Fast Optical Reflectance Measurements during Spin Coating and Annealing of Organic–Inorganic Perovskite Precursor Solutions

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The spin-coating and subsequent low-temperature annealing processes of organic/inorganic halide perovskites are investigated using in situ high-speed spectral reflectance measurements. Methyl ammonium lead triiodide (CH₃NH₃PbI₃, MAPI), methyl ammonium lead tribromide (CH₃NH₃PbBr₃, MAPBr), formamidinium lead triiodide (HC(NH₂)₂PbI₃, FAPI), and triple cation-based (TripleCat) perovskite Cs₀.05(FA₀.83MA₀.17)₀.95Pb(I₀.83Br₀.17)₃ are used as precursor solutions. After ≈1 s of spin coating, interference fringes develop that are used to determine the thickness of the layers. The spontaneous formation of MAPBr and TripleCat perovskite polycrystalline layers is observed during spin coating at room temperature. The phase transition from the other precursor solutions to the polycrystalline perovskite layers is monitored with diffuse reflectance measurements during the low-temperature annealing step. These measurements permit the monitoring of the crystallization process that affects the bandgap of perovskites. Furthermore, it is possible to investigate the phase separation that occurs in perovskite mixtures during annealing by a second relative minimum in the reflectance spectra. The obtained results show that fast reflectance measurements are very useful to characterize kinetics and phase transition. Moreover, this fast experimental method provides insight into the formation of perovskite thin films and allows monitoring these processes on a timescale of some tens of milliseconds.

1. Introduction

Perovskites have made remarkable advances in efficiency in recent years,[1] even though they use inexpensive methods such as spin coating or doctor blading.[2,3] Despite significant progress, perovskites still suffer from lacking long-term stability[4] and higher complexity when moving to mixed-cation perovskites, so-called double-, triple-, or quadruple-cation perovskites,[5–11] that have attracted strong interest recently. Normally, solution-based low-cost processes are used as “black-box” recipes and optimized via brute force processing or machine learning[12,13] without real-time quality control and valuation. Consequently, perovskite synthesis has to be analyzed carefully to identify strategies for process variations and process control to overcome the stability issue and control such complex solutions. There are many publications addressing in situ measurements of the perovskite layer preparation by means of grazing-incidence X-ray diffraction (XRD),[14–23] absorbance,[14,26,27] and photoluminescence (PL) spectroscopy.[26,28–31] However, only a few publications report on reflectometry measurements during annealing of MAPbI₃–Clₓ layers in a narrow-wavelength window from 600 to 950 nm[31] and during the drying process of blade-coated perovskite films at a fixed wavelength of 650 nm.[32]

In this manuscript, we present a detailed experimental investigation and in situ monitoring of the layer formation during spin coating and the subsequent solidification and crystallization processes. For this purpose, fast spectral reflectance measurements were used.

2. Results and Discussion

Figure 1 shows the measured direct reflectance as a function of wavelength and time recorded during spin coating of (a and b) 1 M CH₃NH₃PbI₃ (MAPI), (c) 1 M CH₃NH₃PbBr₃ (MAPBr), (d) 1 M HC(NH₂)₂PbI₃ (FAPI), and (e) 1 M Cs₀.05(FA₀.83MA₀.17)₀.95Pb(I₀.83Br₀.17)₃ (TripleCat). As the solvent, a 4:1 ratio of DMF and DMSO was used. The acceleration of the spin coater to reach 4000 rpm amounted to 5 s. Subsequently, the high revolution speed was kept constant for the remaining time of the experiment. The blue and red colors denote the lowest and highest reflectance, respectively.
Interference patterns and fringes are clearly visible for all perovskite precursor solutions during spin coating. Data acquisition was conducted at a frequency of 100 Hz. This allowed visualizing the fast shift of the interference fringes even during the acceleration step \(t \leq 5\) s of the liquid layer. As an example, this is shown in Figure 1b for MAPI. In the beginning of the spin-coating process, the absorption edge of the iodine-containing solutions at \(\lambda \approx 470\) nm is clearly visible.\(^{[26,31]}\) With increasing spin-coating time the absorption edge shifts to \(\lambda \approx 430\) nm, indicating that the concentration of the solution changes (see green arrows in Figure 1b). This shows that chemical changes of the spin-coating solution can be clearly distinguished from the thinning of the film during spin coating. At longer processing times \(t > 28\) s, the interference fringes disappear due to drying of the precursor solution. For \(t > 28\) s, specular reflectance can no longer be observed and only diffuse scattered light at a much lower intensity can be registered as a result of surface roughening. The time \(t_{\text{end}}\), at which the interference pattern disappears, varies for the different perovskite precursor solutions from about 28 s for MAPI, to 30 s for MAPBr, to 65 s for FAPI, and to 120 s for TripleCat. As the solvent is the same for all precursor solutions, \(t_{\text{end}}\) mainly depends on the interaction of the solvent with the ions in solution. Obviously, the complex formation energy is the highest for TripleCat, medium for FAPI, and the lowest for the MAPI and MAPBr precursor solutions.

The shift of the fringes is also affected by changes in the optical dispersion. As there is only a small change of the position of the absorption edge, changes in the optical dispersion can be neglected. As a solvent, a 4:1 mixture of DMF and DMSO was used. Blue and red denote lowest and highest reflectance, respectively. The green arrows in (b) mark the shift of the absorption in solution within the first seconds of spin coating.

Figure 1. a–f) Spectra of the specular reflectance (in %) as a function of wavelength and time recorded during spin coating of (a, b) MAPI. In (c), (d), and (e, f), the spectra for MAPBr, FAPI, and TripleCat precursor solutions are shown, respectively. Note that (b) and (f) are magnifications of the initial 1–5 s of (a) and 3–3.5 s of (e). As a solvent, a 4:1 mixture of DMF and DMSO was used. Blue and red denote lowest and highest reflectance, respectively. The green arrows in (b) mark the shift of the absorption in solution within the first seconds of spin coating.
solution, which is also the case for the final perovskite layer on the basis of TripleCat precursor solution.\cite{7,11}

Figure 2 shows normalized reflectance spectra of the MAPI solution taken after \( t = 2, 5, 10, \) and 20 s. The data represent individual spectra that were taken from Figure 1a. At \( t = 2 \) s, which is still during the acceleration of the spin coater, the reflectance spectrum shows only very small but a large number of interference fringes. In the first 5 s, the absorption due to iodine species in solution is clearly visible (\( \lambda < 470 \) nm). With increasing spin-coating time, the interference pattern broadens, which leads to a decrease in the number of fringes. This is accompanied by a pronounced increase in the amplitude of the fringes. The light absorption within the precursor solution leads to a damping of the interference fringes for wavelengths below 470 nm. However, there is no structure in the spectra visible that points to the bandgap of the perovskite material.

From the interference fringes the layer thickness \( d \) of the film can be determined from two successive maxima or minima. When the incident light is perpendicular to the sample surface the film thickness is given by\cite{34,38}

\[
d = \frac{\lambda_1 \cdot \lambda_2}{2 \cdot [n(\lambda_2) - n(\lambda_1)]}, \quad \lambda_1 > \lambda_2
\]

where \( \lambda_1 \) and \( \lambda_2 \) correspond to wavelengths where the reflectance exhibits two consecutive maxima or minima and \( n \) is the refractive index.

For the investigated perovskite precursor solutions the dispersion of \( n \) is small between 500 nm < \( \lambda < 1100 \) nm and can therefore be neglected. Moreover, \( n(\lambda) \) is dominated by the solvent. Hence, Equation (1) simplifies to

\[
d = \frac{\lambda_1 \cdot \lambda_2}{2 \cdot n(\lambda_1 - \lambda_2)}, \quad \lambda_1 > \lambda_2
\]

From the spectral data shown in Figure 1, the thickness \( d \) of the perovskite precursor solutions on glass substrates was calculated as a function of the spin-coating time using Equation (2). The resulting \( d \) is shown in Figure 3 as a function of spin-coating time. The interference patterns of the MAPI/MAPBr mixtures resemble that of the MAPI solution in Figure 3 and are therefore not shown.

For the calculations using Equation (2), the following refractive indices for the perovskite precursor solutions were used: \( n = 1.62 \) (MAPI), \( n = 1.6 \) (FAPI, TripleCat, and mixtures of MAPI with MAPBr), and \( n = 1.56 \) (MAPBr). The refractive indices of the precursor solutions were calculated via the molar ratio of the solvents using \( n_{DMF} = 1.43, \quad n_{DMSO} = 1.48, \quad n_{PbI_2} = 3.50,41 \) and \( n_{PbBr_2} = 2.4,42 \) as there are no data available for CH\(_3\)NH\(_3\)I and HC(NH\(_2\))I\(_2\). We chose \( n_{CH_3NH_3I} = n_{HC(NH_2)I_2} = 1.7 \) as found for NH\(_4\)I.\cite{43} The small amount of added CsI was neglected. It should be mentioned that the solvent slowly evaporates during spin coating. This leads to a higher molar ratio of lead compounds versus solvent with time. Initially, this behavior results in an increase in \( n \), which causes a small decrease of the calculated thickness with time (see Equation (2)). For \( t \leq 3 \) s, the thickness varies strongly due to the very low reflectance signals (see Figure 2) but the average thickness is very similar for all precursor solutions and \( d \) varies in the range from 2.2 to 2.5 \( \mu \)m. For \( 3 < t \leq 4 \) s, a pronounced increase of \( d \) is observed for all precursor solutions. The largest increase of about 800 nm is calculated for the TripleCat precursor solution (green stars in Figure 3). This behavior is in accordance with the theory of spin coating of fluids, where a solution wave, depending on density and viscosity of the solution, passes the surface at a specific rotational speed (see sketches in Figure 3, top).\cite{34,40} After passing maximum thickness, the film thickness of the solution decreases strongly and levels out after about 10 s. The more pronounced increase in thickness at about 4 s is the TripleCat precursor solution and the final thicker layer point to a stronger interaction of the ions with the DMF and DMSO molecules.
Table 1 shows the calculated final thickness $d_{\text{end}}$ obtained from the different perovskite precursor solutions at $t_{\text{end}}$ (see Figure 3) and compares the values to measurements taken with a mechanical stylus after annealing. The data from both measurements are in reasonable agreement. However, the error of the measured thickness using a profilometer is much higher due to the development of a rough surface.

To investigate possible crystallization of the perovskite layers during evaporation of the solvent while spin coating, the reflectance was measured for longer times. In addition, the reflectance difference was reduced to about 0.2–1% to highlight changes in the reflectance. Figure 4 shows the spectra of the specular reflectance of MAPI, MAPBr, FAPI, and TripleCat precursor solutions (a–d) for $t > 60$ s during spin coating, which are connected to Figure 1 with a magnified sensitivity of the reflectance between the blue and red color ($\Delta R$: 0.8% for MAPI, 3% for MAPBr, 1% for FAPI, and 0.5% for TripleCat precursor solution).

When the higher reflectance of the interference pattern levels out, MAPI shows no pronounced reflectance (Figure 4a), whereas FAPI (Figure 4c) still exhibits the interference pattern but with a much lower intensity. These observations correlate with XRD investigations on MAPI$^{[21,22]}$ and FAPI$^{[19,23]}$ showing no crystalline XRD pattern related to the perovskite after spin coating and drying. However, the precursor solutions of MAPBr and TripleCat tend to show a structure in the reflectance that develops with time. This reflectance is not associated with the interference pattern but seems to reflect the development of the bandgap of the respective perovskite layer that forms spontaneously during evaporation of the solvent. XRD and absorbance measurements reveal the formation of a crystalline phase of MAPBr with an absorbance onset at about 550 nm.$^{[46]}$ This is related to the yellow-to-blue transition of the reflectance at about 530–540 nm for the MAPBr precursor solution, as shown in Figure 4b, that develops slowly and becomes more pronounced with time. For the TripleCat precursor solution this transition develops abruptly and shows no constant wavelength border but varies from 770 nm at 190 s to about 810 nm at 220 s. It is apparent that this precursor solution shows some unpredicted

| Solution          | MAPI | MAPBr | MAPI:MAPBr (1:1) | MAPI:MAPBr (3:1) | FAPI  | TripleCat |
|-------------------|------|-------|------------------|------------------|-------|-----------|
| $d_{\text{end}}$ (nm) from reflectance data | 430 ± 30 | 320 ± 30 | 340 ± 30 | 380 ± 30 | 370 ± 30 | 500 ± 50 |
| $d$ (nm) from profilometer measurements   | 530 ± 100 | 310 ± 60 | 430 ± 100 | 460 ± 100 | 340 ± 80 | 650 ± 100 |

Figure 4. a–d) Spectra of the specular reflectance (in %) for MAPI, MAPBr, FAPI, and TripleCat precursor solutions as a function of wavelength and at longer spin-coating times using a stretched sensitivity of the reflectance. As a solvent, a 4:1 mixture of DMF and DMSO was used. The dashed lines are guides for the eye. Blue and red denote lowest and highest reflectance, respectively.
behavior in the drying process while spin coating. This border seems to be correlated with the bandgap of the crystalline phase, as for bromine-free TripleCat layers ($\text{FA}_{0.85}\text{Cs}_{0.15}\text{PbI}_3$ and $\text{FA}_{0.758}\text{MA}_{0.152}\text{Cs}_{0.091}\text{PbI}_3$) a black crystalline $\alpha$-phase was observed after spin coating that degraded during long-time XRD processing.\cite{20} However, reflectometry is not able to tell us something about crystalline phases in the solutions or hydrate phases in layers as XRD can do, as observed during spin coating of MAPI\cite{14,47,48} and TripleCat layers.\cite{20}

Finally, the last process step for the formation of perovskite layers is low-temperature annealing. To gain insight into this process, diffuse reflectance spectra were measured with an integration time between 10 and 40 ms. The diffuse reflectance taken at an angle of $\approx 15^\circ$ off normal incidence was referenced to the normal-incidence specular reflectance of a single-side-polished sapphire substrate. All MAPI, MAPBr, and MAPI/MAPBr mixtures were annealed at $T_A = 100^\circ$C, whereas the TripleCat and FAPI layers were annealed at $T_A = 150$ and 165 $^\circ$C, respectively. Figure 5 shows the diffuse spectral reflectance maps of the perovskite layers. Blue and red colors denote lowest and highest values of the reflectance signal, respectively. The yellow/blue boundary reflects strong changes in diffuse reflectance (higher-to-lower values) due to light absorption within the spin-coated layer. During annealing of the layer formed from the MAPI precursor solution, the diffuse reflectance shows a step-like change of this boundary from $\approx 550$ to $\approx 760$ nm (see Figure 5a). This indicates the change from absorption by PbI$_2$ or Pb-related complexes around $\lambda = 550$ nm ($E_g = 2.3$ eV)\cite{49} toward the absorption of methyl ammonium lead triiodide perovskite at $\lambda = 760$ nm ($E_g = 1.6$ eV).\cite{50} The crystallization of such layers was also revealed by XRD investigations.\cite{16,25} This is corroborated by spectrally resolved PL measurements that were taken after the annealing step. The PL spectra are shown as red curves in Figure 5. The layers prepared from the precursor solutions of FAPI and the MAPI/MAPBr mixtures show a similar behavior.

The crystallization of MAPI takes about 7 s at a temperature of 100 $^\circ$C, whereas the crystallization of FAPI requires about 60 s at a much higher temperature of 165 $^\circ$C. A similar trend has been observed by in situ wide-angle X-ray scattering studies.\cite{25} On the
other hand, such a change with annealing time $t_A$ is not observed for the layers prepared from MAPBr and TripleCat precursor solutions. Consequently, MAPBr and TripleCat perovskites are already crystallized in the perovskite lattice structure after the spin-coating process, as also revealed by XRD investigations.\cite{20,46} At this point, it should be mentioned that the influence of the temperature on diffuse reflectance spectra is very small. This can be clearly seen from the already-crystallized MAPBr and TripleCat layers in Figure 5b,d. The time $t_A = 0 \ s$ refers to the start of the measurement. The specimen is placed on the hot plate only an instance before the temperature of the sample is still close to RT, at $t_A = 0 \ s$. Temperature equilibration requires some time. Interestingly, for $t_A = 10 \ s$, only a small shift of $\approx 5 \ nm$ of the border between yellow and blue colors, which indicates the position of the bandgap, is observed (see Figure 5b,d).

However, reflectometry cannot directly measure the energetic position of the bandgap. It measures the reflected light that depends on refractive index, absorption coefficient, and possibly scattering processes. But reflectometry can give an easy to measure hint to these fundamental properties when correlated to other techniques like absorbance and/or XRD techniques.

For the layers prepared from mixed MAPI/MAPBr precursor solutions, the position of the strong change in reflection (from yellow to blue) shifts from $\lambda \approx 570 \ nm$ to $\lambda \approx 640 \ nm$ (ratio 1:1, see Figure 5e) and from $\lambda \approx 550 \ nm$ to $\lambda \approx 700 \ nm$ (ratio 3:1, see Figure 5f), respectively. This behavior correlates with absorbance measurements for such layers yielding an absorption onset at about $650-670 \ nm$ for the 1:1 and 710–730 nm for the 3:1 mixture, respectively.\cite{58,51,52} However, the reflectance data taken on these layers do not allow to clearly identify the position of the bandgap. Especially for the (1:1) mixture, which contains a large amount of MAPBr, a second less-pronounced relative minimum in the reflectance is observed between $\lambda = 700$ and $730 \ nm$ besides the very low reflectance at $\lambda \leq 640 \ nm$. Both mixed perovskites show a red shift of the PL maxima, leading to a similar value of $\lambda \approx 735 \ nm$. This behavior is due to slight demixing of the material, leading to iodine enrichment that is reversible in the dark.\cite{53}

Complete demixing by forming MAPBr crystallites is not observed as no PL signal was measured at around $\lambda = 560 \ nm$ of the mixed material as quantified at high illumination intensities.\cite{54} These observations suggest that PL measurements are not suitable to be used as a measure for the bandgap of mixed MAPI:MAPBr layers.

3. Summary

In summary, fast reflectance measurements on an ms timescale were carried out to monitor the formation of perovskite thin films during spin coating and subsequent annealing. Interference fringes observed in the reflectance measurements allow an in situ monitoring of the layer thickness. In addition, the measurements enable the investigation of changes in the solution at a very early stage of the spin-coating process. The evaporation of the solvent during spin coating results in the spontaneous crystallization of the perovskite layer for MAPBr and TripleCat precursor solutions at longer spin-coating times. On the other hand, MAPI, FAPI, and mixtures of MAPI and MAPBr require low-temperature annealing for crystallization.

During the subsequent annealing process, the diffuse reflectance measured with high sensitivity provides insight into the transformation and crystallization process of the precursor layer to the final perovskite layer. Mixtures of CH$_3$NH$_3$PbI$_3$ and CH$_3$NH$_3$PbBr$_3$ show nonhomogeneous layer formation. The partial demixing of the mixed MAPI:MAPBr layers shows that PL is not a suitable method to determine the bandgap of mixed MAPI:MAPBr layers. Finally, the slower disappearance of the interference fringes for the TripleCat precursor solutions with increasing spin-coating time points to a stronger interaction of the solvents (here DMF:DMSO in the ratio 4:1) with the CH$_3$NH$_3^+$, HC(NH$_2$)$_2^+$, and Cs$^+$ ions compared with MAPI and MAPBr solutions. The interaction is even more pronounced for the TripleCat precursor solution, as the evaporation of the solvent strongly slows down.

4. Experimental Section

The substrates used for the experiments were standard glass plates with an area of $2.5 \times 2.5 \ cm^2$ and thickness of 1 mm. The glass plates were cleaned with ethanol and acetone followed by an ozone cleaning step for 10 min. All chemicals and solutions were stored and processed in a nitrogen-purged glove box. All reflectance measurements were also carried out in the nitrogen-purged glove box.

Solutions used for this investigation were 1M CH$_3$NH$_3$PbI$_3$ (MAPI), 1 M CH$_3$NH$_3$PbBr$_3$ (MAPBr), 1 M HC(NH$_2$)$_2$PbI$_3$ (FAPI), MAPI:MAPBr (1:1), MAPI:MAPBr (3:1), and Cs$_{0.05}$(FA$_{0.85}$MA$_{1.15})_{0.95}$PbI$_{3-x}$Br$_{2x}$ (TripleCat), each dissolved in DMF:DMSO (ratio 4:1).

Spin-Coating Process: About 200 $\mu$l of solution was drop cast on the 2.5 $\times$ 2.5 $cm^2$-sized glass plates. The glass plate was completely covered by the solution. Spin coating comprised the following steps: acceleration from 0 to 4000 rpm within 5 s and final rotation time from 60 to 180 s at 4000 rpm.

Annealing process: The hot plate was set to the desired temperature, as shown in the figures, and the reflectance measurements were carried out just before the perovskite/glass sample was placed on the hot plate.

Reflectance Measurements: A prototype of LayTec’s InsPire system was used inside the glove box, having a fiber-optical head with focusing optics. This head was connected via fibers to the control unit placed outside the glove box, containing a lamp and detector (9 W tungsten lamp and 2048 pixel CCD detector array ranging from 380 to 1100 nm). The measurement spot had a diameter of about 3 mm and was located at about 3 mm from the rotational center of the sample. The fiber-optical head had a large working distance from the sample surface of about 50 cm during spin coating and 20 cm during annealing. The light beam was perpendicular to the sample surface during spin coating, whereas it was placed 15° off-axis to collect diffuse scattered light during the annealing step. The integration times of the spectra varied from 0.2 to 0.5 ms for spin coating and from 10 to 40 ms for annealing. All spectra were normalized to the spectrum of a single-side-polished sapphire wafer, which was measured prior to the experiments.

PL measurements: PL was measured after the annealing step using the 457.8 nm line of an argon-ion laser with an energy density of 80 mW cm$^{-2}$ and a 1024 pixel CCD detector array coupled to a spectrometer, applying an acquisition time of 3 s for the spectrum.

Thickness Measurements: The thickness of the samples was measured using a mechanical stylus profiler from Bruker Corporation (Dektak XT).

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Research data are not shared.

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