Al₂O₃ Underlayer Prepared by Atomic Layer Deposition for Efficient Perovskite Solar Cells

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Perovskite solar cells, as an emergent technology for solar energy conversion, have attracted much attention in the solar cell community by demonstrating impressive enhancement in power conversion efficiencies. However, the high temperature and manually processed TiO₂ underlayer prepared by spray pyrolysis significantly limit the large-scale application and device reproducibility of perovskite solar cells. In this study, low-temperature atomic layer deposition (ALD) is used to prepare a compact Al₂O₃ underlayer for perovskite solar cells. The thickness of the Al₂O₃ layer can be controlled well by adjusting the deposition cycles during the ALD process. An optimal Al₂O₃ layer effectively blocks electron recombination at the perovskite/fluorine-doped tin oxide interface and sufficiently transports electrons through tunneling. Perovskite solar cells fabricated with an Al₂O₃ layer demonstrated a highest efficiency of 16.2% for the sample with 50 ALD cycles (ca. 5 nm), which is a significant improvement over underlayer-free PSCs, which have a maximum efficiency of 11.0%. Detailed characterization confirms that the thickness of the Al₂O₃ underlayer significantly influences the charge transfer resistance and electron recombination processes in the devices. Furthermore, this work shows the feasibility of using a high band-gap semiconductor such as Al₂O₃ as the underlayer in perovskite solar cells and opens up pathways to use ALD Al₂O₃ underlayers for flexible solar cells.

Introduction

Organic–inorganic hybrid perovskite solar cells (PSCs) have in the past few years attracted intense attention in the solar cell community due to the demonstrated high power conversion efficiency (PCE) of above 20%. The high performance of PSCs can mainly be attributed to the excellent properties of the perovskite, such as strong and broad light absorption, long charge-carrier diffusion length, and high ambipolar conductivity. Besides these good material properties, careful perovskite compositional engineering, interfacial materials development, and device configuration optimization are required to create great PSCs. In the standard n-i-p type of PSC configuration (Figure 1a), after the light excitation in the perovskite, the charge separation is driven by the interfacial energy barriers and therefore mainly occurs at the interfaces between the perovskite and the electron transport material (ETM) on one side and between the perovskite and the hole transport material (HTM) on the other. After electron recombination through the ETM and hole conduction through the HTM in the opposite direction, the charges are finally collected at the two conductive contacts, for example, fluorine-doped tin oxide (FTO) at the ETM side and metallic gold at the HTM side. Based on reported energy levels for different components, a diagram representing the charge transfer and transport processes in PSCs is shown in Figure 1b. However, there are also some unfavorable charge recombination processes that occur simultaneously; for example, electrons located in meso TiO₂ and FTO can recombine with holes in the perovskite at the interface. These charge recombination processes could significantly influence the open-circuit voltage \( V_{oc} \) and short-circuit current \( J_{sc} \) and thus the PCE. To avoid the aforementioned recombination processes, an underlayer, also called a compact layer, is a vital component between the current collector FTO and the perovskite layer in obtaining high photon conversion efficiency. However, to date only a few reports have concerned the development of new underlayers for PSCs other than the conventional TiO₂ prepared by spray pyrolysis.

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The underlayer requirements are that it needs to be transparent to visible light, highly compact, and electronically conductive or thin enough to allow for tunneling. In PSCs, the underlayer has been found to show significant influence on the electron recombination kinetics and current-voltage hysteresis. Just as for solid-state dye sensitized solar cells, the compact TiO$_2$ is the most commonly used and efficient underlayer in PSCs. The preparation of the TiO$_2$ underlayer is commonly done by spray pyrolysis of a solution of titanium-containing precursor at above 450 °C. However, the need for high temperature, the use of toxic precursors, and the difficulty in precise control of the preparation parameters significantly limit large-scale application and reproducibility of PSCs. Moreover, underlayers prepared by spray pyrolysis always contain defects such as pinholes, which can be detrimental to the blocking function. In this respect, alternative methods, such as electrochemical deposition, photonic curing, atomic layer deposition (ALD), and sol–gel deposition, have been developed.
for the preparation of TiO₂ layers. However, the thermal post-treatment of TiO₂ underlayers after ALD can cause thermal shrinkage and lead to pinholes. In the case of sol–gel deposition, it is difficult to obtain a pinhole-free underlayer. Other materials have also been explored as underlayers, such as magnesium-doped ZnO, CₓMo₃, and SnO₂. However, most of them had relatively low efficiencies of < 15% in PSCs. Recently, the high band gap semiconductor Al₂O₃ layer has been shown interesting properties as an interfacial interlayer to optimize the charge recombination and thus enhance the solar cell efficiency by 44%. whereas the groups of Snith and Schropp reported that ALD-deposited Al₂O₃ on perovskite showed a great impact on the efficiency, stability, and surface properties of perovskite solar cells.

In this study, based on the above considerations, we have for the first time applied Al₂O₃ grown by ALD, as an underlayer in PSCs. We studied the possibility of electron tunneling through the Al₂O₃ underlayer by investigating the thickness effects on interfacial charge recombination and photovoltaic performance in PSCs. By using an optimal Al₂O₃ underlayer with 50 cycles of deposition in ALD (thickness ≈ 5 nm), the device showed a highest PCE of 16.2% which shows a significant increase by 43% as compared to a PCE of 11.0% for underlayer-free PSCs.

Results and Discussion

Figure 1c and d shows the surface morphology of the bare FTO and 50 cycles (ca. 5 nm) ALD Al₂O₃ coated FTO respectively. The ALD-deposited Al₂O₃ layer homogeneously covers the top of the FTO substrate, as a result of the conformity of the ALD process. Further evidence of this can be found in the uniform spatial distributions of Sn and Al (Figure 1e and f, respectively). This is promising, as the Al₂O₃ underlayer should preferably be very compact without pinholes to inhibit the electron recombination at the FTO/perovskite interface and to obtain high-performance PSCs. To investigate the influence of the Al₂O₃ underlayer thickness in the devices, a series of Al₂O₃ films were deposited with an increasing amount of cycles (20–100 cycles). In this study we varied the amount of cycles between 0 and 100 to prepare films with thicknesses from 0 to 10 nm (Figure 1g). The thickness of the Al₂O₃ is measured with an ellipsometer. The deposition rate of Al₂O₃ by ALD is around 1 Å per cycle. The refractive indices of the FTO/Al₂O₃ films are very similar (1.6–1.7). To study the optical properties of the deposited Al₂O₃ films, the transmittance of the FTO/Al₂O₃ films were measured (Figure 1h). However, thick Al₂O₃ layers, even up to 10 nm, showed little effect on the optical properties of the films.

The quality of the Al₂O₃ underlayers obtained by ALD, in terms of their compactness or electronic conductance, was evaluated electrochemically by using K₃[Fe(CN)₆] as a model redox probe. This method can provide useful information about the quality (compactness) of the underlayers and has been used to study the blocking property of the underlayers for solar cells. Cyclic voltammetry measurements were performed by using a three-electrode setup with FTO/Al₂O₃ (different thicknesses) as the working electrode, Ag/AgCl as the reference electrode, and stainless steel as the counter electrode. The corresponding current flow was recorded when applying different bias potentials on the working electrode (Figure 2a). The inset in Figure 2a shows the current density–voltage (J–V) curve when bare FTO was used as the working electrode; due to the high conductivity of the FTO substrate a typical oxidation/reduction curve is observed with high current density. In contrast, after deposition of the Al₂O₃ layer on FTO glass, the oxidation–reduction peak disappears and instead a monotonously increasing slope is seen in the J–V curve, along with a lowered current density. This confirms that the Al₂O₃ layer on FTO introduces a high electronic resistance that strongly inhibits the charge transfer between the working electrode and the redox species in the solution. Specifically, the current density is significantly decreased with increasing Al₂O₃ thickness from 20 to 100 cycles (Figure 2a); for example, at 0.4 V versus Ag/AgCl the current density is around 20 µA cm⁻² for FTO/Al₂O₃ (50 cycles), which is 20 times lower than that for bare FTO (400 µA cm⁻²). These results indicate that the electron-transfer blocking effect of the ALD Al₂O₃ layer in PSCs can be precisely controlled by adjusting the thickness of Al₂O₃. The J–V response for the optimal FTO/TiO₂ underlayer prepared by high-temperature spray pyrolysis is shown in Figure 2a for comparison. To further study the compactness of the ALD Al₂O₃, we measured the Kelvin probe force microscope (KPFM) mapping of the Al₂O₃ film (Figure 2b). KPFM is a high-resolution spatial surface potential mapping tool, so it is able to check thin film uniformity. To measure the work function of the surface material, we deposited Al₂O₃ by ALD for 20 cycles (2 nm) on a silicon substrate. By doing so, we can probe the uniformity of the Al₂O₃ on silicon substrate because there is a large difference of the work function between silicon and Al₂O₃. Figure 2b shows the surface potential mapping in a 1 μm x 0.5 μm area, with a very uniform surface potential distribution throughout the whole area. Figure 2c shows the 3D potential mapping and the small work-function fluctuation (less than 20 mV) again demonstrates the high compactness of the ALD Al₂O₃.

The Al₂O₃-based underlayers with different thicknesses were tested in solar cells with the device configuration shown in Figure 1a. Figure 3a shows the cross-sectional image of the PSCs, showing that the previously optimized thicknesses for meso-TiO₂, perovskite and HTM are about 150, 500, and 300 nm. The perovskite material used in this work is the previously developed mixed-ion perovskite ([((CH₃NH₃)₂)ₓ(CH₃NH₂)₁₋ₓPb(I₀.₃₂Br₀.₆₈)]₀.₇₀Br₀.₃₀). The surface morphology of the perovskite film is depicted in Figure 3b, showing an average grain size of 300 nm. Furthermore, the perovskite film shows large grains and is free of pinholes, which is crucial for achieving high-performance PSCs. Figure 3c shows the J–V curves of the devices based on the different thickness Al₂O₃ underlayers and the corresponding photovoltaic parameters are listed in Table 1. The underlayer-free PSCs showed a PCE of 11.0%, with Jsc of 18.5 mA cm⁻², Voc of 0.99 V, and fill factor of 0.71. The PCEs of the underlayer-PSCs increased with increasing Al₂O₃ thickness, with the highest PCE of 16.2% for an Al₂O₃ thickness of 5 nm. The smaller decrease in Voc and Jsc as compared to a PCE of 11.0% for underlayer-free PSCs is probably due to the high conductivity of the FTO substrate at typical oxidizing conditions.
values. The device with an approximately 5 nm-thick AlO_x underlayer (from 50 ALD cycles) had the best performance (Figure 4b) with a PCE of 16.2% (J_{sc} = 22.8 mA cm^{-2}, V_{oc} = 1.06 V, FF = 0.67), compared to 12.3, 13.1, and 14.7% for the devices based on AlO_x underlayers with thicknesses of about 2, 3, and 4 nm, respectively. However, when the AlO_x thickness increases to more than 5 nm, the devices show lower performances with PCEs of 13.0, 10.4, and 0.2% for AlO_x thicknesses of approximately 6, 7, and 10 nm, respectively (Figure 4b). Therefore, the thickness of the AlO_x underlayer has a great impact on the solar cell performance, as previously reported.[33] These results also show that the ultrathin AlO_x can conduct electrons effectively through tunneling, as well as blocking the recombination efficiently in PSCs, as recently reported for a similar system where ALD-deposited thin AlO_x films were found to be sufficient to conduct the charges between the perovskite and a HTM.[32]

To better understand the FF losses for thicker AlO_x films, dark current measurements were performed for the devices (Figure 3d). In PSCs, the dark current is primarily determined by the series resistance of the components in the devices. Since the same ETM and HTM were used for all devices discussed herein, the differences in dark current could provide useful information on the series resistance of the complete device. As the AlO_x thickness increases from 2 nm to 10 nm, the dark current decreases at forward bias (Figure 3d), showing a very similar trend in electrochemical behavior to that shown in Figure 2. This indicates that the thick AlO_x layer leads to high series resistance in the device. The high resistance of AlO_x will induce difficulties of the electron conduction from the perovskite/TiO_x to the FTO and thus reduce the charge collection efficiency. Therefore, the difference in their series resistance could be one of the main reasons for the decreasing J_{sc} values for thicker AlO_x films (Table 1).

To better understand the lower J_{sc} for the thinner AlO_x films, the incident photon-to-current conversion efficiency (IPCE) curves (Figure 4a) and the J_{sc} values of the devices (Figure 4b) were measured. The PSC with 50 cycles of AlO_x ALD showed the highest IPCE and the integrated J_{sc} values were consistent with the obtained J_{sc} in Table 1. The thinner AlO_x films showed lower IPCE values than the 50 cycles sample. It is possible that these films are not thick enough to hinder recombination between the FTO and the perovskite, which could also explain the lower V_{oc} values for these thicknesses. When the thickness of AlO_x is higher than the optimal condition (5 nm), the J_{sc} becomes lower, which can be explained by the high electron transfer resistance through the AlO_x, in accordance with the electrochemical characterization (Figure 2) and the dark current measurements (Figure 3d). It should be noted that the IPCE for 30 cycles AlO_x is slightly higher than that for 40 cycles AlO_x. We suggest that there are probably three electron transfer pathways that exist under operating conditions, including electron transfer through defects (such as pinholes) in the AlO_x, electron tunneling through the AlO_x layer, and electron recombination with the holes in perovskite both through pinholes and tunneling through the AlO_x layer. Therefore, the J_{sc} obtained in the device is the combined result.

Figure 2. a) Cyclic voltammetry curves of 10 mM K_{3}[Fe(CN)_{6}] in 0.1 M KCl aqueous solution with FTO, FTO/TiO_x (spray pyrolysis), and FTO/AlO_x (different thicknesses) layers as working electrodes in a three-electrode setup. The reference electrode is Ag/AgCl (3 M KCl) and the counter electrode is stainless steel. The area of the working electrode is fixed at 1.25 cm^2. b) Surface potential mapping of 2 nm AlO_x on silicon substrate with a dimension of 1 μm x 0.5 μm by Kelvin probe force microscopy (KPFM). c) 3D potential mapping of 2 nm AlO_x on silicon substrate by KPFM.
of the above processes. In the 30 cycles Al₂O₃ sample, electron injection is probably dominated by the defects, and recombination also occurs through these defects, whereas for 40 cycles Al₂O₃, the pinholes are probably less abundant, meaning that electron injection is mainly accomplished through tunneling, although the pinholes may still be important for recombination. Therefore, the higher probability of electron transfer through defects induced a higher \( J_{sc} \) value for 30 cycles Al₂O₃ and thus higher IPCE, as compared to 40 cycles Al₂O₃. However, for the 50 cycles Al₂O₃ sample, the device has the minimum electron recombination loss of all of the devices, probably owing to lower amounts of pinholes than the thinner Al₂O₃ films. The device also still has electron injection from the perovskite through Al₂O₃ by tunneling, giving the optimal balance between charge injection and charge recombination, thus giving the highest \( J_{sc} \) value. The solar cell \( J_{sc} \) is highly dependent on the interfacial electron transfer efficiency and the charge collection efficiency. When the Al₂O₃ thickness is changed, both the electron transfer resistance from the perovskite to FTO (current collector) and the shunt resistance are highly influenced. Therefore, we believe that there is a trade-off between low recombination and efficient electron transfer. Figure 4c and Table 1 show the device performance statistics and it can be clearly seen that the PSC with an Al₂O₃ underlayer with 50 cycles performed much more efficiently than the other thicknesses. Therefore, it can be concluded that the optimal thickness of Al₂O₃ layer for high-performance perovskite solar cells is obtained by ALD through 50 cycles.

As reported previously, the underlayer also has a significant influence on the \( J-V \) hysteresis in PSCs\(^ {20}\). We therefore measured the \( J-V \) curves of the device without underlayer and the optimal device (5 nm Al₂O₃ thickness), using both forward and reverse scan directions (Figure 4d and e, respectively). The underlayer-free device showed around 1% absolute efficiency difference between the forward and backward scans. In contrast, the corresponding device with 5 nm Al₂O₃ containing exhibited very little hysteresis with PCEs of 16.2 and 16.3% in backward

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Figure 3. a) Cross-sectional image of the complete PSCs without Al₂O₃ underlayer. b) Surface morphology of the perovskite crystals. c) \( J-V \) curves of the PSCs based on Al₂O₃ underlayer with different thicknesses under AM 1.5 illumination (100 mW cm\(^{-2}\)). d) Dark current of PSCs based on Al₂O₃ underlayers with different thicknesses.
Figure 4. a) IPCE curves of PSCs. b) $J_{sc}$ statistics of the devices with and without $\text{Al}_2\text{O}_3$. c) Histogram of the device efficiencies. d) Current–voltage hysteresis of the underlayer-free devices. e) Current–voltage hysteresis of the devices based on $\text{Al}_2\text{O}_3$ underlayer (50 cycles). f) Transient photovoltage decay measurements of devices without underlayer and with $\text{Al}_2\text{O}_3$ underlayer (50 cycles). g) Mechanism of the tunneling through high band gap semiconductor $\text{Al}_2\text{O}_3$ at the interface between FTO and perovskite.
(\(V_m\) to \(J_m\) and forward \(U_m\) to \(V_m\)) directions, respectively. A similar study suggests that the low \(J-V\) hysteresis could be due to the fact that the underlayer, in this case ALD-prepared Al\(_2\)O\(_3\), is ultrathin and at the same time has a uniform morphology.\(^\text{[20]}\) In these regards, ALD is a promising method by which to potentially develop high-efficiency and hysteresis-free perovskite solar cells.

As discussed above, using a device incorporating a 50-cycle Al\(_2\)O\(_3\) underlayer gave an improved \(V_m\) of 1.06 V, compared to 0.99 V for the underlayer-free PSC, even though both devices used the same ETM and HTM. To further elucidate this difference, transient photovoltage decay (TPVD) was performed on the complete devices. TPVD measurements were conducted on the PSCs under open-circuit conditions by applying a light perturbation on a constant light intensity of 100 mW cm\(^{-2}\).\(^{[16, 37]}\) By monitoring the photoinduced voltage decay, information on electron recombination can be qualitatively extracted. The PSC with an Al\(_2\)O\(_3\) underlayer of 50 cycles shows much slower photovoltage decay than the underlayer-free device (Figure 4f), which indicates a longer electron lifetime for the Al\(_2\)O\(_3\)-based device. A longer lifetime for the device with the Al\(_2\)O\(_3\) underlayer could be the result of reduced recombination for this sample, which would correspond well with the increase in \(V_m\) that we observed for the cells (Table 1). We therefore believe that the Al\(_2\)O\(_3\) underlayer does indeed prevent recombination. The insulator Al\(_2\)O\(_3\) is acting as an energy barrier due to its high band gap. Since the energy barrier for tunneling electrons is lower than for tunneling holes from the perovskite, and at some Al\(_2\)O\(_3\) thickness it therefore becomes noticeably easier to tunnel electrons compared to holes through the layer (Figure 4g). Thus this tunnel oxide layer can effectively block recombination paths while allowing transport of the excited electrons.

**Conclusions**

In conclusion, we have prepared compact and homogeneous Al\(_2\)O\(_3\) underlayers by atomic layer deposition (ALD) for perovskite solar cells (PSCs). By controlling the thickness of Al\(_2\)O\(_3\), we could control the electron-transfer resistance and thus the electron recombination rate in the perovskite solar cells. We found that the thickness of the Al\(_2\)O\(_3\) underlayer significantly affects the series resistance, and electron recombination kinetics of the device, and thus their \(J_m, V_m\) and solar cell efficiency. By using the optimal Al\(_2\)O\(_3\) thickness of 50 cycles, a high power conversion efficiency (PCE) of 16.2% was achieved with only a small hysteresis compared to the 11.2% for underlayer-free PSCs. We therefore believe that the low-temperature processed Al\(_2\)O\(_3\) underlayer prepared by ALD is promising for other types of solar cells and for making flexible PSCs. In addition, the possibility of tunneling through Al\(_2\)O\(_3\) as well as its high blocking effect, provides a great potential for solar cell interface engineering to further enhance the photovoltaic performance of perovskite solar cells.

**Experimental Section**

**Preparation of Al\(_2\)O\(_3\) by ALD**

The ALD Al\(_2\)O\(_3\) underlayers were grown by a hot-wall Picosun ALD R200 reactor, using trimethylaluminum (TMA) as the Al precursor and H\(_2\)O as the counter reactant at a substrate temperature of 200 °C. An ALD pulse cycle of TMA/N\(_2\) purge/H\(_2\)O/N\(_2\) purge was employed with corresponding pulse lengths of 0.1, 4, 0.1, and 6 s, respectively, resulting in a saturated growth rate of 0.1 nm per cycle.

**Electrochemical characterization**

For the electrochemical characterization of the underlayers, a three-electrode setup was used; the working electrode was bare FTO, FTO/TiO\(_2\) underlayer, or FTO/Al\(_2\)O\(_3\) underlayer; the reference electrode was Ag/AgCl; the counter electrode was stainless steel; the electrolyte was 10 mM K\(_2\)(Fe(CN)\(_3\))\(_6\) in 0.1 M KCl. Cyclic voltammetry was used to characterize the quality of the underlayers. The voltage scan was from 0 V to 0.6 V versus Ag/AgCl and the current density was recorded.

**Device fabrication and characterization**

FTO glasses were first cut into rectangles with dimension of 1.5 cm x 2.5 cm, as required for solar cells. Then the FTO substrates were cleaned with three steps by using water, acetone, and ethanol (around 0.5 L containers). The Al\(_2\)O\(_3\) underlayers with different thicknesses were then prepared by ALD with a controlled number of deposition cycles. For reference, bare FTO or FTO with a thin layer of the TiO\(_2\) blocking layer were prepared. The TiO\(_2\) underlayer was deposited on the FTO by spray pyrolysis of isopropanol-based solution (0.2 m titanium isopropoxide and 2 m acetylacetone in isopropanol). Then a layer of mesoporous TiO\(_2\) was deposited on the aforementioned substrates by spin coating of TiO\(_2\) dispersion (30 nm TiO\(_2\) particles in ethanol). The perovskite film was formed by spin-coating a perovskite precursor solution on the substrates, followed by sintering at 100 °C for 1 h. The precursor solution contained FAI (CH\(_3\)NH\(_3\))\(_3\)I (1 m), Pb\(_3\) (1.1 m), MABr (0.2 m), and PbBr\(_2\) (0.2 m) in anhydrous DMF/DMSO = 4:1 v/v. The perovskite solution was spin-coated in a two-step program; first at 1000 rpm for 10 s and then at 4000 rpm for 30 s. During the second step, chlorobenzene (100 mL) was poured onto the spinning substrate 15 s prior to the end of the program. Finally the hole-transport material spiro-OMeTAD solution (70 m\(_\text{m}\)) was spin coated on the perovskite film, followed by deposition of 80 nm gold evaporation. The hole-transporting materials were doped with lithium bis(trifluoromethylsulfonyl)imide (LiTFSI), tris(2-(1H-pyrazol-1-yl)-4-tert-butylpyridi dine) cobalt(III) tris[trifluoromethylsulfonyl]imide (FK209), and 4-tert-butylpyridine (TBP), at molar ratios of 0.5, 0.03, and 3.3, respectively. Scanning electron microscopy and energy-dispersive X-ray spectroscopy were employed to investigate the morphological properties of Al\(_2\)O\(_3\) underlayer and elemental components. The instruments used were the FEI Nova NanoSEM 450 FEGSEM and the MERLIN Field Emission SEM (Zeiss, Germany). A black metal mask with an area of 0.125 cm\(^2\) was used during the measurement of current–voltage characteristics, IPCE, and transient photovoltage decay measurements. Kelvin probe force microscopy was performed on a Dimension Icon AFM Bruker using SCM-PIT tip in tapping mode.
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Conflict of interest

The authors declare no conflict of interest.

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