Silver is a low-cost candidate electrode material for perovskite solar cells. However, in such cells the silver electrodes turn yellow within days of device fabrication. The color change is also accompanied by a dramatic decrease in the power conversion efficiency when compared to otherwise identical devices using gold electrodes. Here, it is shown that the color change results from silver oxidation to silver iodide, due to a reaction with iodine in methyl ammonium lead perovskite. The change in X-ray diffraction and X-ray photoelectron spectroscopy is discussed. Exposure to air accelerates corrosion of the Ag electrodes when compared to dry nitrogen gas exposure. However, iodine not reacted with silver is observed by X-ray photoelectron spectroscopy even for the perovskite solar cell kept in dry nitrogen gas. It is proposed that silver iodide is formed when methyl ammonium iodide migration is facilitated by the small pinholes in the hole transport layer spiro-MeOTAD.

1. Introduction

Perovskites CH$_3$NH$_3$PbX$_3$ [X = I, Cl, or Br] have recently attracted attention as exciting, low-cost, photovoltaic materials because of their strong light absorption across almost all visible wavelengths,$^{[1–3]}$ long exciton diffusion lengths,$^{[4]}$ long charge-carrier lifetimes,$^{[5]}$ and high carrier mobilities$^{[6–8]}$ that contribute to exceptional power conversion efficiencies (PCE). In 2009, Miyasaka and co-workers reported that CH$_3$NH$_3$PbI$_3$ (MAPbI$_3$) was used as an absorber in a solar cell showing a PCE of 3.8%.$^{[2]}$ Since then, PCEs for perovskite solar cells have continued to increase, with the latest record topping 20%.$^{[9–11]}$

Currently, the most common electrode material for high-efficiency, halide-based perovskite solar cells is Au.$^{[4,10]}$ Au is much more expensive than other metals; the price of gold in 2014 was more than 65 times that of Ag, based on cumulative average spot prices at the London Gold Fix. In low-cost organic solar cells, which are somewhat similar in structure and manufacture to perovskite solar cells, the use of Ag electrode metal accounts for 7% of the total manufacturing cost.$^{[12]}$ Further decrease in cost can be achieved by using Ag nanowires.$^{[13]}$ In solar cells with inverted structures Al is commonly employed as top electrode. Al is much cheaper than Ag. However, Al has been reported to be associated with issues such as air-exposure induced oxidation and interdiffusion of Al atoms into the organic layer.$^{[14]}$

Ag is a possible alternative electrode material. Ag has been used for perovskite solar cell electrodes and for characterization of MAPbI$_3$. Unfortunately, Ag electrode suffer from corrosion or contamination in devices containing perovskites. For example, we observed that Ag electrodes on a perovskite solar cell became discolored and turned yellow several days after device fabrication. We also observed lower PCE when compared to a device with Au electrodes. Snaith and co-workers reported that Ag becomes corroded in contact with perovskite films and suggested silver halide formation as the cause.$^{[15]}$ Namboothiry and co-workers reported that the PCE dropped drastically after 50 d of storage under humid air conditions for their Glass/FTO/TiO$_2$/perovskite/P3HT/Ag solar cell devices. They attributed the decreased PCE to Ag or P3HT degradation.$^{[16]}$ Recently, Cheng and co-workers studied stability of encapsulated, planar-structured MAPbI$_3$ with an Ag back-contact electrode layer at elevated temperature and humidity using scanning electron microscopy (SEM) and X-ray diffraction (XRD).$^{[31]}$ They observed PbI$_2$ (001) contamination in devices containing perovskites. For example, we observed that Ag electrode suffer from corrosion or contamination in devices containing perovskites. For example, we observed that Ag electrode suffer from corrosion or contamination in devices containing perovskites. For example, we observed that Ag electrode suffer from corrosion or contamination in devices containing perovskites.

In the current study, we fabricated perovskite solar cell devices with Ag electrodes and stored them in the dark in ambient air or dry N$_2$. We identified AgI by XRD and XPS (X-ray photoemission spectroscopy), and confirm that this is the cause of Ag electrode corrosion. We suggest a route for AgI formation and possible ways to limit or prevent corrosion of Ag electrodes that are critical for low-cost solar cell device fabrication.

2. Results and Discussion

The composition of corroded Ag can help identify the source of the corrosion. In this case, the most likely suspect is the...
mental Section to test these possibilities (MAI) or Pb. We prepared samples as described in the Experimental Section to test these possibilities (Table 1). Li⁺ salt-doped spiro-MeOTAD was used as the hole transport layer for this study. We used doped spiro-MeOTAD to reproduce the most widely employed device chemistries.© 2015 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim

Table 1. Device structure and storage conditions of the samples prepared and analyzed in this study.

<table>
<thead>
<tr>
<th>Sample name</th>
<th>Device structure and storage conditions</th>
</tr>
</thead>
<tbody>
<tr>
<td>S1</td>
<td>Glass/FTO/TiO₂/MAPbI₃/spiro-MeOTAD</td>
</tr>
<tr>
<td>S2</td>
<td>Glass/FTO/TiO₂/MAPbI₃/spiro-MeOTAD/Ag(60 nm), 1 h after Ag deposition</td>
</tr>
<tr>
<td>S3</td>
<td>Glass/FTO/TiO₂/MAPbI₃/spiro-MeOTAD/Ag(60 nm), stored three weeks in N₂ (H₂O &lt; 0.1 ppm, O₂ &lt; 0.1 ppm)</td>
</tr>
<tr>
<td>S4</td>
<td>Glass/FTO/TiO₂/MAPbI₃/spiro-MeOTAD/Ag(60 nm), stored three weeks in air (dark) relative humidity = approximately 50%</td>
</tr>
<tr>
<td>S5</td>
<td>Glass/spiro-MeOTAD/Ag(36 nm), stored one week in air (dark) relative humidity = approximately 50%</td>
</tr>
<tr>
<td>AgI</td>
<td>Glass/carbon tape/AgI powder</td>
</tr>
<tr>
<td>Ag</td>
<td>Glass/Ag, 1 h after Ag deposition</td>
</tr>
</tbody>
</table>

Another important observation from the XRD data is that the XRD peaks from perovskite decrease in intensity as a function of time. Samples stored for a longer time—especially those stored in air (S3), and three weeks after Ag deposition for samples stored in air (S4). The XRD spectrum changed as a function of time. Initially, it consisted of a simple combination of XRD peaks from Ag and spiro-MeOTAD/MAPbI₃ films (Figure 1). Several days after device fabrication, Ag electrodes turned strongly yellow on Sample S4. In contrast, the Ag electrode on the doped spiro-MeOTAD layer without MAPbI₃ (S5) did not show any color change. The observed stable behavior of Sample S5 strongly suggests that the lead component is the cause of the Ag electrode change in not the underlying doped spiro-MeOTAD layer. After three weeks, a spectrum from the sample stored in N₂ (S3) showed XRD peaks at 2θ = 22.3°, 23.8°, and 39.2° (Figure 1). These peaks can be assigned to AgI (100), AgI (002), and AgI (111), respectively, indicating that newly formed AgI constitutes a significant component after storage in air for three weeks. On the other hand, the sample stored in N₂ for three weeks (S3), the fresh sample (S2), and the fresh sample without an Ag electrode (S1) did not show any AgI peaks. After Ag deposition (S2), we observed the XRD peak at 2θ = 38.1°, which can be assigned to AgI (AgI). This peak was continuously observed in samples that were stored three weeks in either N₂ or air (S3 and S4), confirming that Ag was not completely converted to AgI after three weeks of storage in air.

Another important observation from the XRD data is that a strong decrease in intensity of perovskite related peaks, even approaching the level of noise. Substrate peaks are still clearly visible, so the film is not so thick as to obscure the substrate. X-rays easily pass through the entire film with little attenuation, so the decrease in intensity of perovskite peaks is indicative of a loss of crystalline perovskite, which is consistent with the formation of a substantial amount of AgI.

We performed high resolution X-ray photoelectron spectroscopy (HRXPS) analysis on the samples to understand the chemical nature of the surface. A relatively large amount of iodine was detected in Sample S1. (Figure S1, Supporting Information.) This is likely due to the large pinholes in spiro-MeOTAD films, which permit detection of underlying, exposed perovskite. Controversy exists regarding the peak position assignments for Ag⁺ and Ag⁰ states.³⁴, ³⁸ Ag 3d HRXPS peaks clearly shift from metallic to a lower binding energy that is characteristic of AgI (Figure 2, Figure 3, and Figure 4). We assign the Ag metal (3d₅/₂ = 368.3 eV and Ag⁻ (3d₃/₂ = 368.17 eV) peaks.³⁴, ³⁹ Our assignments of Ag⁺ and Ag⁰ (AgI) with Ag⁺ showing higher binding energy values are also consistent with our X-ray excited...
Auger spectroscopy\cite{39,40} results shown in Figure S8, Supporting Information. A detailed description of the XPS curve-fitting procedure can be found in the Experimental Section. Sample S4 shows high binding energy shoulders for the Ag 3d\textsubscript{5/2} peak at 368.1 eV and for the Ag 3d\textsubscript{3/2} peak at 374.1 eV. This indicates that the chemical states of Ag in the electrodes changed during 3 weeks of storage in ambient air.

Chemical shifts of Ag cannot be explained by physisorption of MAI or I\textsubscript{2} onto the surface of the electrodes. Instead, these chemical shifts clearly indicate that Ag has reacted. We fitted Ag 3d core-level peaks with asymmetric shapes for two Ag chemical states: Ag metal (red) and Ag-I (blue). Background due to inelastic scattering was subtracted using the Shirley method.\cite{41} Curve-fitting based on two Ag chemical states fits the spectra well. This agrees with the hypothesis of Snaith co-workers that degradation is due to AgI formation.\cite{15} In the Ag 3d region, the ratio of the integrated area of AgI to the total integrated area of the Ag peak on Sample S4 was 26.3\% (Table 2). This value, when compared to the 35.5\% of atomic ratio determined for pure AgI (1.02 eV), therefore, there could be another chemical state of iodine beside AgI, and that the chemical shift is consistent with iodine in MAI, but not I\textsubscript{2}. The electronegativity of Pb is greater than that of Ag and similar to those of C and N, so it might be expected to exhibit a similar chemical shift in the I 3d spectrum. However, migration of PbI\textsubscript{2} to the Ag electrode top surface can be ruled out because no Pb 4f peak was detected in HRXPS spectra (Supporting Information, Figure S2). The possibility that the yellow material on the electrode might be PbI\textsubscript{2}, or that the perovskite was incompletely covered can likewise be excluded.

Clear peaks related to iodine were observed in the spectral region between 615 and 635 eV for the MAPbI\textsubscript{3}/spiro-MeOTAD/Ag sample (Figure 3). Peak positions in the spectrum from Sample S4 coincide with those of the reference AgI spectrum with peaks at 619.5 eV for I 3d\textsubscript{5/2} and 631.1 eV for I 3d\textsubscript{3/2}.\cite{34} XPS was fully consistent with AgI formation in the electrodes of perovskite solar cells. Relative atomic ratios were determined based on the HRXPS data after normalization considering atomic sensitivity factors (ASFs) of 18.04 and 33.64 for the Ag 3d and I 3d core-levels, respectively.\cite{42} Iodine was detected in Sample S2, 1 h after preparation. This means that

<table>
<thead>
<tr>
<th>Sample name</th>
<th>I/Ag</th>
<th>Pb/Ag</th>
<th>Ag(I)/total Ag</th>
</tr>
</thead>
<tbody>
<tr>
<td>S2 MAPbI\textsubscript{3}/spiro-MeOTAD/Ag, 1 h</td>
<td>0.009 ± 0.003</td>
<td>No signal</td>
<td>0.02 ± 0.01</td>
</tr>
<tr>
<td>S3 MAPbI\textsubscript{3}/spiro-MeOTAD/Ag, after three weeks (N\textsubscript{2})</td>
<td>0.061 ± 0.002</td>
<td>No signal</td>
<td>0.00 ± 0.01</td>
</tr>
<tr>
<td>S4 MAPbI\textsubscript{3}/spiro-MeOTAD/Ag, after three weeks (air)</td>
<td>0.355 ± 0.005</td>
<td>No signal</td>
<td>0.26 ± 0.01</td>
</tr>
<tr>
<td>AgI</td>
<td>0.998 ± 0.008</td>
<td>No signal</td>
<td>1</td>
</tr>
</tbody>
</table>

\textsuperscript{a}Standard deviations in the table were estimated based on curve-fitting analysis.
less than 1 hour after Ag deposition, some iodine had already reached the top surface of the otherwise fresh Ag electrode. In addition, iodine elemental signals were observed in Sample S3, with peaks at 619.1 and 630.6 eV, which are different than those of AgI. Thus, these iodine signals suggest migration of an iodine-containing compound. A solid–solid chemical reaction must occur after electrode deposition to form AgI. Candidates for the iodine-containing compound include an organic iodide, such as MAI, HI, and/or I2.

Chemical shifts of MAI should be similar to other organic iodides because of the similar electronegativity of carbon and nitrogen. The observed lower binding energy from Sample S2 suggests that MAI or another organic iodide is more likely than I$_2$. The binding energy of MAI is 619.0 eV$^{[43]}$ while that of I$_2$ is 619.9 eV$^{[44]}$. If the contamination were from I$_2$, the peak would be expected to show higher binding energy than AgI.

The valence region of HRXPS spectra (Figure 4) also supports our assertion that AgI forms in the electrode. Spectral shapes of valence spectra from Samples S2 and S3 are similar to that of metallic Ag. However, Sample S4 shows a different spectral shape. New peaks are observed at binding energies of 2.5 and 5.5 eV, respectively. These new peaks coincide with those of AgI$^{[14]}$ suggesting AgI formation. Likewise at the top of the valence band, there is a new peak at 6.3 eV (inset, Figure 4). The spectrum from Sample S4 is a combination of the spectra of AgI and Ag, consistent with a mixture of the two materials in the electrodes. Also for Sample S3, which shows a small AgI peak in the Ag 3$d$ spectrum, there is a rise in baseline around 6.3 eV, consistent with a smaller amount of AgI mixed with pure Ag.

It is clear that AgI forms in the top surface of Ag electrodes. We further studied the source of iodine for this reaction. The iodine-containing compound could come from the perovskite, migrate through the spiro-MeOTAD film, then react with and diffuse through the Ag.

For Sample S4, although the shift in the I 3$d$ peak is what would be expected for iodine in MAI, the XPS signal for N 1$s$ is weak due to the low ASF (approximately 1.8) and is further masked and complicated by the Ag 3$d$ satellite region (insets in Figures S3 and S4, Supporting Information). On the basis of roughly estimated peak intensities, there is twice as much carbon as iodine. The carbon is either a product of dissociation of perovskite or from a separate source of contamination. One might wonder whether the Ag could have been contaminated by an iodine-containing compound in the atmosphere of the laboratory. However, we did not detect iodine on a fresh Ag film deposited on glass (Figure S5, Supporting Information) that was treated similarly to Ag films on MAPbI$_3$/spiro-MeOTAD. Thus, iodine appears to originate from the film beneath the spiro-MeOTAD layer surrounding the Ag electrode, but migrates to the top of the Ag electrode. Subsequent formation of AgI leads to increase in solar cell performance.$^{[15,16,31]}$

The observed decrease in PCE is most likely a result of one or multiple factors such as (1) energy level alignment mismatch at the AgI/spiro-MeOTAD interface, (2) energy level alignment mismatch at the AgI/Ag interface, (3) lower conductivity of AgI in comparison with Ag (Ag is a semiconductor).

Based on the above observations we propose a likely mechanism with five steps (Figure 5): (1) spiro-MeOTAD layer has pinholes as initial state and H$_2$O in air diffuses into pinholes. (2) H$_2$O-induced decomposition of MAPbI$_3$ gives rise to iodine containing volatile species (e.g., MAI and/or HI).$^{[45,46]}$ (3) Migration of the iodine containing volatile compound (e.g., MAI and/or HI) from the MAPbI$_3$ layer to the bottom and top Ag layer. (4) Surface diffusion of the iodine containing volatile species (e.g., MAI and/or HI). (5) AgI formation. H$_2$O in air can reach the spiro-MeOTAD/perovskite interface through the pinholes in the spiro-MeOTAD layer, which are reported to have an average diameter of $\approx$135 nm and a density of $\approx$3.72 holes $\mu$m$^{-2}$$^{[47]}$. We observed pinholes in the spiro-MeOTAD layer on MAPbI$_3$ (Figure S6, Supporting Information). H$_2$O in air is well known to accelerate decomposition of MAPbI$_3$.$^{[45,46]}$ Decomposition of MAPbI$_3$ accelerated by H$_2$O could be the starting point of this reaction. MAI results from decomposition when H$_2$O reaches the MAPbI$_3$. The iodine containing volatile species (e.g., MAI and/or HI) has a relatively high vapor pressure in ambient$^{[48,49]}$ and migrates to the top surface of the spiro-MeOTAD film through the pinholes induced by concentration gradient driven diffusion. In the end, the iodine containing volatile species (e.g., MAI and/or HI) reaches the Ag electrodes by surface diffusion. Interestingly, iodine signals were also observed by HRXPS on an Au top electrode in MAPbI$_3$/spiro-MeOTAD/Au samples (Figure S7, Supporting Information). The peak position of I 3$d$ at 618.8 eV indicates that migration of a iodine-containing compound occurs independently of the presence of Ag. Iodine has a strong affinity for metals.$^{[50,51]}$ In the final step of the process, MAI reacts with Ag to form AgI, corroding the electrode. Alternative pathways such as formation of LiI and LiPbI$_3$ (substitution of CH$_3$NH$_3^+$ by Li$^+$) were considered in our

![Figure 5. Schematic illustration of a proposed mechanism of AgI formation based on XPS and XRD data. (1) H$_2$O in air enters pinholes in the spiro-MeOTAD layer. (2) Decomposition of MAPbI$_3$ gives rise to iodine containing volatile compound (MAI and/or HI). (3) Migration of the iodine containing volatile compound from the MAPbI$_3$ layer corroding the electrode from both the top and bottom surface of Ag layer. (4) Surface diffusion of the iodine containing volatile compound. (5) AgI formation.](image-url)
material system (CH₃NH₃PbI₃/spiro-MeOTAD). However, we were unable to observe the XPS Li 1s signal that is expected to be at a binding energy of ≈55 eV (i.e., the signal is below the instrument detection limit). Also, our XRD results (Figure 1) suggest the presence of only CH₃NH₃PbI₃ and AgI compounds as the major components. Nevertheless, a small amount of LiI and LiPbI₃, i.e., below the instrument detection limit, might be present and further experiments are necessary to prove their presence.

Based on the experimental observations, we propose that if some measures can be taken to prevent or slow down the decomposition of perovskite and/or AgI formation, Ag would be a viable electrode material for low-cost perovskite solar cells. The hole transport material between the top electrode and perovskite is expected to play a critical role in resolving this problem. We must understand the mechanism of pinhole formation in spiro-MeOTAD on MAPbI₃, and then find ways to prevent it from happening. Possibly another iodine-blocking layer will also be needed. Other spin-coating conditions, compositions, or alternative hole transport layers need be tested. For example, recently many inorganic hole transport layers such as NiOₓ, CuSCN, CuI, and CsₓSnI₆ have been reported,[30,52-58] which may resolve the present issue.

3. Conclusions

We investigated corrosion of metal Ag electrodes on MAPbI₃/spiro-MeOTAD, characterized by XRD and HRXPS. This characterization demonstrates that Ag electrodes are corroded to produce AgI. The effect is accelerated by exposure to air, compared with pure nitrogen. Iodine was observed by XPS even on samples kept in N₂. We propose that MAI migrates through the spiro-MeOTAD layer, aided by pinholes. Further study on the origin of pin-holes in spiro-MeOTAD films or alternative hole-transport materials are required to avoid using prohibitively expensive Au in low-cost perovskite solar cells.

4. Experimental Section

**MAI Synthesis**: MAI was synthesized according to a literature procedure.[9] Briefly, hydroiodic acid solution was gradually added to methyl amine ethanol solution, continuously stirred in an ice-bath. Ethanol and water from the mixed solution were removed using a rotary evaporator (BUCHI, Rotavapor R-3). Precipitated yellow crystals were dissolved in hot ethanol, and cooled in a refrigerator (5 °C) for recrystallization. Subsequently, crystals were filtered and washed with tetrahydrofuran and diethyl ether, resulting in a white crystalline powder. After drying in a vacuum, MAI was kept in N₂. H₂O < 0.1 ppm and O₂ < 0.1 ppm.

**Sample Preparation**: Fluorine-doped tin oxide (FTO) glass (Pilkington, 7 Ω sq⁻¹) was used as a substrate. The device structure was FTO/TiO₂/ MAPbI₃/spiro-MeOTAD/Ag. A compact layer of TiO₂ ≈70 nm thick was prepared via spray pyrolysis using a precursor solution of acetylacetone, Ti(IV) isoproxyde and anhydrous ethanol (3:3:2) on a preheated hot plate at 480 °C. The MAPbI₃ perovskite layer was made using a modified sequential deposition method.[80] First, PbI₂ thin films (∼100 nm) were deposited by thermal evaporation in a vacuum chamber (<10⁻⁶ Torr). Substrate temperature was kept at 20 °C during preparation of the PbI₂ films. After deposition of the PbI₂ layer, samples were immersed in a MAI (10 mg mL⁻¹) solution in 2-propanol for 30 s in N₂. Samples were annealed at 108 °C for 15 min to prepare the MAPbI₃ perovskite layer. Then a hole transport layer was spin-coated at 2000 rpm for 60 s using a mixture of three materials:[60] spiro-MeOTAD (2,2’,7’,7’-tetrakis(N,N-di-p-methoxy-phenylamine)-9,9’-spirobiﬂuorene (Merck) dissolved in chlorobenzene (72.5 mg mL⁻¹), 17.5 µL of Li-bis(trifluoromethanesulfonyl)-imide (Sigma) dissolved in acetonitrile (52 mg/100 µL), and 28.8 µL of tert-butylpyridine (Sigma). Finally, 60 nm of Ag or Au was deposited by thermal evaporation to form a top electrode.

**Characterization**: Films were characterized by X-ray diffraction (D8 Bruker) using Cu Ka x-rays and a Pathfinder 0D detector. θ-2θ scans were performed using a resolution of 0.02 degrees per step.

The measurement technique allows for bulk measurement of the entire film from FTO to Ag. For HRXPS measurements, we used monochromated AlKα (hv = 1486.6 eV) and a delay-line detector with a 180° hemispherical, 165 mm mean radius analyzer in an AXIS Ultra DLD (Kratos Surface Analysis). Binding energy for XPS was calibrated by setting the Fermi edge (E₀ = 0 eV) and Au-4f 7/2 (84.0 eV) on a clean Au surface. Energy resolution was less than 0.5 eV for HRXPS. X-ray-induced sample damage was monitored by taking five consecutive spectra and comparing them. Acquisition time for each scan varied from 10 to 20 s, depending on core level regions. The five scans were averaged to a single spectrum if no changes were observed among them. Analysis of XPS data was performed in CasaXPS 2.3.16 software. Ag metal and AgI powder XPS reference spectra were fitted using asymmetric, Gaussian-Lorentzian line shapes. Shirley-type background was subtracted to account for inelastic scattering processes.[11] The same parameters (Gaussian-Lorentzian ratio, asymmetry function, binding energy, and peak width) obtained from reference sample fitting results were used when fitting Ag-coated perovskite film spectra and only the intensity was allowed to vary during the fitting process. The spin-orbit coupling energy (separation of 3d½ and 3d½ doublet) ΔE = 6.0 eV[61, 62] and intensity ratio I(3d½)/I(3d½) = 1.5 were constrained. The atomic concentrations of different chemical elements were extracted from XPS intensity ratios after proper normalization using atomic sensitivity factors.[46]

The topographic image of the glass/FTO/TiO₂/MAPbI₃/spiro-MeOTAD sample was acquired by atomic force microscopy (ASYLUM Research MFP 3D) in tapping mode.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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