

Spatial Atomic Layer Deposition of Nitrogen-doped Alumina Thin Films for High-Performance Perovskite Solar Cell Encapsulation

Authors: Hatameh Asgarimoghaddam^a, Qiaoyun Chen^{a,b}, Fan Ye^a, Ahmed Shahin^a, Olivia Alexandra Celeste Marchione^a, Bo Song^b, Kevin Philip Musselman^{a,*}

^a Department of Mechanical and mechatronic Engineering, University of Waterloo, Waterloo, Ontario, Canada

^b Laboratory of Advanced Optoelectronic Materials, Suzhou Key Laboratory of Novel Semiconductor Materials and Devices, Suzhou key Laboratory of Macromolecular Design and Precision Synthesis, College of Chemistry, Chemical Engineering and Materials Science, Soochow University, Suzhou 215123, China

* kevin.musselman@uwaterloo.ca

Abstract:

An atmospheric-pressure spatial atomic layer deposition (AP-SALD) system is used to deposit nitrogen-doped alumina (N-AlO_x) thin-film-encapsulation layers. The rapid nature of the AP-SALD process facilitates deposition of 60-nm layers directly on perovskite solar cells at 130 °C with no damage to the temperature-sensitive perovskite and organic materials. Varying the bubbling of a NH₄OH precursor varied the nitrogen concentration from 0.08 to 0.68 atomic %. These small concentrations were found to have a significant impact on the structural properties of the films and their moisture barrier performance. The N-AlO_x thin films had slightly higher growth rates than undoped AlO_x, less unwanted hydroxyl and carbon content, and were smoother and more compact, which was attributed to a higher flux of reactive species from the volatile NH₄OH. Optical calcium tests showed that the N-AlO_x films had lower water-vapor-transmission rates ($\sim 10^{-5}$ g/m²/day) than undoped AlO_x films and the transmission was minimized for 0.28% nitrogen. The increased compactness of the N-AlO_x films is expected to minimize nanoscale percolation pathways, whereas higher nitrogen-defect concentrations may facilitate water permeation through these pathways. The stability of n-i-p and p-i-n perovskite solar cells under standard ISOS-D-1 and ISOS-D-3 testing conditions was significantly enhanced by the encapsulation layers. An N-AlO_x encapsulation layer with 0.28% nitrogen improved the T₈₀ value of a p-i-n formamidinium

methylammonium lead iodide solar cell from 144 hrs to 855 hrs (ISOS-D-1) and 52 hrs to 300 hrs (ISOS-D-3).

KEYWORDS: Alumina (AlO_x), Nitrogen doping, Atmospheric-pressure spatial atomic layer deposition (AP-SALD), Thin film encapsulation (TFE), Perovskite solar cells (PSCs).

1. Introduction:

Organic-inorganic hybrid perovskite solar cells (PSCs) have attracted great attention due to their high power conversion efficiency (PCE) and low manufacturing cost[1]. Although PSCs have already achieved comparable performance to Si-based solar cells, the long-term stability of these devices under real operating conditions remains a challenge[2], [3]. Both the external environment and intrinsic factors are known to contribute to PSC degradation[4], such that a combination of intrinsic stabilization and protection from the environment will be necessary to produce stable PSCs[5]. Among all the external factors affecting the durability of PSCs, moisture is the most challenging one to mitigate and plays an important role in the degradation process[6]. It was established that the most promising technique to enhance the stability of a PSC is full encapsulation of the device, which will be necessary for commercialization[7]. The encapsulation can act as a barrier, restricting the diffusion of moisture and protecting the perovskite active layer from deterioration, as shown in the n-i-p and p-i-n PSCs in Figure 1a,b[8].

Thin-film encapsulation (TFE) is one of the most promising candidates for the encapsulation of PSCs. Single-layer thin films are attractive because of the simplicity of the manufacturing process compared to multilayer encapsulation methods that require multiple processing steps[9]. Thin films can be applied as dense, pinhole-free barriers against moisture and oxygen yet remain lightweight and thin enough to not adversely affect the mechanical flexibility of the solar stack. Therefore, they can be compatible with roll-to-roll processing[10]. Furthermore, thin films can be deposited directly onto the PSC and used in conjunction with glass-to-glass and polymer encapsulation[5].

To fabricate the TFE, different kinds of deposition processes have been adopted including plasma-enhanced chemical vapor deposition (CVD), sputtering, and atomic layer deposition (ALD)[11].

Unfortunately, such methods require a high energy input or temperature, which can degrade the perovskite material[10]. The challenge lies in the fact that the barrier properties of inorganic TFE layers are greatly influenced by the deposition temperature[12]. For example, decreasing the ALD process temperature reduced the barrier performance of an AlO_x TFE, since the films had lower densities and a large amount of carbon-related impurities and hydroxyl groups[13]. Hence there is commonly a trade-off between achieving good TFE barrier properties and damaging the perovskite material. Moreover, these vacuum deposition processes are expensive and have limited throughput[11]. Therefore, it is crucial to develop scalable TFE methods that can maximize the barrier performance while minimizing damage to the perovskite during the encapsulation process[14].

In this respect, atmospheric-pressure spatial atomic layer deposition (AP-SALD) is very promising. AP-SALD is an emerging method for rapid, open-air deposition of thin films[15], [16]. In contrast to conventional ALD, spatial ALD processes separate the chemical precursors in space rather than in time. In AP-SALD, precursors flow towards the substrate in different physical locations with the substrate moving back and forth, as shown in Figure 1c-d. Films are grown by alternatively exposing the substrate to the precursors, which are separated by inert gas regions[17]. AP-SALD can be up to two orders of magnitude faster than conventional ALD and its open-air nature makes it cheaper and easier to scale up[18]. These characteristics make AP-SALD very attractive for the deposition of TFE layers at a temperature that is high enough to provide good barrier properties and at a speed that is fast enough to avoid perovskite damage. Initial demonstrations of AP-SALD on top of metal-halide perovskite materials have included the deposition of a ZnO charge-injection layer on $\text{CH}_3\text{NH}_3\text{PbBr}_3$ in a perovskite LED[19] and TiO_2 and SnO_2 electron-transport layers on the perovskite of a PSC[20], [21]. However, little work has been done to produce TFE layers for PSCs using AP-SALD.

Aluminum oxide (Al_2O_3) is an attractive moisture barrier owing to its combination of adhesion, mechanical strength, chemical inertness, and ultralow water-vapor transmission rates on the order of 10^{-4} to 10^{-6} g per day per m^2 [9]. It has been previously established that an ultrathin ALD Al_2O_3 film deposited

between perovskite and spiro-OMeTAD layers can isolate the perovskite layer from moisture, thus enhancing the stability of PSCs[22]. However, as discussed above, conventional ALD is not practical for preparing effective Al_2O_3 TFE layers due to its low throughput and need for prolonged substrate heating. When depositing Al_2O_3 by ALD, it has been shown that decreasing the process temperature impedes the reaction between the trimethyl aluminum (TMA) and H_2O , generating unreacted residues that create defects in the films, making them more permeable to water vapor[23]. Recent work from our group attempted to overcome these conflicting requirements by using an AP-SALD system to rapidly deposit Al_2O_3 thin films on partial PSC stacks[24]. However, Al_2O_3 TFE layers deposited by AP-SALD have yet to be characterized in detail and incorporated into full PSCs. Furthermore, the composition of AP-SALD Al_2O_3 TFE layers has yet to be studied and optimized.

Metal oxynitrides, for example, are used as a gas-barrier coating in the food packaging industry due to their excellent oxygen- and water-vapour-barrier performance[25]. Improvements in a number of film properties have been gained by replacing aluminium oxide with aluminium oxynitride[26], [27]. This is due to the fact that variable concentrations of aluminum, oxygen, and nitrogen lead to the development of a ternary AlO_xN_y system with tuneable properties. The film properties can be tailored between those of pure Al_2O_3 and aluminum nitride (AlN), depending on the application requirements[28]. It was reported that anion doping of Al_2O_3 can decrease the defect density and oxygen and moisture diffusion[29]. Nitrogen-doped alumina (N- AlO_x) has been successfully deposited using chemical vapor deposition, ALD, and plasma-enhanced ALD[30], [31]; however, studies have shown that the gas-barrier properties of Al-based films depend on many factors, including the film thickness and type of deposition technique[25], [27]. To the best of our knowledge, AP-SALD N- AlO_x films have not been demonstrated or studied.

In this work, N- AlO_x films are deposited by AP-SALD and their deposition rate, microstructure and barrier properties are studied as a function of the film composition. The N- AlO_x films are then employed as TFE layers on both p-i-n and n-i-p perovskite solar cells, as shown in Figure 1a,b. The rapid AP-SALD process prevents degradation of the perovskite layer and the N- AlO_x composition is optimized to maximize

the PSC stability, which is measured using International Summit on Organic Photovoltaic Stability (ISOS) protocols[32]. As a result, we successfully demonstrate a more than five-fold enhancement in the stability of the PSCs with a single TFE layer deposited rapidly in open-air.

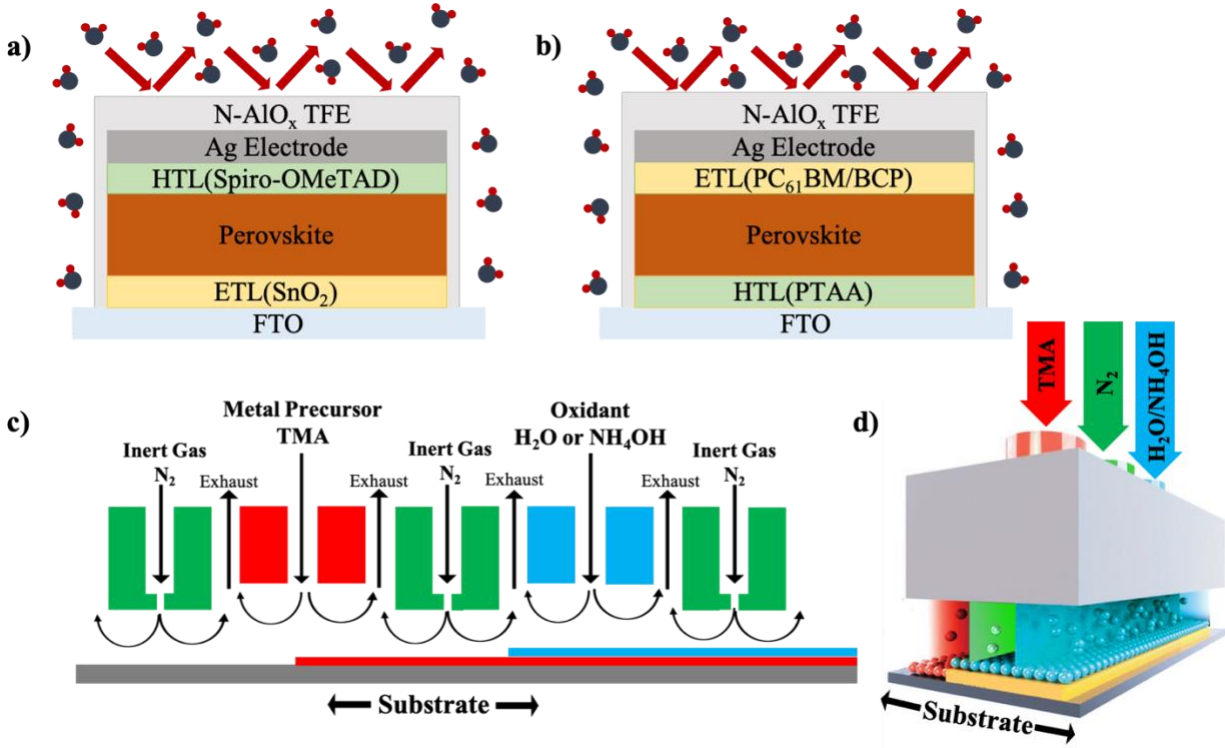


Figure 1. Schematic of a) n-i-p and b) p-i-n perovskite-solar-cell structures. c) Principle of a close-proximity AP-SALD reactor, where the precursor half-reaction zones are separated by inert gas curtains. By moving the substrate horizontally underneath the reactor, the two half reactions will take place sequentially to form an ALD monolayer. d) A schematic of the reactor head used in our AP-SALD system. Aluminum precursor (red), inert nitrogen (green), and oxidant and nitrogen-dopant (blue) gas streams are shown.

2. Results and discussion:

AlO_x and N-AlO_x layers were deposited in open-air conditions using our custom-built, dual atmospheric-pressure spatial atomic layer deposition/chemical vapor deposition (AP-SALD/SCVD) system, which employs a close-proximity reactor-head configuration, as shown in Figure 1c,d[24], [33]. Trimethylaluminum (TMA) and distilled water were used as metal and oxygen precursors, respectively. Ammonium hydroxide (NH₄OH) solution (28% ammonia (NH₃) in water) was used as an oxidant to deposit nitrogen-doped AlO_x thin films. Vapors were generated by bubbling nitrogen gas through the chemicals and combining the vapors with a carrier line of nitrogen gas (see Experimental Methods for full details). The

nitrogen doping was controlled by varying the NH_4OH bubbling rate between 25 and 100 SCCM, as shown in Table 1. Since the process occurs in open air, oxygen and water vapor are always present as oxidants. Hence, varying the NH_4OH bubbling rate alters the relative concentrations of NH_3 and oxidant to which the substrate is exposed. The substrate was placed on a heated substrate stage set to 130 °C and positioned underneath the reactor head with a vertical separation of 100 μm . The heated stage was oscillated back and forth at the speed of 50 mm/s to expose the substrate to the alternating precursor flows and deposit films with nanoscale thickness control.

Table 1. Compositions of AlO_x and N-AlO_x thin films, as determined by x-ray photoelectron spectroscopy.

Samples	AP-SALD deposition conditions			Film Composition				
	Water bubbling rate (SCCM)	NH_4OH bubbling rate (SCCM)	Oxidant Carrier gas flow rate (SCCM)	N at%	Al at%	O at%	O/Al	C at%
AlO_x	100	0	150	-	24.89	45.17	1.81	29.93
0.08N- AlO_x	0	25	225	0.08	27.22	44.23	1.62	25.72
0.28N- AlO_x	0	50	200	0.28	32.17	41.83	1.30	25.71
0.57N- AlO_x	0	75	175	0.57	33.16	42.53	1.28	23.73
0.68N- AlO_x	0	100	150	0.68	34.26	43.55	1.27	21.50

2.1. Thin film characterization

X-ray photoelectron spectroscopy (XPS) was performed to determine the chemical composition of AlO_x and N-AlO_x thin films deposited using 120 oscillations in 6 minutes (Table 1). The atomic percentage of nitrogen was found to vary between 0.08% and 0.68% for the doped films and names were assigned according to the different doping levels (e.g, 0.68N- AlO_x for the film with 0.68% nitrogen). The relatively low atomic percentages of nitrogen are expected because breaking of Al-O bonds by nitrogen atoms is not thermodynamically favored. Furthermore, the low-temperature and atmospheric-processing conditions are expected to limit the incorporation of nitrogen, as compared to vacuum-based deposition techniques[34]. The O/Al ratio is seen to vary from 1.81 to 1.27 in Table 1 as the nitrogen-doping increases. The incorporation of nitrogen into the alumina lattice can alter the surface chemistry and result in a decrease in

the surface-oxygen concentration. Nitrogen can occupy oxygen vacancies or form new nitrogen-aluminum bonds, leading to the removal of oxygen atoms from the surface. Moreover, N doping was reported to suppress formation of oxygen-related defects, such as non-lattice oxygen and OH- groups, in AlO_x , which also reduces the surface-oxygen concentration[29]. The carbon content ranged from approximately 21% to 30% and is attributable to adventitious carbon on the film surface and residual carbon from the TMA precursor.

The O1s and Al2p XPS spectra of the 60-nm-thick AlO_x and 0.28N- AlO_x are shown in Figure 2a,b and d,e. The O1s and Al2p XPS spectra of the other N- AlO_x films are provided in Figure S1 of the Supporting Information and are similar to those of the 0.28N- AlO_x film. Deconvolution of the O1s peaks by Gaussian fitting in Figure 2a,b revealed peaks at 530.9 and 532.2 eV, which correspond to lattice oxygen (i.e., Al-O) and non-lattice and surface oxygen (e.g., OH-, hydroxyl groups), respectively[34], [35]. The fraction of the O1s signal attributable to these two components was calculated for the AlO_x and N- AlO_x films based on the area under the corresponding XPS peaks and is shown in Figure 2c. The O-H signal can be attributed in part to the water precursor used, consistent with previous reports[26], [34]. It is known that thermal deposition at low temperatures using H_2O as the oxidant usually results in a large amount of OH-groups on the film surface, due to incomplete reaction of the precursors and the high desorption energy of water at low temperatures[36], [37]. Notably, the Al-O fraction of the O1s peak is higher for all the N- AlO_x films than for the AlO_x film in Figure 2c and increases with the amount of nitrogen doping. Deconvolution of the Al2p spectra is shown in Figure 2d,e. The main peak with a binding energy of 74.3 eV corresponds to the Al-O bond, consistent with the 530.9 eV peak in the O1s spectra (Figure 2a,b)[38]. Another peak with higher binding energy (75.5 eV) was observed which could be assigned to the Al-OH bond[39]. For the 0.28N- AlO_x film in Figure 2e, a third peak with small intensity and lower binding energy (73.3 eV) was observed and assigned to the Al-N bond[26], [35]. Figure 2f shows the fraction of the Al2p signal attributable to the Al-O, Al-OH, and Al-N bonds as a function of nitrogen-doping level. An increase in the Al-N signal is observed with increasing doping concentration, as expected. The decrease in the amount of

Al-OH with increased nitrogen doping in Figure 2f is consistent with the decreasing O-H contribution observed for the O1s spectra in Figure 2c.

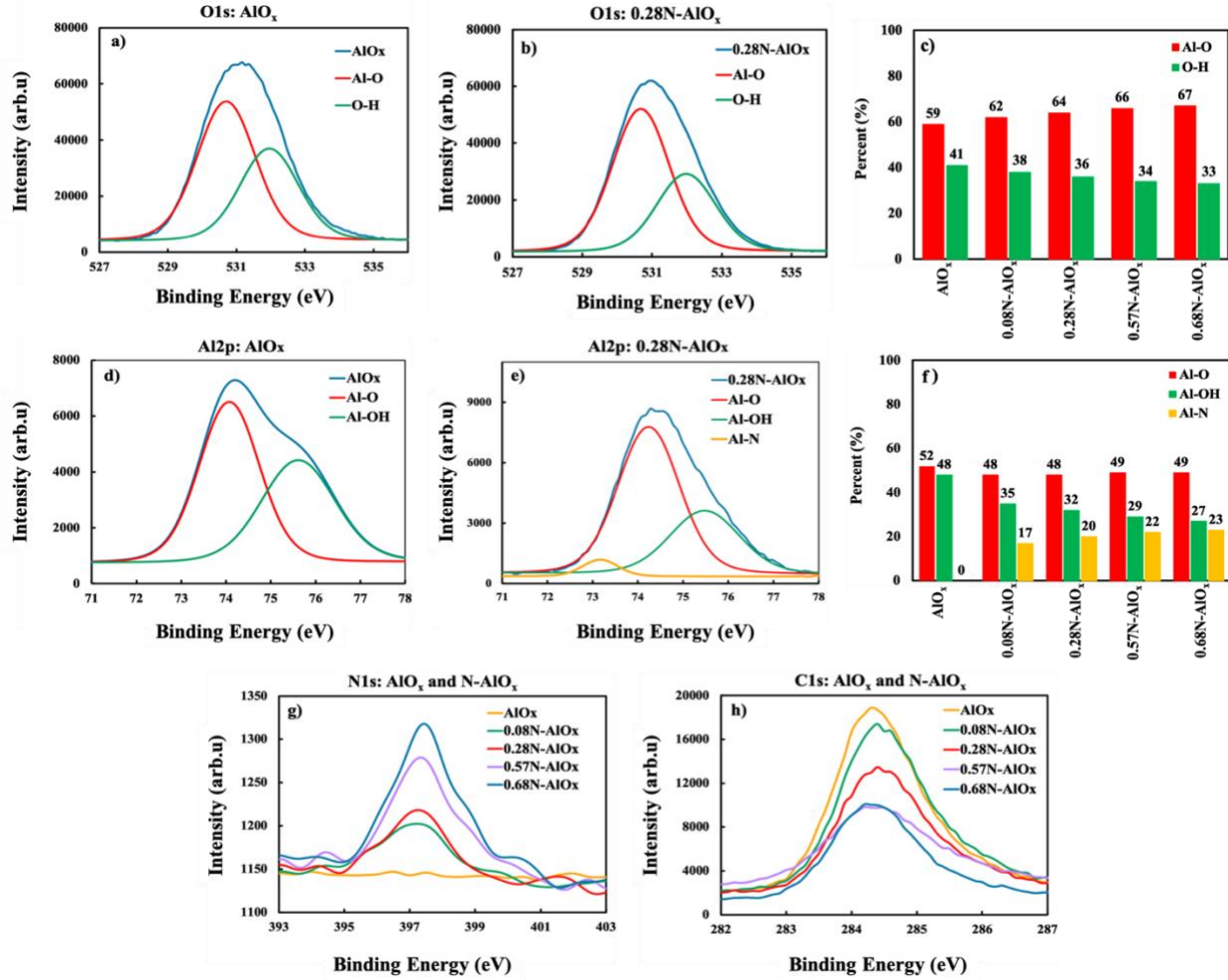


Figure 2. O1s XPS spectra of a) AlO_x and b) 0.28N-AlO_x films. c) The fraction of the O1s XPS signal attributable to Al-O and O-H components for AlO_x and N-AlO_x films. Al2p XPS spectra of d) AlO_x and e) 0.28N-AlO_x films. f) The fraction of the Al2p signal attributable to Al-O, Al-OH, and Al-N in AlO_x and N-AlO_x films. g) N1s and h) C1s XPS spectra of AlO_x and N-AlO_x films.

The N1s spectra in Figure 2g further confirm that nitrogen is incorporated into the N-AlO_x films. The peak located at 397.2 eV is attributed to Al-N bonds [29], [35] and its intensity increased as the NH₄OH bubbling rate was increased from 25 SCCM (0.08N-AlO_x) to 100 SCCM (0.68N-AlO_x). Figure 2h shows the C1s spectra of the films. The intensity of the C1s peak decreases with nitrogen doping, consistent with the carbon content reported in Table 1. The same trend was observed after sputtering the films for 10

seconds to mitigate the effect of adventitious carbon on the film surface (Table S1 of the Supporting Information). The atomic percentage of carbon decreased from 7.9% in AlO_x to 3.1% in a 0.68N- AlO_x film.

Comparing the Gibbs free energy for the reaction of TMA with water and NH_3 using thermodynamic data showed that the reaction of TMA with water is slightly more thermodynamically favorable[40], [41]. However, it is important to note that other factors, such as reaction kinetics can also play a significant role. In general, the reaction kinetics of TMA with water and NH_3 follow a similar pathway, which includes adsorption of the precursor on the substrate, surface reaction, and desorption of by-products. However, the kinetics of this reaction can be affected by the precursor supply and availability of reactive sites on the substrate surface. The higher vapor pressure of NH_3 than H_2O (30 times higher at 20 °C)[29] should result in a higher flux of reactive species. This larger flux of reactive NH_3 species with N-doping is consistent with the increasing Al-N signal and decreasing Al-OH signal (Figure 2f), and is expected to result in more effective removal of the methyl groups[34], consistent with the reduced C1s signal (Figure 2h).

Therefore, the XPS showed that the N-doping suppresses the formation of oxygen-related defects, such as residual hydroxyl groups, and reduced the carbon content, which is expected to improve the compactness of the films[29]. A high carbon concentration is undesirable in gas diffusion barrier films, as the carbon provides a penetration pathway[42]. Similarly, oxygen-related defects, including hydroxyl groups, can provide a permeation pathway in AlO_x [25], [43]. Thus, the N-doping may be expected to improve the barrier properties of the encapsulation layer.

To study the uniformity, compactness and roughness of the AlO_x and N- AlO_x films, ellipsometry, scanning electron microscopy (SEM) and atomic force microscopy (AFM) were conducted. Figure 3a,b shows photographic images of AlO_x and 0.28N- AlO_x films deposited on a silicon substrate using 120 substrate oscillations. Both films are uniform and the same uniformity was observed for all doping levels (Figure S2, Supporting information). SEM images of the AlO_x and 0.28N- AlO_x films in Figure 3c,d confirmed the pinhole- and crack-free nature of the thin films, indicating a high uniformity well-suited for TFE. SEM images for all doping levels are shown in Figure S2 and show similarly high uniformity. Figure

3c shows some randomly distributed particles on the surface of the AlO_x thin film, which could result from gradual powder formation on the underside of the AP-SALD reactor head, indicating that some mixing of the precursors in the gas phase may have occurred, which is discussed further below. Ellipsometry thickness maps are presented in Figure 3e,f for the AlO_x and 0.28N-AlO_x films. The variation of thickness is very low over areas of approximately $30 \times 30 \text{ mm}^2$.

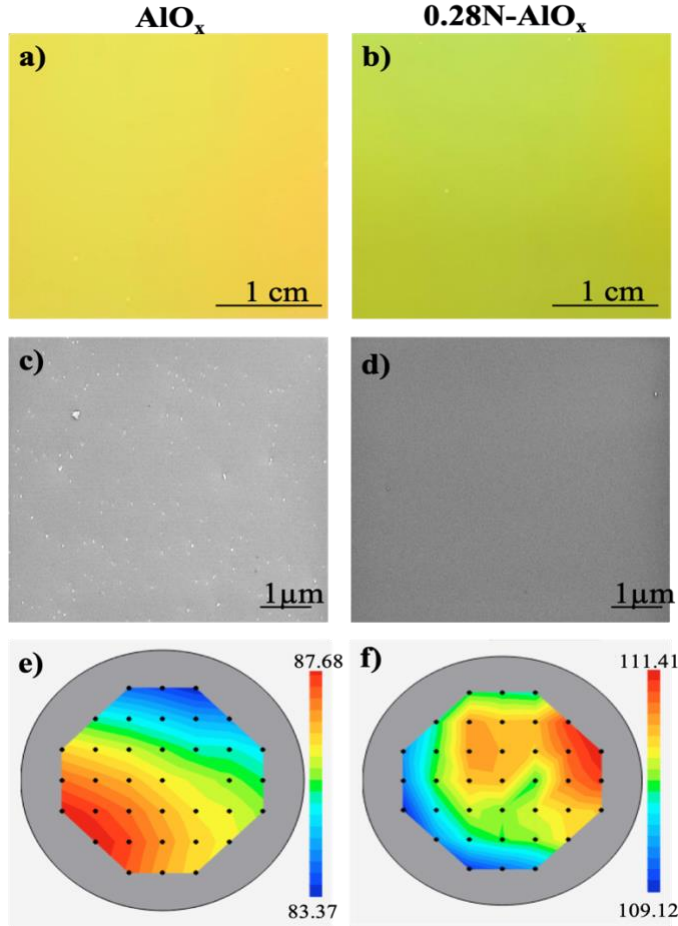


Figure 3. Uniform, pinhole-free AP-SALD films deposited on Si wafers using 120 substrate oscillations. Photographic images of a) AlO_x and b) 0.28N-AlO_x . SEM images of c) AlO_x and d) 0.28N-AlO_x . Ellipsometry thickness distribution maps (in nm) of e) AlO_x and f) 0.28N-AlO_x over a $30 \times 30 \text{ mm}^2$ area.

By plotting the film thickness as a function of the number of AP-SALD oscillations (Figure 4a), the growth per cycle (GPC) was obtained for each doping level. One AP-SALD oscillation is equivalent to two conventional-ALD precursor-reactant cycles as the substrate oscillates back and forth under the reactor. Linear trends are observed for all doping levels, indicating a constant GPC. A growth of 0.66 nm/oscillation

is determined for pristine AlO_x , which is equivalent to 0.33 nm/cycle. GPCs of 0.11-0.14 nm/cycle are typically reported in literature for alumina films grown by spatial ALD using similar process conditions[44], [45]. The higher GPCs observed here suggest that atmospheric-pressure spatial chemical vapor deposition (AP-SCVD) likely occurred due to some precursor mixing in the gas phase, i.e., the gas flow rates and reactor-substrate spacing were such that the TMA and water/ NH_4OH precursors were not perfectly isolated by the inert N_2 gas. AP-SCVD conditions are attractive for device manufacturing, since higher deposition rates are obtained, while still producing smooth, pinhole-free, conformal films with thicknesses proportional to the number of cycles[46]. It was previously shown that AP-SCVD deposition was obtained using a reactor-substrate spacing of 50 μm and different flow rates for the metal and oxidant precursors[47]. In this work, an even larger reactor-substrate spacing of 100 μm was used to ensure some mixing of the precursors in the gas phase above the substrate. The GPC of 0.33 nm/cycle for the undoped AlO_x films indicates that approximately 2 to 3 monolayers were deposited each cycle.

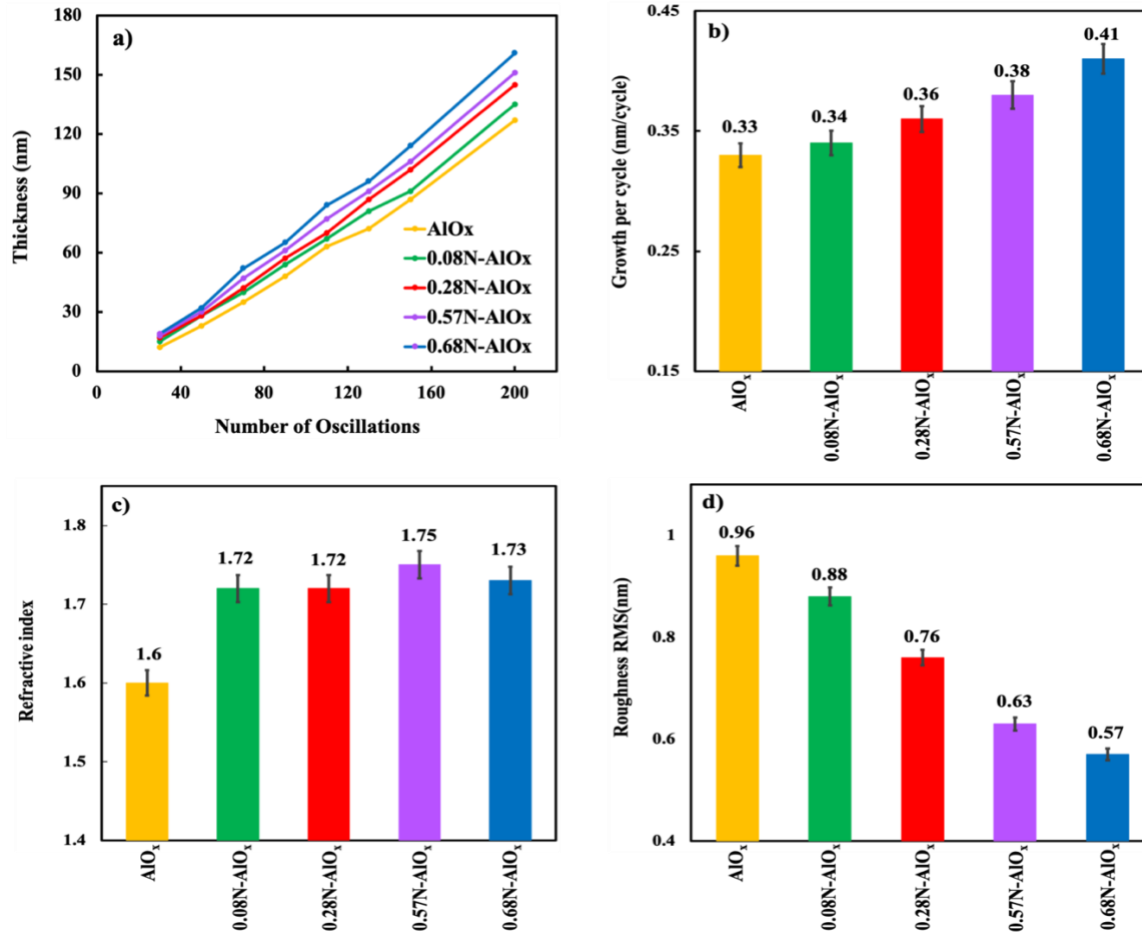


Figure 4. a) Film thickness as a function of the number of AP-SALD oscillations for different nitrogen-doping levels on silicon substrates. b) GPCs, c) refractive indices, and d) surface roughness for different nitrogen-doping levels. (Refractive indices and surface roughness were measured for 60-nm-thick films deposited on silicon substrates.)

The GPC was observed to increase with nitrogen doping, with values between approximately 0.34–0.41 nm/cycle for different N-AlO_x compositions, as shown in Figure 4b. This is consistent with the XPS results that indicated that the higher vapor pressure of NH₄OH facilitates a greater flux of reactive species and more complete surface reactions. Furthermore, the nitride ion (1.40 Å) is 0.08 Å larger than the oxide ion (1.32 Å) such that N-AlO_x films are expected to be thicker than AlO_x films for otherwise identical growth conditions[48].

The refractive indices were measured by ellipsometry to be 1.60 for the AlO_x and 1.72–1.75 for the N-AlO_x, as shown in Figure 4c. These matched well with the 1.53–1.78 range reported previously for Al₂O₃[38]. The N-AlO_x thin films showed higher refractive indices than AlO_x, indicating an improved film

compactness/density[49]. This is consistent with the lower OH- and carbon contents of the N-AlO_x films observed by XPS (Figure 2).

Surface roughness is another critical coating characteristic that should be minimized for high-quality encapsulation layers[12]. The roughness of the films with different nitrogen-doping levels is shown in Figure 4d. The surfaces of all the N-AlO_x films were smooth with root-mean square (RMS) roughness between 0.57 nm and 0.88 nm, slightly smaller than that of the AlO_x thin (0.96 nm). A reduction in surface roughness has previously been reported for nitrogen-doped ALD films and is attributed here to the substitution of larger N³⁻ ions for O²⁻ during the deposition and/or reduction of oxygen related defects (such as surface and non-lattice oxygen)[50], [51]. The compact, smooth nature of these films make them good candidates for gas-diffusion barriers[52].

2.2. Water-vapor transmission rate

Water-vapor-transmission rates (WVTRs) are the steady state rates at which water vapor can penetrate through a film. Ultralow WVTRs between 10⁻⁴ and 10⁻⁶ g/(m² day) are required for stable operation of thin film photovoltaic devices[53], but no commercial instrumentation is available to measure ultralow WVTRs. In this study, we employed an optical calcium (Ca) test to evaluate the gas diffusion barrier properties of the AlO_x and N-AlO_x thin films. AlO_x and N-AlO_x films with thicknesses of 60 nm (confirmed by ellipsometry) were deposited directly on top of thermally evaporated Ca films in approximately 4 minutes. A 60 nm thickness was chosen for the TFE layers because a previous study of alumina TFE layers deposited by conventional ALD showed an improvement with thickness up to ~80 nm[54]. Thicker AlO_x layers may be expected to provide slightly better encapsulation; however, practical considerations (deposition time and cost) favor thinner layers for commercialization. Furthermore, it has been demonstrated for ALD films that the improvement in barrier properties with thickness can be sub linear and can show a low thickness dependence[55].

The Ca films were initially metallic and opaque. Then the encapsulated Ca films were exposed to ISOS-D-1 testing conditions[32] (25 °C and 55%RH). Transmission of water through the encapsulation

films resulted in oxidation of the Ca to calcium hydroxide, which made the film transparent. The oxidation/transparency of the Ca films was monitored by photographic imaging to determine the WVTR of the TFE layers using a method reported previously[56] (see Experimental Methods for full details). Notably, since the AlO_x and N- AlO_x TFEs were deposited directly on the Ca film, the photographic imaging can identify the location of defects in the encapsulation layers.

Pictures of the Ca films encapsulated with the AlO_x and 0.28N- AlO_x films are shown in Figure 5. a,b after different testing durations. Pictures of the Ca films encapsulated with the 0.08N- AlO_x , 0.57N- AlO_x and 0.68N- AlO_x films are shown in Figure S3 and show similar trends. A red background was used to allow the oxidation and hence the defects and weak spots in the encapsulation layer to be directly visualized. The images of the Ca film encapsulated with a 60 nm AlO_x TFE in Figure 5. a showed the presence of a few circular spots on the Ca film after 3 h, which are identified as oxidized regions. After 7 h, these circular spots have grown and a few additional new small circular spots are noticeable. These images clearly indicate that these oxidized Ca regions are circular areas that grow radially in size with time. This behavior suggests the existence of some pinhole defects in the AlO_x coating, which are likely caused by particles on the initial Ca film[57]. Particles are expected to mask the underlying Ca film from AlO_x encapsulation and provide a permeation path for water[58], as shown schematically in Figure 6a.

Also, the appearance of new oxidization area may be due to water traveling through hydroxyl defects in the AlO_x TFE[43]. In other words, these defects may be caused by water corrosion of the AlO_x film[59]. Defects caused by water corrosion were described previously in a study of H_2O permeation in Al_2O_3 ALD films of different thicknesses grown at different temperatures[60]. The study proposed that water-vapor permeation does not rely on pinholes in ALD films, which we contend have few, if any, pinholes. Instead, it occurs by H_2O permeating along chains of chemical defect clusters like the OH^- defects shown in Figure 6b[60]. It is likely that these percolation paths did not exist initially at early times and instead were formed progressively with time resulting from H_2O corrosion of the AlO_x film[60]. The circular spots continue to grow and then merge together. After 42 h, the photographic image in Figure 5. a shows nearly complete

oxidation of the Ca film. The reaction of water with Ca metal to form calcium hydroxide ($\text{Ca}(\text{OH})_2$) results in a 27% increase in volume. Calcium hydroxide can also readily react with CO_2 to form calcium carbonate (CaCO_3). This reaction results in a further increase in volume to a total of 31% (aragonite) or 42% (calcite) above the original Ca volume[61]. This expansion may crack the TFE layer and degrade its barrier properties.

As shown in Figure 5. b, the 0.28N- AlO_x TFE layer showed a similar oxidation pattern but at later times, indicating that the permeation rate for water molecules through the 0.28N- AlO_x TFE was lower than for the AlO_x TFE. It was previously reported that the probability that a percolation pathway exists will increase as the OH- defect concentration increases[43]. Our XPS results showed that by introducing N into N- AlO_x , the OH- defect concentration was decreased. Therefore, the N- AlO_x films enter the blooming phase slower than the AlO_x film, indicating lower WVTR values.

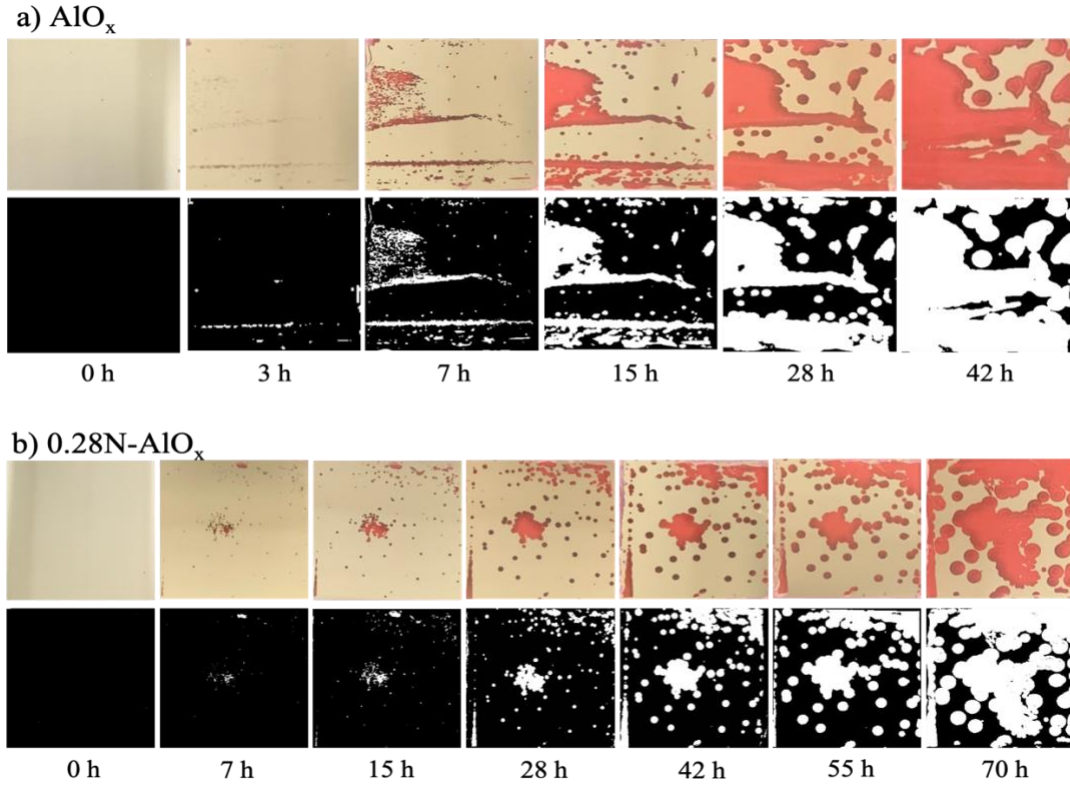


Figure 5. Real pictures and high-contrast black-and-white images of $1.8 \text{ cm} \times 1.8 \text{ cm}$ Ca films encapsulated with a) AlO_x and b) 0.08N- AlO_x barrier films with a thickness of 60 nm after storage in ISOS-D-1 (25°C and 55% RH) conditions for increasing time intervals.

The WVTR values were obtained by analyzing the oxidized area of the Ca films. The images were first converted into black-and-white images (Figure 5. a-b), where the white areas correspond to oxidized Ca. The oxidized surface area was then plotted as a function of time and the slope of the plot ($\Delta A/\Delta t$) was used to determine the WVTR, as shown in Figure S4 (see Experimental Methods for full details)[59]. The WVTR values of the different TFE layers are summarized in Table 2.

Table 2. WVTR values for the 60-nm-thick TFE layers deposited with AP-SALD at ISOS-D-1 (25 °C and 55% RH) and ISOS-D-3 (65 °C and 85% RH).

TFE layer	WVTR ($\text{g m}^{-2} \text{ day}^{-1}$) at ISOS-D-1 (25 °C and 55% RH)	WVTR ($\text{g m}^{-2} \text{ day}^{-1}$) at ISOS-D-3 (65 °C and 85% RH)
AlO_x	6.5×10^{-5}	7.8×10^{-4}
0.08N- AlO_x	2.7×10^{-5}	7.1×10^{-4}
0.28N- AlO_x	1.34×10^{-5}	5.7×10^{-4}
0.57N- AlO_x	3.8×10^{-5}	6.3×10^{-4}
0.68N- AlO_x	4.4×10^{-5}	5.9×10^{-4}

WVTR values on the order of $10^{-5} \text{ g/m}^2/\text{day}$ and $10^{-4} \text{ g/m}^2/\text{day}$ were measured at 25 °C/55% RH and 65 °C/85% RH, respectively. Attempts to compare the reported WVTR values is not easy because most Ca-test studies have not been described in detail. In addition, many of the assumptions associated with oxidation-area methods have not been clearly defined or verified by these studies[53]. Furthermore, the wide range of temperatures and relative humidities used to measure the WVTR values make it impossible to compare WVTR values from Ca-test results. In general, higher temperatures and higher relative humidity will produce larger WVTR values[32]. Nonetheless, the WVTR values in Table 2 indicate that all the films are good barriers to water-vapor permeation. It is important to note that due to the atmospheric nature of the TFE deposition, residual water may be trapped within the substrate or barrier layers, which was previously shown to influence the measured WVTR value in H_2O -based techniques[53]. This implies that the WVTR measurements in Table 2 may slightly overestimate the actual WVTR through the TFE layers. The N- AlO_x TFE layers consistently showed lower WVTR values compared to the undoped AlO_x . It is also

seen in Table 2 that the WVTR values decrease by increasing the N concentration up to 0.28% but that adding more nitrogen (0.57% or 0.68%) increased the WVTR slightly. Water-vapor transmission depends on the nature of defects and pinholes, surface morphology, and chemical interactions between water molecules and surface species[62]. Water molecules arriving on the top surface take energetically favorable permeation pathways including micron-scale defects and smaller tortuous pathways, as shown in Figure 6. The absence of pinholes on the surface of the AlO_x and N-AlO_x , as revealed by SEM in Figure 3c,d, suggests that the water-vapor diffusion through the TFE was not controlled by micron-scale defects. Instead, the AlO_x and N-AlO_x films are expected to contain nanoscale tortuous pathways that are probably of central importance in controlling WVTR values. With this in mind, the lower WVTRs observed for the N-AlO_x films are consistent with the higher refractive indices that indicated these films are more compact than the AlO_x . The interaction of water molecules with surface species is also expected to contribute to the permeation mechanism, especially if the primary transport mechanism is through a percolation permeation pathway. Thus, in order to understand the effect of the nitrogen doping on the WVTR values, we need to consider the role of available interaction sites in N-AlO_x films. The XPS results (Figure 2g) confirmed the incorporation of nitrogen atoms into the alumina lattice, either by replacing oxygen atoms, or by occupying interstitial sites. These nitrogen defects can act as energy wells, which can trap water molecules and delay their permeation through the thin film. However, excess nitrogen may be expected to facilitate water permeation through a percolation pathway by creating a network of interconnected energy wells that allow water vapor to flow through the material more easily. A high concentration of trapping sites may lead to multilayer absorption of water, resulting in surface diffusion or capillary condensation between pore walls (Figure 6c), which increases water vapor permeation and WVTR values[62]. It was shown in other studies that immediately after deposition, the AlO_xN_y surface is more hydrophilic than AlO_x [62], further suggesting that nitrogen may facilitate vapor penetration in the N-AlO_x thin films. Once water molecules reach the tortuous pathways, they can interact strongly with the more hydrophilic pore walls (i.e., those with nitrogen defect sites), causing some water molecules to dissociate and oxygen to become trapped locally. The noninteracting hydrogen species would then need to re-form into water molecules to complete the

permeation process. This may be facilitated by simultaneous permeation of oxygen gas[62]. Thus, while further study of the permeation mechanisms is warranted, the evidence presented here suggests that nitrogen doping of the TFE improves their barrier properties by increasing the compactness of the films (reducing the size and/or number of nanoscale permeation pathways) but that the nitrogen defects may facilitate permeation through these pathways as their concentration increases.

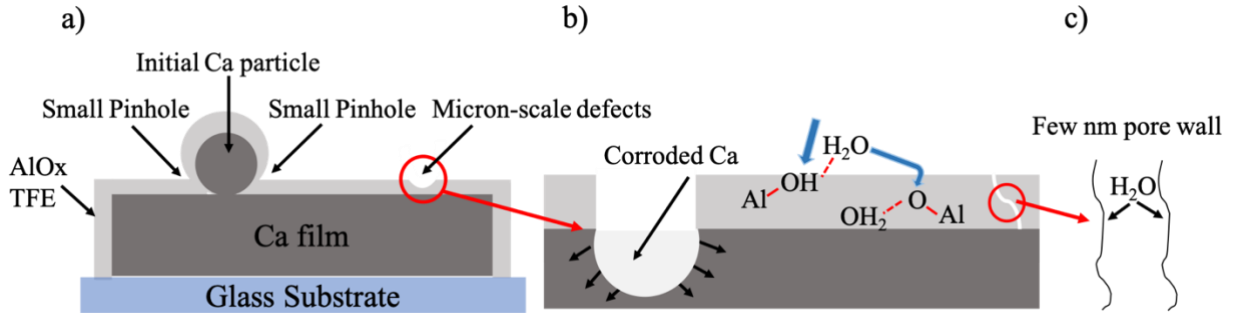


Figure 6. Schematic of a) pinholes and micron scale defects on AlO_x thin film encapsulation layer, b) Ca corrosion and the percolation paths formed progressively with time resulting from H_2O permeating along chains of chemical defect clusters like OH^- defects, and c) surface diffusion of water through pore walls.

2.3. Perovskite solar cell characterization

To assess whether deposition of the TFE layers causes any damage to the light-absorbing perovskite layer, a 60-nm 0.28N- AlO_x TFE layer was deposited directly on a 200-nm formamidinium methylammonium lead iodide ($\text{FA}_{0.92}\text{MA}_{0.08}\text{PbI}_3$) perovskite film using 80 AP-SALD oscillations in only 4 minutes. Ellipsometry was used to ensure the 60-nm thickness. Figure 7a shows the XRD patterns of the perovskite film before and after deposition of the 0.28N- AlO_x TFE layer. The pattern is unchanged, demonstrating that negligible change occurs to the perovskite during the rapid deposition of the TFE layer at 130 °C. Typical peaks at 14.10°, 23.47°, 28.42°, and 30.89° corresponding to the (110), (202), (220), and (222) planes of the tetragonal perovskite phase are present in both cases[63]. The positions of the peaks are consistent before and after the deposition of the 0.28N- AlO_x TFE layer, indicating that no significant structural alterations occur in the perovskite film. No impurity phases, neither pure PbI_2 nor FAI tetragonal phase are detected, indicating a high level of phase purity.

To examine whether the AP-SALD/SCVD process influences the PSC performance, 60-nm-thick 0.28N-AlO_x TFE layers were then deposited on PSCs using 80 AP-SALD oscillations in 4 minutes. In order to identify any effect of the PSC configuration on the performance of the TFE layers, PSCs with 2 different structures were fabricated: a n-i-p structure consisting of FTO/SnO₂/FA_{0.92}MA_{0.08}PbI₃/Spiro-OMeTAD/Ag, as well as a p-i-n structure consisting of FTO/PTAA/FA_{0.92}MA_{0.08}PbI₃/PC₆₁BM/BCP/Ag, as illustrated in Figure 1a,b.

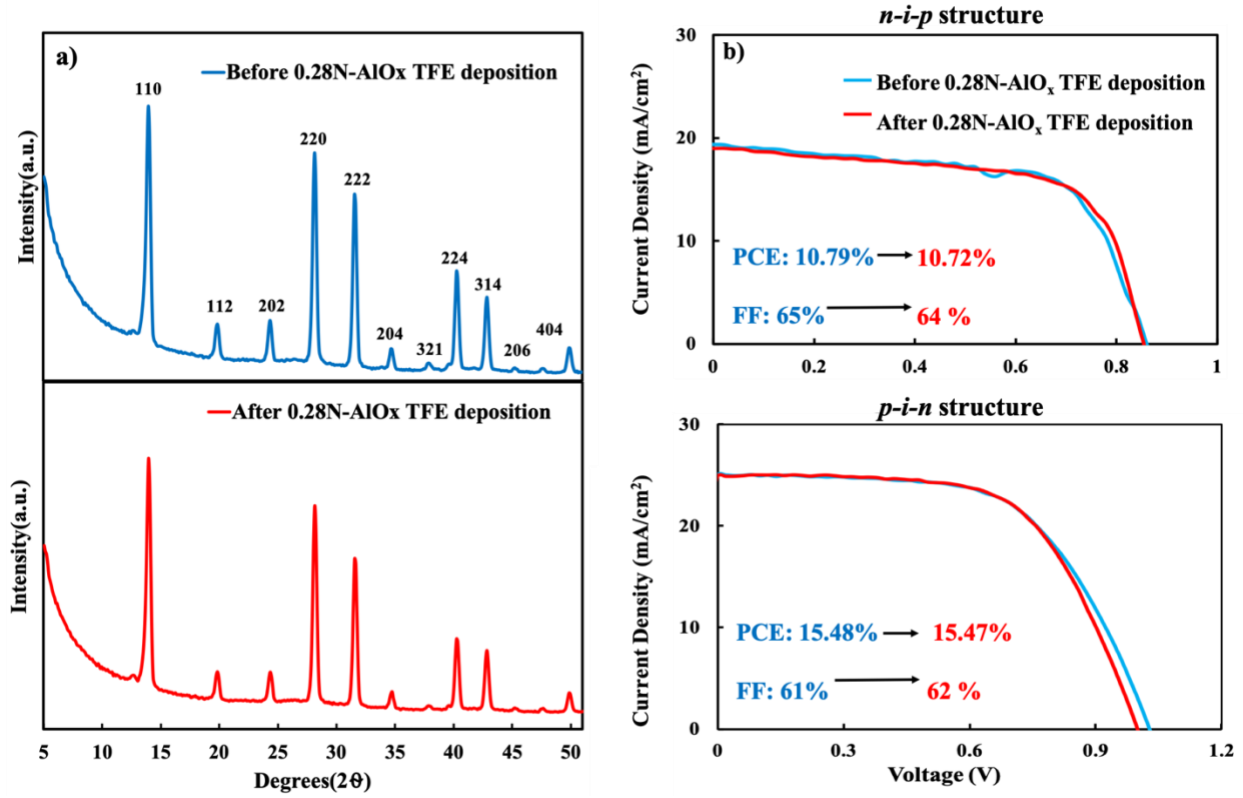


Figure 7. a) X-ray diffraction (XRD) spectra of a perovskite layer, b) J-V characteristics of n-i-p structure and p-i-n structure perovskite solar cells before and after deposition of 60 nm 0.28N-AlO_x TFE layer with SALD.

The current-density/voltage (J-V) curves measured under simulated solar illumination in air for the p-i-n and n-i-p solar cells before and after deposition of the 60-nm 0.28N-AlO_x TFE layers are shown in Figure 7b. The power conversion efficiencies (PCE) and fill factors (FF) of the PSCs are listed inside the Figure. The J-V curves are nearly identical, indicating that the deposition of the TFE layer had no obvious effect on the performance of the solar cells. Even the n-i-p PSC with Spiro-OMeTAD exhibited no

degradation during the AP-SALD/SCVD process at 130 °C. The $\text{FA}_{0.92}\text{MA}_{0.08}\text{PbI}_3$ perovskite layer used in this study is expected to be unstable above approximately 150 °C[63] and most PSCs suffer from thermal stress at high temperatures due to the poor thermal stability of the organic small-molecule-based hole-transporting materials, including Spiro-OMeTAD and additives[64]. Spiro-OMeTAD has shown a low thermal stability above 85 °C due to a large drop in the glass transition temperature (T_g), which causes severe recrystallization[65]. Hence the slow deposition rate of conventional ALD has limited its use for the deposition of TFE on PSCs due to the need for prolonged heating at ALD reaction temperatures. In contrast, the much shorter AP-SCVD times used in this work allow higher deposition temperatures (e.g., 130 °C), which lead to dense, conformal and uniform oxide films[17].

2.4. Stability tests for perovskite solar cells

To study the performance of the TFE layers developed in this work, the PSC performance was then monitored over extended periods under different environmental test conditions. n-i-p and p-i-n PSCs were coated with 60 nm of AlO_x or N- AlO_x with different nitrogen concentrations, as illustrated in Figure 1a,b. The encapsulated cells and control cells without an encapsulation layer were exposed to accelerated test conditions ISOS-D-1 (dark, 25 °C, 55%RH) and ISOS-D-3 (dark, 65 °C, 85% RH)[32] and the PCEs of the cells were monitored. At least two PSCs were tested in each condition to ensure data reproducibility. Figure 8a,b presents the normalized PCEs as a function of time for the two device architectures under ISOS-D-3 (65 °C, 85% RH) conditions. Similar figures for the ISOS-D-1 conditions are included in the supporting information (Figure S5), and the results are summarized in terms of T_{80} values in Figure 8c,d.

It can be seen in Figure 8a,b that the stability of the devices increased markedly by applying an encapsulation layer. For example, the n-i-p device without encapsulation in Figure 8a degraded to 80% of its original efficiency in 35 h (T_{80} = 35 h)[32], which is attributed to the rapid permeation of moisture into the devices leading to accelerated decomposition of the perovskite layer and degradation of its interface with charge transport layers[66]. In contrast, all encapsulated n-i-p PSCs in Figure 8a displayed T_{80} values greater than 98 h. Similarly, the p-i-n PSCs in Figure 8b showed a T_{80} = 53 h without encapsulation and T_{80}

values greater than 180 h with encapsulation. The AlO_x and N-AlO_x TFE layers act as a first barrier, slowing down the ingress of H_2O and oxygen from the ambient and the egress of volatile species from the device. This blocking of decomposed volatile components has been reported to cause saturation of the gaseous decomposed components inside the cells, which hinders the decomposition process[5].

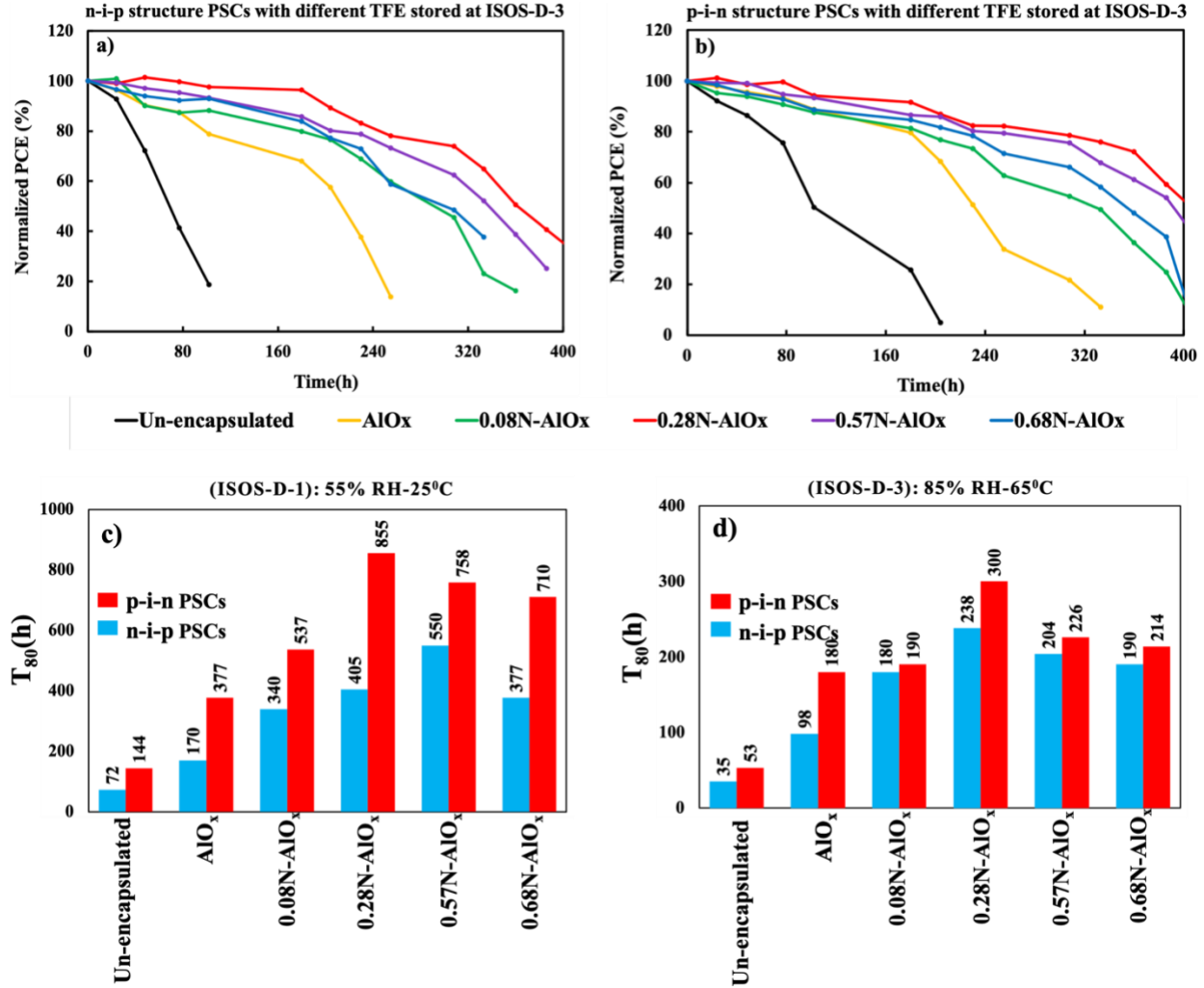


Figure 8. Normalized PCE versus time for a) n-i-p and b) p-i-n PSCs encapsulated with different thin film encapsulation layers kept at ISOS-D-3 conditions (65 °C and 85%RH). The PCE values were normalized to their initial PCE value. The T_{80} values of the p-i-n and n-i-p PSCs with different thin film encapsulation layers in c) ISOS-D-1 and d) ISOS-D-3 conditions.

Figure 8c and d show the T_{80} values of the p-i-n (red) and n-i-p (blue) PSCs with the various TFE layers for the ISOS-D-1 and ISOS-D-3 conditions, respectively. As expected, the T_{80} values are higher for the ISOS-D-1 conditions (25 °C and 55%RH) than the ISOS-D-3 conditions (65 °C and 58%RH), as the

diffusivity of water vapour through the encapsulation obeys Fick's law and hence is related to the humidity level and temperature. It is observed that the devices with N- AlO_x TFE showed better stability than those with AlO_x TFE, consistent with the lower WVTR values. The p-i-n PSCs with AlO_x TFE, for example, showed T_{80} values of 377 hrs and 180 hrs in ISOS-D-1 and ISOS-D-3 conditions, respectively, whereas the p-i-n PSCs with the 0.28N- AlO_x TFE layers showed T_{80} values of 855 hrs (ISOS-D-1) and 300 hrs (ISOS-D-3). It is seen in Figure 8c,d that the optimal nitrogen concentration is around 0.28%, consistent with the lowest WVTR values reported in Table 2. The N-doping improves the film compactness and the nitrogen defects may trap water molecules and hinder their diffusion; however, higher nitrogen concentrations facilitate permeation, possibly due to multilayer adsorption of water driven by the high concentration of trapping sites[62]. Therefore, the key requirement to produce a better barrier layer is to increase the density and compactness of the coatings as much as possible and reduce the number of water diffusion pathways by optimizing the N concentration.

It is seen in Figure 8c,d that the p-i-n devices (red) are more stable than the n-i-p devices (blue), regardless of the encapsulation. The T_{80} value is almost 2 and 1.5 times longer for the un-encapsulated p-i-n PSCs stored in ISOS-D-1 and ISOS-D-3 conditions, respectively. The perovskite's rate of degradation is strongly linked to the humidity level as well as the type of layer placed on top of the perovskite. It was pointed out by several studies that the hole-transport layer (in n-i-p structure) and electron-transport layer (in p-i-n structure) are able to hinder moisture ingress toward the perovskite layers underneath[67]. In our study, doped Spiro-MeOTAD (hole-transport layer) and $\text{PC}_{61}\text{BM}/\text{PCB}$ (electron-transport layer) covered the perovskite in the n-i-p and p-i-n structures, respectively. Stability issues in n-i-p PSCs are frequently linked to the poor stability of the Spiro-MeOTAD, which may suffer from cracking during the fabrication process[68]. This would expose the perovskite and device degradation may be accelerated. It was also shown that exposure to moisture and applying thermal stress made pinholes in the Spiro-OMeTAD layer, which could promote moisture ingress into the perovskite layer and lead to rapid degradation[69]. Here, the generally hydrophobic nature of the top electron-transport layer (PC_{61}BM) would seem to be beneficial

for preventing moisture ingress, even under the accelerated conditions of ISOS-D-3 (65 °C and 85%RH), as shown in Figure 8d.

A summary of previous reports on TFEs can be found in Table S2, highlighting the perovskite device structure, encapsulation materials and the stability performance. Although it is difficult to directly compare available results due to the inconsistency in testing conditions used and parameters reported, it is seen that the WVTR values measured for the N-doped TFE (e.g., 1.34×10^{-5} g/m²/day in ISOS-D-1 conditions for the 0.28N-AlO_x) are similar to or less than previous reports and the T₈₀ values (e.g., 855 hr in ISOS-D-1 conditions for the 0.28N-AlO_x) are also very promising. Notably, most of these previous reports are for TFE layers deposited using prohibitively slow vacuum ALD processes, whereas we used a roll-to-roll-compatible atmospheric process that deposited the films in a fraction of the time. Our study clearly confirmed that the AP-SALD AlO_x and N-AlO_x films are promising single-layer TFE for preventing moisture ingress and improving the stability of PSCs. In addition to providing stability-enhancing TFE layers for both n-i-p and p-i-n PSCs, AP-SALD/SCVD layers, including N-AlO_x and SnO_x, among others, also have the potential to be used as efficiency- and stability-enhancing interfacial layers [70].

3. Conclusion

In this work, we used atmospheric-pressure spatial CVD to produce uniform AlO_x and N-AlO_x thin films with different nitrogen concentrations for encapsulation of PSCs. The thin-film-growth rate was slightly higher for the N-AlO_x films than the AlO_x films, which was attributed to an expected greater supply of the more volatile NH₄OH precursor and the larger nitrogen ions. The GPCs were observed to be around 0.33 nm/cycle for the AlO_x and 0.34 to 0.41 nm/cycle for the N-AlO_x films, providing precise control over the film thickness. The N-AlO_x films showed higher refractive indexes than the AlO_x films, indicating an increased film density, which was again attributed to more complete surface reactions facilitated by the volatile NH₄OH. Introducing nitrogen reduced the RMS roughness to below 0.88 nm, compared with 0.96 nm for the AlO_x film. XPS showed that the nitrogen bonded to the aluminum and N-doping suppressed the formation of carbon- and oxygen-related defects, such as residual hydroxyl groups.

Both the AlO_x and N-AlO_x films showed outstanding barrier properties with WVTR values on the order of 10^{-5} and $10^{-4} \text{ g m}^{-2} \text{ d}^{-1}$ at accelerated conditions of $25^\circ\text{C}/55\% \text{ RH}$ and $65^\circ\text{C}/85\% \text{ RH}$, respectively. The N-AlO_x films showed lower WVTR values, which was attributed to the higher film density, trapping of water molecules by N-rich defect sites, and the lower concentration of OH- defects on the N-AlO_x film surface, as water-vapor transmission through thin films can occur by permeation of H_2O molecules along chains of chemical defect clusters like hydroxyl groups. The lowest WVTR was observed for the N-AlO_x films with 0.28% nitrogen; higher concentrations of nitrogen defects may provide permeation pathways for water transmission.

The rapid nature of the AP-SCVD technique enabled deposition of the TFE without damage to the heat-sensitive materials used for PSC fabrication (i.e., perovskite and Spiro-OMeTAD). Fabricated p-i-n PSCs were slightly more stable than n-i-p devices, which was attributed to the poor stability of Spiro-OMeTAD in the n-i-p PSCs and the hydrophobic nature of PCBM in the p-i-n PSCs. The TFE layers significantly improved the device stability by preventing moisture permeation; a p-i-n PSC encapsulated with a 0.28N- AlO_x TFE layer maintained 80% of its initial PCE after exposure to 25°C and 55% RH for 855 hours, whereas an equivalent unencapsulated device was only stable for 144 hrs. Again, the largest stability enhancements were observed for the N-AlO_x TFE layers with 0.28% nitrogen, consistent with the WVTR measurements.

Thus, the AP-SCVD AlO_x and N-AlO_x thin films presented here provide a promising new PSC-encapsulation route, not only for lab-scale studies but also for high-throughput commercialization efforts. Additional research is warranted to further optimize the composition and properties of these TFE layers, further elucidate their transmission mechanisms, and apply them to different PSC architectures.

4. Experimental

4.1. Deposition of AlO_x and N-AlO_x thin films

Nitrogen was used as a carrier gas to deliver the precursor vapors from liquid sources to the AP-SALD/SCVD reactor head, which has parallel gas outlet channels along its bottom surface. The TMA

bubbler flow rate was set to 20 SCCM, with a nitrogen carrier flow rate of 105 SCCM. For undoped AlO_x , the water bubbler was set to 100 SCCM, with a nitrogen carrier flow rate of 150 SCCM. For N- AlO_x , the flow through the NH_4OH (28% NH_3 in water) bubbler was set to 25, 50, 75 or 100 SCCM, and the corresponding carrier flow to 225, 200, 175 or 150 SCCM respectively, so that the total flow into the reactor was kept constant at 250 SCCM. NH_3 has a higher vapor pressure (10.78 psi) than water (0.27 psi)[71], so it preferentially evaporates, leading to an enrichment of NH_3 in the vapor phase, which facilitates the nitrogen doping. However, doping AlO_x with nitrogen is challenging because the breaking of Al-O bonds by nitrogen atoms is not thermodynamically favored[34]. Thus, a competition exists between the preferential evaporation of NH_3 and the thermodynamic barrier associated with nitrogen atoms breaking Al-O bonds. The NH_4OH solution was replenished frequently to avoid the depletion of NH_3 . The inert nitrogen gas flow rate was set to 750 SCCM, which was divided amongst six outlet channels.

4.2. Ca tests to measure WVTR values

Due to the lack of commercial instruments that can measure ultralow WVTRs, most efforts have relied on the oxidation of metallic Ca films to determine H_2O permeability rates[72]. The oxidized area method was introduced by Kumar et al[56].

To prepare the Ca films, 2.8 cm $\times$ 2.8 cm glass slides were cleaned in an ultrasonic bath with deionized water, acetone, and isopropanol. The blown-dried substrates were transferred into a N_2 glovebox then they were dried using a hotplate at 150 °C for 1 h and cooled down in a petri dish inside the glovebox. Kapton tape was used to attach 3D-printed shadow masks to the glass slides. The masks covered a 5 mm strip on each side of the glass substrate and left a 1.8 $\times$ 1.8 cm² area in the middle section to be coated with a Ca film. A 200-nm Ca film was thermally evaporated in the glovebox with a deposition rate of approximately 2 Å/s and the film thickness was monitored using a quartz crystal sensor. The Ca films were opaque with a mirrorlike appearance.

In order to minimize the exposure to air, the Ca samples were vacuum sealed inside the glovebox and transfer to the AP-SALD system, where the vacuum bag was opened immediately prior to TFE

deposition. The Ca-coated samples were then placed on the AP-SALD stage and encapsulation layers were deposited directly on the Ca film. A 60 nm thickness was chosen for the TFE layers because a previous study to measure the barrier performance showed an improvement with barrier thickness up to 80 nm[54]. Although the ALD and CVD growth mechanism for AlO_x is well understood on most of surfaces, it is reported that metal-oxide deposition on metal surfaces is quite different due to a very slow nucleation process, resulting in a different growth rate[73]. In the case of the Ca surface, a detailed growth mechanism has not been reported yet, but the deposition of all AlO_x thin films on calcium was monitored using ellipsometry to ensure that 60-nm-thick TFE layers were deposited. After the desired TFE thickness was deposited, the AlO_x -coated Ca samples were removed from the AP-SALD system and transferred to a N_2 glove box to seal the edge using epoxy glue. A poor edge seal can allow moisture ingress through the edge and impact the test results and duration[72].

The samples were then placed into an ESPEC SH-222 benchtop environmental chamber and measurements were taken at two conditions: 25 °C and 55% RH in the dark (ISOS-D-1) and 65 °C and 85% RH in the dark (ISOS-D-3). A Nikon D7100 camera was used to monitor the samples visually. In order to take pictures, the samples were briefly removed from the environmental chamber every 15 minutes to 1 h for the duration of the sample test. IMAGEJ software was used to convert color images of the encapsulated Ca films to black and white images. The color images were first converted to gray-scale images. A gray-scale threshold value was then set to produce binary images of black and white pixels. The gray-scale threshold value was determined visually based on a comparison between the colored image and the black-and-white image. Based on this procedure, IMAGEJ was then able to provide an accurate measurement of the white areas that correspond to oxidized Ca film. In some instances, poor resolution and sample lighting led to inaccuracies in the converted photographic images. These errors could be minimized through careful observation, manually removing the reflections from the measured oxidized area and excluding the degradation from the edges from the evaluation.

The WVTR, or permeation rate, P , was determined from the photographic images using[53]:

$$P = n \frac{M(H_2O)}{M(Ca)} \delta \cdot h \cdot \frac{\Delta A}{\Delta t} \quad \text{Equation 1}$$

In Equation 1, n is a stoichiometric coefficient which is 2 for water oxidation, $M(H_2O)=18.015$ g/mol is the molar mass of water and $M(Ca)=40.078$ g/mol is the molar mass of Ca. $\delta=1.54$ g/cm³ is the bulk density of Ca and $h=200$ nm is the height of the Ca metal film. The change in oxide area is represented by ΔA and the time interval, in days, between the photos is Δt . Plotting the oxidized area (A) versus time results in a graph that shows the rate at which the Ca film is oxidized. As an example, a $\Delta A/\Delta t$ graph and calculation steps for one TFE was provided in Figure S4.

4.3. Perovskite solar cell fabrication

4.3.1. n-i-p cell fabrication

Devices were fabricated on fluorine-doped tin oxide (FTO) coated glass (1.6 cm × 1.6 cm, 14Ω/sq). Initially the FTO-coated glass was cleaned sequentially under ultrasonication in detergent, DI water, acetone, ethanol and isopropanol for 30 min for each solvent, and then dried on a hotplate at 150 °C for at least 2 h. Before usage, the cleaned FTO was treated with ultraviolet ozone for 30 min.

An electron-transport layer of tin oxide nanoparticles (2.67% SnO₂, diluted with Milli-Q water) was deposited by spin-coating at 3000 rpm for 30 s and annealed in ambient air at 150 °C for 30 min. The samples were transferred while hot ($T = 150$ °C) to a N₂ glovebox (H₂O and O₂ levels ~1 ppm). The perovskite layer was fabricated by a two-step deposition method and each solution was filtered through 0.45 μm polytetrafluoroethylene syringe filters. First, 1.5 mol L⁻¹ PbI₂ was dissolved in dimethylformamide (DMF)/dimethyl sulfoxide (DMSO) (9:1 by volume) and stirred at 70 °C for 10 h. The warm PbI₂ was spin-coated at 4000 rpm for 20 s, and then a drop of the mixed solution containing FAI: MAI: MACl (90 mg: 9 mg: 9 mg in 1 mL of IPA) was added to the spinning substrate for 30 s. The as-prepared samples were annealed at 150 °C for 8 min, and slowly cooled to room temperature.

To prepare the hole transport layer, 30 μL of 4-*tert*-butyl pyridine, 29 μL of tris(2-(1H-pyrazol-1-yl)-4-*tert* butylpyridine)cobalt(III) tri[bis(trifluoromethane)sulfonimide] (Co-TFSI) (300 mg Co-TFSI in 1 mL

acetonitrile), and 18 μL of bis(trifluoromethane) sulfonimide lithium salt (Li-TFSI) stock solution (520 mg Li-TFSI in 1 mL acetonitrile) were added to 1000 μL of a 72.3 mg Spiro-OMeTAD solution in chlorobenzene. The hole-transport layer was deposited on top of the perovskite layer at a spin rate of 3000 rpm for 30 s. The films were allowed to dry in an open petri dish overnight in the glovebox. Finally, 100-nm-thick Ag top electrodes was deposited by thermal evaporation at a base pressure of 5×10^{-6} torr.

4.3-2. p-i-n cell fabrication

The procedures for cleaning the FTO-coated glass and depositing the perovskite and Ag layers were identical to those of the n-i-p device. After cleaning the FTO-coated glass, a layer of PTAA (2 mg/mL in toluene) was spin-coated onto the cleaned FTO substrates at 5000 rpm for 30 s and the substrates were annealed at 100 °C for 10 min in the glove box. It was noted that to increase the coverage of the perovskite films on the PTAA, the PbI_2 solution was deposited by spin-casting. A layer of PC_{61}BM (20 mg mL^{-1} in chlorobenzene) was spin-coated on the perovskite films at 1500 rpm for 30 s and annealed at 100 °C for 7.5 min. Then a BCP layer (0.75 mg mL^{-1} in IPA) was prepared by spin-coating at 3000 rpm for 30s.

4.4 Characterization

A FilmSense FS-1EX ellipsometer with a wavelength range of 200–1800 nm was used to measure the thicknesses and refractive indexes of the N-AlO_x and AlO_x films, which were modeled using the Cauchy formula.

Surface roughness were measured using a Dimension 3100 AFM. SEM images were captured using a Zeiss Leo 1530 with an acceleration voltage of 5 kV. A VG Scientific ESCALAB 250 XPS system was used to determine the elements present in the prepared thin films using $\text{Al K}\alpha$ X-rays. XRD measurements were performed by grazing incidence X-ray diffraction (GIXRD) using a PANalytical X'Pert Pro MRD diffractometer with $\text{Cu K}\alpha$ radiation.

A Sciencetech UHE-NL-150 Class AAA Solar Simulator was used to conduct the J-V measurements under simulated solar illumination (AM 1.5G). The solar cell area was calculated to be 0.1695 cm^2 , an

irradiance of 100 mW/cm² was set using a NIST-calibrated silicon reference solar cell, and the voltage was swept from 1.1 V to −0.1 V with a sweep rate of 0.02 V/s. To assess the PSC stability under different environmental conditions, the samples were stored in the SH/SU-222 environmental chamber. The performance of the PSCs with different TFE layers were compared to their initial performance measured at T = 0 hrs.

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Supporting Information

Spatial Atomic Layer Deposition of Nitrogen-doped Alumina Thin Films for High-Performance Perovskite Solar Cell Encapsulation

Authors: Hatameh Asgarimoghaddam^a, Qiaoyun Chen^{a,b}, Fan Ye^a, Ahmed Shahin^a, Olivia Alexandra Celeste Marchione^a, Bo Song^b, Kevin Philip Musselman^{a,*}

^a Department of Mechanical and mechatronic Engineering, University of Waterloo, Waterloo, Ontario, Canada

^b Laboratory of Advanced Optoelectronic Materials, Suzhou Key Laboratory of Novel Semiconductor Materials and Devices, Suzhou key Laboratory of Macromolecular Design and Precision Synthesis, College of Chemistry, Chemical Engineering and Materials Science, Soochow University, Suzhou 215123, China

* kevin.musselman@uwaterloo.ca

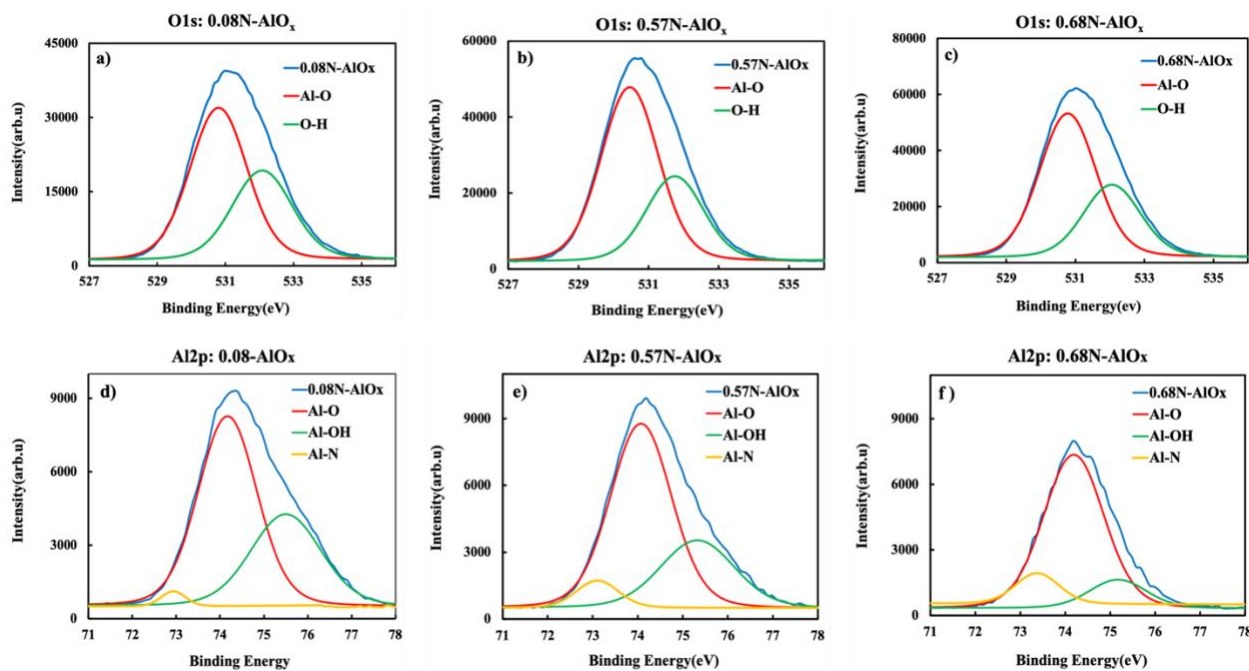


Figure S1. O1s XPS spectra of a) 0.08N-AlO_x, b) 0.57N-AlO_x, and c) 0.68N-AlO_x thin films. Al2p XPS spectra of d) 0.08N-AlO_x, e) 0.57N-AlO_x, and f) 0.68N-AlO_x thin films.

Table S3. Compositions of AlO_x, 0.28N-AlO_x and 0.68N-AlO_x thin films on silicon substrates, as determined by x-ray photoelectron spectroscopy after sputtering for 10 seconds.

Samples	Al at%	O at%	C at%	N at%	O/Al
AlO _x	35.28	56.82	7.91	-	1.61
0.28N-AlO _x	37.38	57.51	4.85	0.26	1.53
0.68N-AlO _x	38.09	58.09	3.11	0.72	1.52

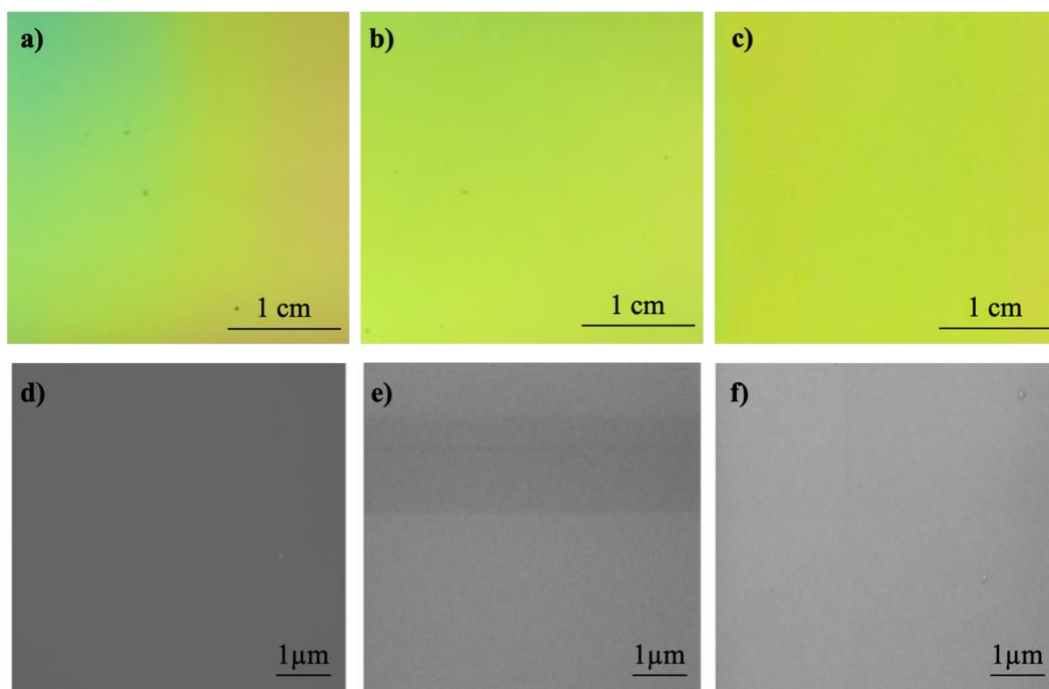
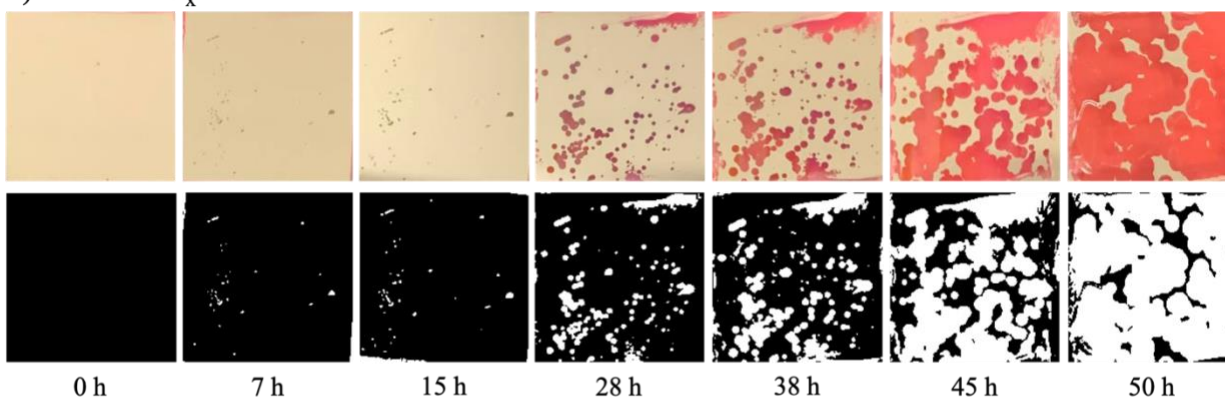
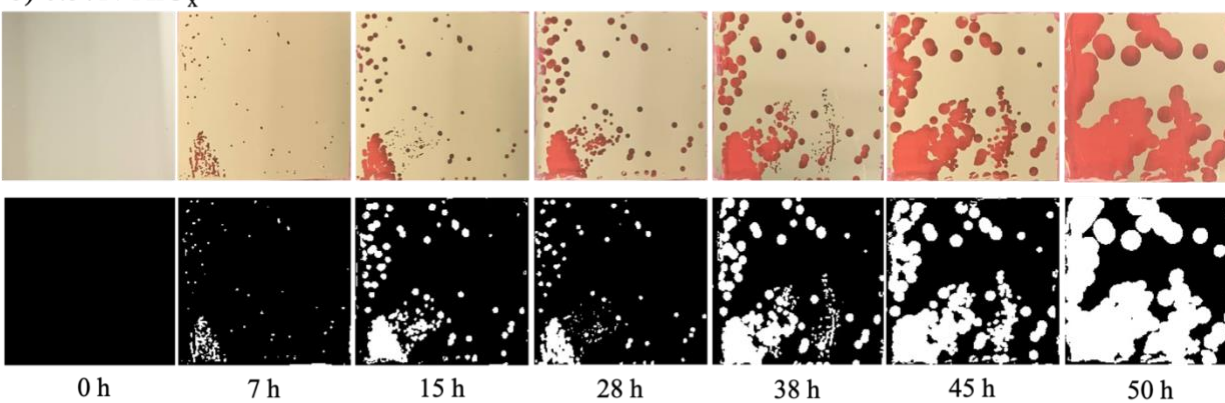


Figure S2. Photographic images of a) 0.08N-AlO_x, b) 0.57N-AlO_x, and c) 0.68N-AlO_x. SEM images of d) 0.08N-AlO_x, e) 0.57N-AlO_x, and f) 0.68N-AlO_x films deposited using 120 AP-SALD oscillations.

a) 0.08N-AlO_x



b) 0.57N-AlO_x



c) 0.68N-AlO_x

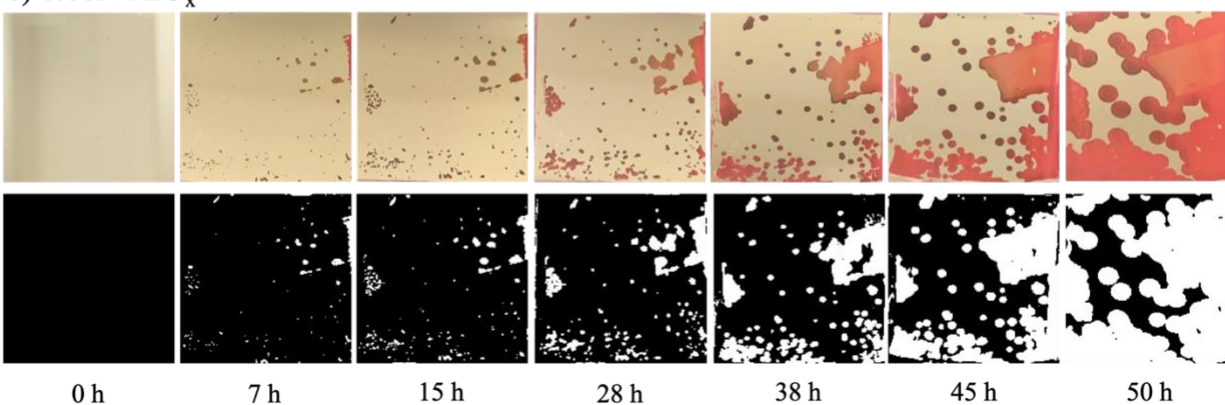


Figure S3. Real pictures and high-contrast black-and-white images of 1.8 cm × 1.8 cm Ca films encapsulated with a) 0.08N-AlO_x, b) 0.57N-AlO_x, and c) 0.68N-AlO_x barrier films with a thickness of 60 nm after storage in ISOS-D-1 (25°C and 55% RH) conditions for increasing time intervals.

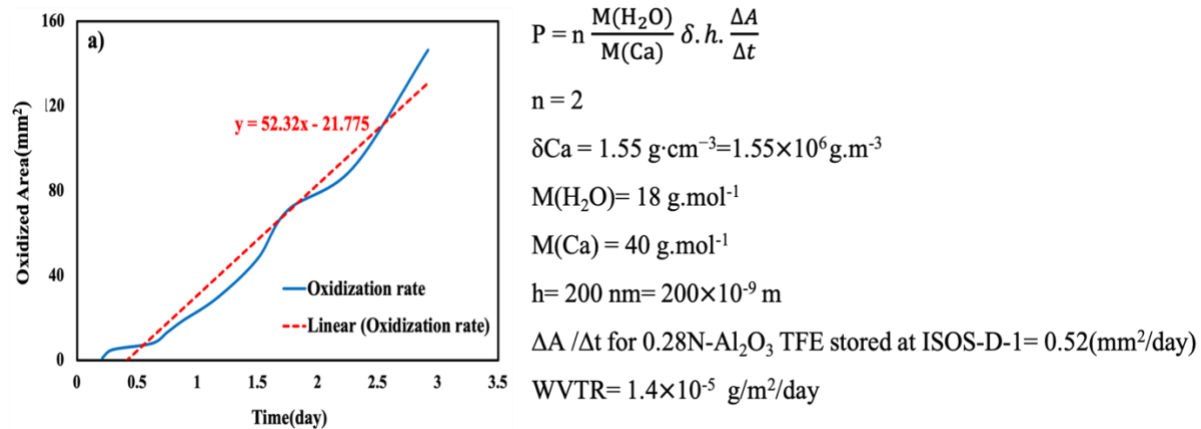


Figure S4. The oxidized surface area as a function of time for a Ca film with a 60-nm 0.28N-AlO_x TFE stored at ISOS-D-1 conditions. The slope of the plot corresponds to the oxidization rate of the Ca ($\Delta A/\Delta t$) needed to calculate WVTR value. A sample WVTR calculation is also provided (see Experimental section for further details).

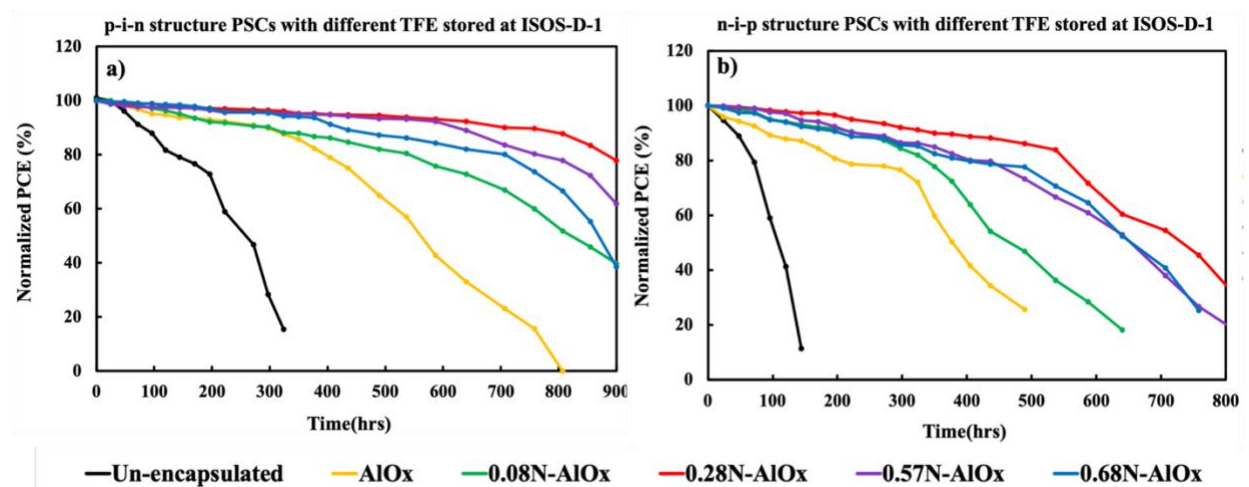


Figure S5. Normalized PCE versus time for a) p-i-n structure and b) n-i-p structure perovskite solar cells encapsulated with different thin film encapsulation layers kept at ISOS-D-1 conditions (25°C and 55%RH). The PCE values were normalized to their initial PCE value.

Table S2. Summary of representative PSCs and their stabilities at different test conditions encapsulated with different materials and methods in literature.

PSC structure	Encapsulation material and method	WVTR ($\text{g m}^{-2} \text{d}^{-1}$)	Long term stability	references
Glass/FTO/TiO ₂ /(FAPbI ₃) _{0.85} (MAPbBr ₃) _{0.15} /HTL/Au	ALD-Al ₂ O ₃ TFE	1.8×10^{-2} (at 45 °C, 100%RH)	25% reduction in PCE after 2250 h at 25 °C and 50% RH in dark	[1]
FTO/c-TiO ₂ /mp-TiO ₂ /MAPbI ₃ /PTAA/Au	ALD-Al ₂ O ₃	9.0×10^{-4}	97% of its initial PCE after 300 h at 50 °C, 50% RH	[2]
ITO/PEDOT:PSS/perovskite/PC ₆₁ BM/ZnO(CBL)/Ag	ALD-Al ₂ O ₃	9.0×10^{-4}	Over 90% of its initial PCE after 10 days at 30 °C, 65% RH	[3]
Glass/ITO/NiO/MAPbI ₃ /PC ₆₁ BM/ALD-TiO ₂ /Ag	ALD-Al ₂ O ₃	9.0×10^{-4}	93% of its initial PCE after 1000 h at 25 °C, 40– 60% RH)	[4]
ITO/NiO/MAPbI ₃ /PC ₆₁ BM/ TiO ₂ /Ag	ALD-Al ₂ O ₃	9.0×10^{-4}	97% of its initial PCE after 1000 h at ambient conditions	[5]
ITO/CH ₃ NH ₃ PbI ₃ /SnO ₂ /spiro-MeOTAD/Ag	PEALD- Al ₂ O ₃ + EG	1.3×10^{-5}	96% of its initial PCE after 2000 h at ambient condition	[6]
FTO/TiO ₂ /MAPbI ₃ / spiro-MeOTAD /Au	Spin coated- Al ₂ O ₃	9.0×10^{-4}	95% of its initial PCE after 350 h at simulated full sunlight	[7]
Glass/FTO/mp-TiO ₂ /bl-TiO ₂ / MAPbI ₃ /PTAA/Au	iCVD- pV ₃ D ₃ /ALD- Al ₂ O ₃ Multilayer TFE	8.5×10^{-5}	97% PCE retained after 300 h shelf at 50 °C and 50% RH.	[8]
Glass/FTO/c-TiO ₂ /MAPbI ₃ / SpiroOMeTAD/MoO ₃ /Al	ALD-SiO ₂ TFE+ UV- curable epoxy glue sheet	10^{-4}	11% PCE loss after 432 h outdoor aging test (ISOS- O-1)	[9]
ITO/NiO/Cs _{0.17} FA _{0.83} Pb(Br _{0.17} I _{0.83}) ₃ /PC ₆₀ BM/ITO/Ag	ALD- SnO ₂ /zinc tin oxide (ZTO)	-	Stable after 1000 h at 85 °C and 85% RH	[10]
ITO/TiO ₂ /C ₆₀ /Perovskite/PTAA/Au	Hexamethyldi siloxane (HMDSO) TFE	-	Maintained 92% initial PCE after 3100 h storage at 85 °C, 25% RH	[11]
IZO-PET/TiO ₂ / MAPbI ₃ /spiro-OMeTAD/Au	Commercial barrier film from Viewbarrie	1×10^{-3}	Maintained initial PCE after 500 h storage in ambient conditions	[12]