub>O<sub>3</sub> was used as an encapsulation layer which effectively protected the underlying PbI<sub>2</sub> film<sup>[78]</sup>.

High-performance flexible PSCs need transparent electrodes with low fabrication temperature and reduced charge recombination losses. ALD layers could meet these requirements. Jin *et al.* have proposed a flexible electrode structure, silver nanowires (AgNWs)/ZnO/ALD TiO<sub>2</sub> with excellent transparency and electrical and mechanical characteristics<sup>[28]</sup>. The ALD TiO<sub>2</sub> layer was applied to effectively passivate the charge recombination defects on the ZnO layer and protect the perovskite layer from decomposition. The power conversion efficiency (PCE) of this flexible PSC reaches 17.11%, comparable to that of 18.26% of rigid devices. Finally, it maintained 77% of initial PCE after 2,000 bending cycles with a radius of 6 mm<sup>[28]</sup>. Because of the inferior gas barrier properties of plastic substrates, flexible devices often suffer from intrinsic problems of poor stability under ambient environments. Lin *et al.* investigated the stability of flexible PSCs under illumination for polyisobutylene (PIB)-, 1H,1H,2H,2H-perfluorooctyltriethoxysilane (PFOTES)/ZnO-, and ALD Al<sub>2</sub>O<sub>3</sub>-based polyethylene naphthalate/indium tin oxide (PEN/ITO) substrates<sup>[79]</sup>. Due to the compact and uniform ALD films, ALD Al<sub>2</sub>O<sub>3</sub>-based devices showed the best T<sub>80</sub> (Normalized PCE of 0.8) value (increased from 80 h to over 350 h) under maximum power point (MPP) tracking under 1 sun illumination in ambient conditions [60%-70% relative humidity (RH)]<sup>[79]</sup>.

ALD layers always act as diffusion barriers, buffer layers, and recombination layers in tandem solar cells. Traditionally, all-perovskite tandem solar cells require several spin-coating steps, which limited the device area. For large areas, ALD is a scalable preparation technique to fabricate large area functional layers due to its good expandability. To overcome the problem of reaction between interfacial halide and metal electrode, Xiao *et al.* introduced a thin conformal diffusion barrier (CDB) consisting of 10 nm ALD SnO<sub>2</sub> to an all-perovskite tandem module<sup>[80]</sup>. The CDB layer could extract vertical electrons and serve as the lateral diffusion barrier between interconnecting subcells. The ITO/ALD SnO<sub>2</sub>/Ag junction showed good ohmic contact, demonstrating that the CDB layer supported effective electrical interconnection between two subcells. Finally, they achieved a certified PCE of 21.7% with aperture area of 20.25 cm<sup>2</sup>, and the modules with CDB maintained 75% of their initial efficiency for 500 h upon MPP tracking under 1 sun illumination in ambient conditions while the modules without CDB decreased to less than 50% after 20 h<sup>[80]</sup>. Yu *et al.*



**Figure 6.** A scheme of the applications of ALD in different types of PSCs. (A) Perovskite material and encapsulation layer on flexible and scalable substrates. Reprinted with permission from ref. [78]. Copyright 2016 American Chemical Society. (B) Charge extractor and diffusion barrier in all-perovskite tandem solar modules. Reprinted with permission from ref. [80]. Copyright 2022 The American Association for the Advancement of Science. (C) Recombination layer in flexible all-perovskite tandem solar cells. Reprinted with permission from ref. [60]. Copyright 2019 Elsevier.

have developed a new strategy to activate the unreactive PCBM substrate and deposit an impermeable ALD sputtering buffer  $\text{SnO}_x$  layer [22]. For allowing the near-infrared light to pass through and be absorbed in the bottom subcell, tandem solar cells need the top subcell to be optical transmission; the dense ALD films are vital for the perovskite/silicon tandem solar cells when preparing transparent conductive oxides (TCOs) and avoid damage to the perovskite during sputtering. For demonstration, optimized ALD layers were employed as sputtering buffer layers in semi-transparent (ST) devices. As a result, the ratio of working devices to both working and non-working devices of optimized ST devices was almost 100%, exhibiting the excellent anti-sputtering ability [22]. As for all-perovskite tandem solar cells, the ideal recombination layer could enable voltage addition and optical loss reduction between the subcells. Palmstrom *et al.* introduced a modified structure with a ALD layer ( $\text{C}_{60}/\text{PEIE}/\text{ALD AZO}$ ) to enhance the composite between low bandgap and wide bandgap perovskite layers, reducing solvent degradation of the active layer during solution deposition [60]. Recently, ALD  $\text{SnO}_x$  layers provided a promising solution to enhance carrier-selective contacts in tandem PSCs. Xiong *et al.* controlled the O:Sn ratio by varying the purge time of the oxygen source [81]. They found that the perovskite degraded apparently when the ratio increased, and the electrical properties became worse when the ratio decreased. By modifying the gradient compositions of the ALD  $\text{SnO}_x$  layer, the charge extraction ability was enhanced. Finally, they achieved a PCE of 28.9% and retained 95% of its initial efficiency for 500 h upon MPP tracking under AM 1.5G illumination for a  $1.0 \text{ cm}^2$  monolithic perovskite/silicon tandem solar cell [81].

Stability issues in moisture, oxygen, and light exposure are key challenges for PSCs. As shown in Table 4, ALD could act as encapsulation barriers against external environmental factors, thereby improving the long-term stability of PSCs. As for p-i-n structure PSCs, Brinkmann *et al.* prepared 20 nm ALD  $\text{SnO}_x$  with water vapor transmittance as low as  $7 \times 10^{-5} \text{ g m}^{-2} \text{ d}^{-1}$ , showing the excellent water vapor barrier properties [55]. The ALD  $\text{SnO}_x$  layer could prevent decomposition products from being expelled from perovskite. Under inert atmosphere, the unencapsulated perovskite underwent thermal decomposition, as observed by

**Table 4. Recent studies on improving the stability of perovskite devices by ALD**

Buffer layer	Architecture	Efficiency	Storage condition	Stability of devices	Ref.
BCP	ITO/NiO <sub>x</sub> /PTAA/Al <sub>2</sub> O <sub>3</sub> /FAMACs/PCBM/BCP/Ag	N/A	Under UV light (365 nm) in air for 20 days; N <sub>2</sub> atmosphere (at 65 °C) for 1,080 h; Ambient air (at 25 °C, 60%RH) for 1,440 h; Heated at 85 °C with 85%RH in N <sub>2</sub> atmosphere for 110 h	A strong diffraction peak of PbI <sub>2</sub> was detected, and the color of the film faded from dark brown to yellow; Normalized PCE decreased to 0.70; Normalized PCE decreased to 0.73; Normalized PCE decreased to 0.22	[82]
ALD SnO <sub>x</sub>	ITO/NiO <sub>x</sub> /PTAA/Al <sub>2</sub> O <sub>3</sub> /FAMACs/PCBM/ALD SnO <sub>x</sub> /Ag	21.10%	Under UV light (365 nm) in air for 40 days; N <sub>2</sub> atmosphere (at 65 °C) for 1,080 h; Ambient air (at 25 °C, 60%RH) for 1,440 h; Heated at 85 °C with 85%RH in N <sub>2</sub> atmosphere for 680 h	A strong diffraction peak of PbI <sub>2</sub> was detected, and the color of the film faded from dark brown to yellow; Normalized PCE decreased to 0.82; Normalized PCE decreased to 0.85; Normalized PCE decreased to 0.38	
Modified-ALD SnO <sub>x</sub>	ITO/NiO <sub>x</sub> /PTAA/Al <sub>2</sub> O <sub>3</sub> /FAMACs/PCBM:EVA/ALD SnO <sub>x</sub> /Ag	22.06%	Under UV light (365 nm) in air for 40 days; N <sub>2</sub> atmosphere (at 65 °C) for 1,080 h; Ambient air (at 25 °C, 60%RH) for 1,440 h; Heated at 85 °C with 85%RH in N <sub>2</sub> atmosphere for 800 h	A slight diffraction peak of PbI <sub>2</sub> was detected, and the color of the film showed no big change; Normalized PCE decreased to 0.90; Normalized PCE decreased to 0.92; Normalized PCE decreased to 0.85	
BCP	FTO/NiO <sub>x</sub> /Me-4PACz/perovskite/C <sub>60</sub> /BCP/Cu	24.29%	N <sub>2</sub> atmosphere (85%RH) for 10 h; MPP tracking at 85 °C in ambient air for 15 h; 85%RH at 85 °C for 150 h; Operated under 1 sun illumination in ambient air (30%-50%RH at 65 °C) for 67 h	Normalized PCE decreased to 0.65; Normalized PCE decreased to 0.61; Normalized PCE decreased to 0.78; Normalized PCE decreased to 0.90	[83]
ALD SnO <sub>x</sub>	FTO/NiO <sub>x</sub> /Me-4PACz/perovskite/C <sub>60</sub> /ALD SnO <sub>x</sub> /Cu	24.42%	N <sub>2</sub> atmosphere (85%RH) for 10 h; MPP tracking at 85 °C in ambient air for 15 h; 85%RH at 85 °C for 150 h; Operated under 1 sun illumination in ambient air (30%-50%RH at 65 °C) for 140 h	Normalized PCE decreased to 0.45; Normalized PCE decreased to 0.85; Normalized PCE decreased to 0.80; Normalized PCE decreased to 0.90;	
ALD AlO <sub>x</sub>	FTO/NiO <sub>x</sub> /Me-4PACz/perovskite/C <sub>60</sub> /ALD AlO <sub>x</sub> /Cu	24.61%	N <sub>2</sub> atmosphere (85%RH) for 10 h; MPP tracking at 85 °C in ambient air for 15 h; 85%RH at 85 °C for 150 h; Operated under 1 sun illumination in ambient air (30%-50%RH at 65 °C) for 1,150 h	Normalized PCE decreased to 0.80; Normalized PCE decreased to 0.97; Normalized PCE decreased to 0.90; Normalized PCE decreased to 0.90	
Spiro-OMeTAD	FTO/ALD SnO <sub>2</sub> /perovskite/Spiro-OMeTAD/ALD V <sub>2</sub> O <sub>5-x</sub> /Au	23.15%	Ambient air (at 24 °C, 20%RH) for 576 h; Operated under continuous AM 1.5G light illumination and a constant bias of 0.85 V without a UV cutoff filter for 130 h	Normalized PCE decreased to 0.318; Normalized PCE decreased to 0.712	[84]
ALD V <sub>2</sub> O <sub>5-x</sub>	FTO/ALD SnO <sub>2</sub> /perovskite/Spiro-OMeTAD/ALD V <sub>2</sub> O <sub>5-x</sub> /Au	23.02%	Ambient air (at 24 °C, 20%RH) for 576 h; Operated under continuous AM 1.5G light illumination and a constant bias of 0.85 V without a UV cutoff filter for 130 h	Normalized PCE decreased to 0.905; Normalized PCE decreased to 0.949	
Spiro-OMeTAD	F:SnO <sub>2</sub> /SnO <sub>2</sub> /perovskite/Spiro-OMeTAD/Au	19.1%	Ambient air for 300 days	Normalized PCE decreased to 0.38	[85]
ALD Al <sub>2</sub> O <sub>3</sub>	F:SnO <sub>2</sub> /SnO <sub>2</sub> /perovskite/Spiro-OMeTAD/ALD Al <sub>2</sub> O <sub>3</sub> /Au	19.4%	Ambient conditions for 300 days	Normalized PCE decreased to 0.84	
Spiro-OMeTAD	FTO/ALD SnO <sub>2</sub> /SnO <sub>2</sub> NPs/perovskite/Spiro-OMeTAD/Au	21.29%	Operated under continuous AM 1.5G light illumination and a constant bias of 0.85 V without a UV cutoff filter for 120 h	Normalized PCE decreased to 0.832	[86]
ALD TiO <sub>2</sub>	FTO/ALD SnO <sub>2</sub> /SnO <sub>2</sub> NPs/perovskite/Spiro-OMeTAD/ALD TiO <sub>2</sub> /Au	20.68%	Operated under continuous AM 1.5G light illumination and a constant bias of 0.85 V without a UV cutoff filter for 120 h	Normalized PCE decreased to 0.965	

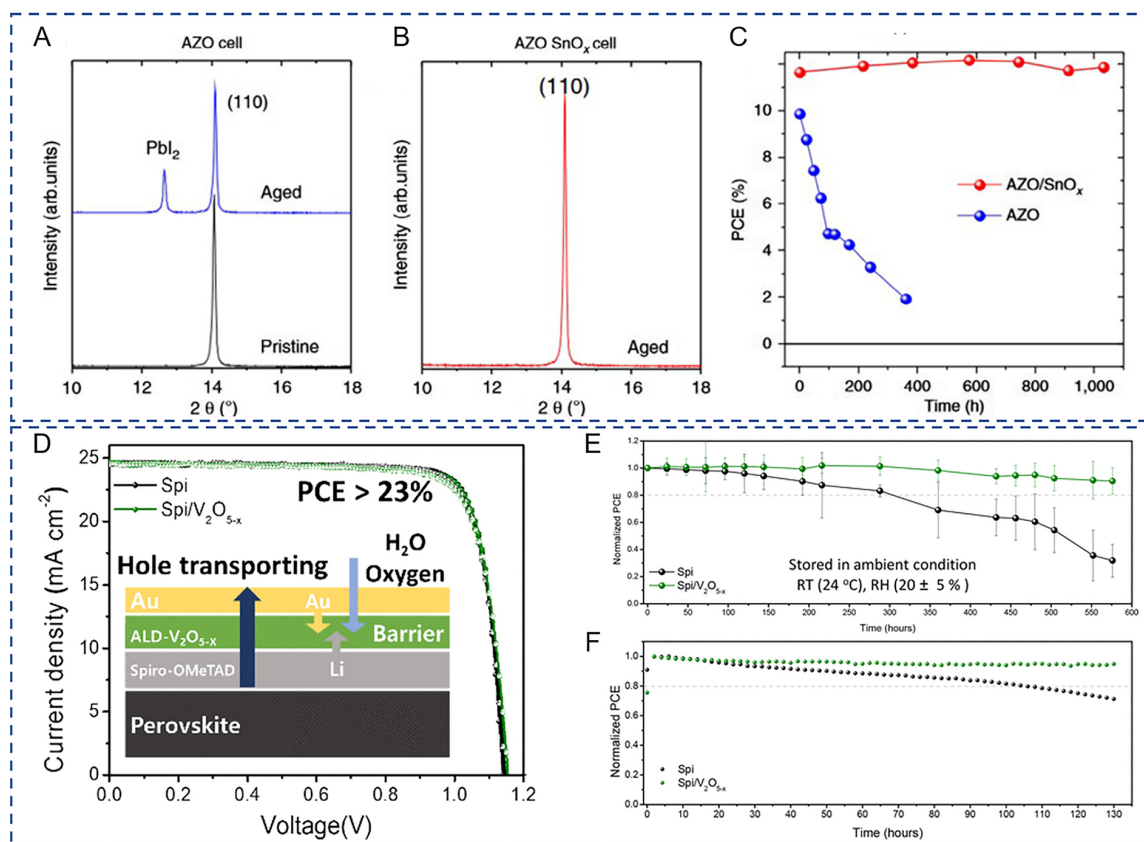
characteristic peaks of  $\text{PbI}_2$  [Figure 7A and B]. However, the ALD  $\text{SnO}_x$ -based device effectively hindered the outer diffusion of the decomposition products, significantly improving the thermal stability of the PSCs [Figure 7C]<sup>[55]</sup>. Li *et al.* used the modified ALD  $\text{SnO}_x$  by ester groups of poly(ethylene-co-vinyl acetate) as a self-encapsulated interface, resulting in retaining 85% of the initial PCE after storage 85 °C with RH of 85% for over 800 h<sup>[82]</sup>. The choice of ALD materials is essential for the long-term stability level of PSCs. Recently, Zheng *et al.* systematically investigated the long-term stability and the underlying decomposition mechanisms of ALD  $\text{SnO}_x$ -based PSCs<sup>[83]</sup>. It was found that ALD  $\text{SnO}_x$ -based PSCs exhibited higher susceptibility to degradation, surpassing even the degradation levels observed with bathocuproine (BCP) under humid conditions. It further revealed that the ALD  $\text{SnO}_x$  layer triggered a phase transition in the perovskite when exposed to moisture, transitioning from the black cubic phase to the yellow  $\delta$  phase despite the presence of a thin layer of fullerene between the  $\text{SnO}_x$  and the perovskite. Instead of  $\text{SnO}_x$ , ALD  $\text{AlO}_x$  layers emerged as a transformative strategy, sufficiently bolstering the humidity and thermal stability of the cells without affecting device efficiency. The optimized ALD  $\text{AlO}_x$  PSCs exhibited a PCE of 24.61% and maintained 88% of its initial efficiency after MPP tracking under 1 sun illumination for 1,350 h at 65°C in ambient air<sup>[83]</sup>. As for n-i-p PSCs, ALD  $\text{V}_2\text{O}_{5-x}$  deposited on the top of a Spiro-OMeTAD layer was utilized to block the moisture and oxygen, enhancing the stability by preserving the photovoltaic  $\alpha$ -FAPbI<sub>3</sub> phase and eliminating the leakage of both Li ions from the intermediate layer and Au ions from the electrode [Figure 7D]. Finally, the PCE of ALD  $\text{V}_2\text{O}_{5-x}$ -based devices retained 90.5% of their initial efficiency after 576 h while that of the devices without ALD  $\text{V}_2\text{O}_{5-x}$  encapsulation layer reduced to 31.8% of the initial values in ambient condition (25%RH at 24 °C). In addition, the PCE of ALD  $\text{V}_2\text{O}_{5-x}$ -based devices maintained 94.9% of the initial efficiency after 130 h, while that of the devices without ALD  $\text{V}_2\text{O}_{5-x}$  encapsulation layers decreased to 71.2% of the initial PCE under operating conditions [Figure 7E and F]. The improved stability for PSCs with ALD  $\text{V}_2\text{O}_{5-x}$  was ascribed to the barrier function of ALD films and the retarded diffusion of Au electrodes by passivation of ALD layers<sup>[84]</sup>.

## CONCLUSION AND OUTLOOK

This paper reviews the influences of atomic layer precursors, deposition temperatures and reaction substrates on the physical and chemical properties of ALD films and the performance of PSCs. For the precursor, some metal sources may damage the substrate (such as perovskite, carrier transport layer, *etc.*). The physical properties (such as density, permeability, and resistivity) of the films prepared with different oxygen sources may change. Moreover, oxygen sources may also influence the device performance of PSCs, especially on FF. The deposition temperature also influences the characteristics of ALD films and the performance of ALD devices. The optimal deposition temperature can be obtained by testing the band gap, resistivity and absorptivity of the films prepared at different temperatures. The ALD substrate is also a crucial factor in the process of ALD. In the field of non-perovskite, there have been many studies on the substrate-inhibited island growth mode of ALD film. However, in perovskite, the reaction mechanism of ALD on different substrates is unclear, and most relevant studies are related to the stability of ALD perovskite devices prepared on various substrates and the water vapor barrier ability of ALD films.

At present, ALD is increasingly used in the carrier transport and encapsulation layers of PSCs. Therefore, this paper summarizes the influential factors (Especially for the reaction substrates) that need attention in preparing ALD films for PSCs, along with related solutions, which are conducive to the efficient and large-scale fabrication of PSCs and the related tandem cells.

Several challenges associated with ALD processing in perovskites need to be addressed:



**Figure 7.** (A and B) XRD analysis of PSC with AZO and AZO/SnO<sub>x</sub> before and after being heated in N<sub>2</sub> atmosphere for six days. (C) Thermal stability test (N<sub>2</sub> atmosphere at 60 °C). Reprinted with permission from ref. [55]. Copyright 2017 Nature Publishing Group. (D) Performance and structure of ALD V<sub>2</sub>O<sub>5-x</sub>-based-PSC. (E) Ambient stability test (20%RH at 24 °C). (F) Operated stability test under AM 1.5G illumination. Reprinted with permission from ref. [84]. Copyright 2022 American Chemical Society.

### Precursor selection and compatibility

Precursor selection is influenced by various factors, including chemical stability, vapor pressure, and reactivity. In the context of perovskite ALD, the choice of precursors must strike a delicate balance between providing the desired chemical composition and ensuring compatibility with the substrate material. For instance, while highly reactive precursors may offer enhanced film growth rates, they may also pose challenges in terms of substrate damage or film quality degradation due to uncontrolled reactions at the substrate surface. The compatibility between precursors and substrates encompasses several aspects, including adsorption kinetics, surface diffusion, and reaction kinetics. A precursor that exhibits favorable interactions with the substrate surface, such as strong adsorption and controlled surface diffusion, is more likely to result in uniform film growth. Conversely, mismatches in precursor-substrate compatibility can lead to non-uniform film coverage, defects, and reduced film quality. More experimental characterizations and computational models are needed to provide deeper insights into precursor-substrate interactions, guiding the optimization of ALD processes for diverse applications in PCSs.

### Interfacial engineering

ALD enables the deposition of ultrathin, conformal layers with atomic-level precision, making it well-suited for interface engineering applications. It also offers opportunities for interface modification at the interface between the charge transport layers and electrodes. By depositing thin interfacial layers to promote adhesion, reduce interfacial resistance, and enhance charge collection efficiency, ALD can improve the

overall device performance and stability. Achieving precise control over interfacial properties, such as energy level alignment and interface roughness, is essential for maximizing device efficiency and stability.

### **Film uniformity**

Achieving uniform deposition of functional layers using ALD across large-area substrates is crucial for scalability. Addressing issues such as precursor diffusion, surface coverage, and reaction kinetics to ensure uniform film deposition is essential.

### **Scalability and cost**

Scaling up ALD processes for PSC production requires the development of high-throughput deposition methods compatible with large-area substrates. Addressing challenges related to deposition rate, precursor utilization, and equipment scalability is essential for transitioning ALD from laboratory-scale research to industrial-scale production. Cost-effective deposition techniques are necessary for the commercialization of PSCs. Optimizing ALD processes to minimize precursor consumption, reduce deposition time, and increase equipment efficiency can help lower production costs and make PSCs more competitive with traditional silicon-based photovoltaics.

## **DECLARATIONS**

### **Authors' contributions**

Proposed the topic of this mini review: Yu B, Yang Y

Performed literature survey: Yu B, Zhang J

Prepared the manuscript: Yu B, Zhang J

Collectively discussed and revised the manuscript: Yang Y, Yu D

Review, conceptualization, and supervision: Mai Y, Chen X

### **Availability of data and materials**

Not applicable.

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### **Conflicts of interest**

All authors declared that there are no conflicts of interest.

### **Ethical approval and consent to participate**

Not applicable.

### **Consent for publication**

Not applicable.

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