Controlling the Morphology of $CH_3NH_3PbBr_3$ Perovskite Films on Planar Substrates

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ABSTRACT

Hybrid organic-inorganic metal halide perovskites have recently emerged as one of the most promising new materials for photovoltaics, reaching efficiencies up to 20.1% over a period of only five years. However, for the planar heterojunction device architecture - likely the most commercially scalable design for perovskite solar cells – controlling film morphology remains a significant challenge, inhibiting both device performance and the investigation of fundamental material properties. In this study, surface silane-functionalization of planar substrates was employed together with the addition of hydrobromic acid to the perovskite precursor solution to improve perovskite film uniformity with controlled crystal size and reduced surface roughness.

Keywords

Perovskites, bromide, surface fuctionalization, solar cells, morphology, planar substrates, silanes.

INTRODUCTION

In recent years hybrid organic-inorganic metal halide perovskites have been one of the most talked about trends in solar cell technology, mainly due to their unprecedented performance improvements over a very short period of time. It has been only five years since the beginning of widespread research on perovskite photovotaics, yet their efficiencies have soared to 20.1%, rivaling those of more conventional bulk and thin film technologies [1]. Solar cells made from perovskites possess the benefits of being lightweight, low cost and easy to fabricate with simple solution or vapor processing techniques [2]. Moreover, the tunable band gap of these materials makes them ideal candidates for affordable thin-film tandem solar cells, which can reach extremely high efficiencies, but so far have been restricted only to certain niche markets such as the aerospace industry due to high material and production costs [3].

Perovskites possess a range of optical and electrical properties that make them attractive for photovoltaic applications. Their charge carrier mobilites and carrier diffusion lengths are significantly higher than those of organic films and colloidal quantum dots used to make solar cells, and are comparable to those of CdTe and polycrystalline silicon [4] [5]. Perovskites also have been shown to exhibit long carrier lifetimes (up to 2 μs), which are similar to those in GaAs, and photoluminescence efficiencies up to 70% [6] [7]. Thus non-radiative recombination in these materials is relatively low, supporting high open-circuit voltages. Consequently, if film thickness and morphology can be optimized for maximum absorption, with limited losses in charge carrier transport and extraction, high device efficiencies can be expected. Nevertheless, such optimization requires a good understanding of the fundamental properties of the material, which is an active area of research for hybrid organic-inorganic perovskites.

One of the largest limitations for the theoretical understanding, and thus performance, of perovskite photovoltaics is the lack of adequate control of the material's morphology and crystal quality. The presence of pinholes and poor crystallinity have often been cited as the cause of lower device efficiencies and have been a limiting factor for adequate optical characterization of these materials [4] [8]. The purpose of this study was thus to develop methods for controlling the morphology of perovskite films as necessary for both optoelectronic characterization and device integration.

In particular, focus was put on the less well studied bromide-based perovskites ($CH_3NH_3PbBr_3$), due to their relatively high (2.2 eV) band gap making them well suited for applications requiring semiconductors with large open-circuit voltages such as water splitting for solar fuels and, particularly, tandem solar cells. The perovskites were also deposited specifically on planar substrates, which represent the simplest, and, arguably, most easily scalable solar cell design for these materials, and also makes them well suited for optical characterization.

The major problem with obtaining continuous $CH_3NH_3PbBr_3$ films on smooth substrates so far has been poor nucleation. It appears that it is energetically more favorable for the perovskites to form individual crystals than to nucleate uniformly over the surface. Thus in this study substrate functionalization with silanes was employed along with the addition of hydrobromic acid to the precursor solution to improve substrate-perovskite interaction, and to obtain better control over the nucleation and growth kinetics of the material.

METHODS

Surface silane functionalization

Two types of substrates of roughly the same size (15x15 mm) were used for this study - smooth glass and monocrystalline, polished n-type silicon. Identical functionalization procedures were followed for both materials. The substrates were first sonicated in acetone, rinsed with isopropanol and dried under an N_2 stream, then transferred to a 1:1 solution of deionized (DI) water and 37% hydrochloric acid (HCl) and left to sit for 30 minutes. The substrates were subsequently rinsed with DI water and isopropanol, and dried under a stream of N_2. Lastly, to remove the remaining contaminants from the surface and to make it hydroxyl-terminated for funtionalization, the substrates were plasma treated by exposing them to an O_2 plasma at 50 W for 2 minutes.

The substrates were then functionalized with the aim of improving perovskite-substrate interaction. The silanes used for surface functionalization were: 95% (3-Mercaptopropyl)trimethoxysilane (MPTS) and 99% (3-Aminopropyl)trimethoxysilane (APTMS). It was hypothesized that the thiol functional groups in MPTS would bind to the lead in the perovskite, and that the amino groups in APTMS would replace some of the organic cations ($CH_3NH_3^+$) in the $CH_3NH_3PbBr_3$ lattice. Both solution- and vapor-phase functionalization was used. For the solution-based approach the substrates were immersed in a solution of 50 ml isopropanol, 500 µl deionized water and 500 µl of the corresponding silane. For optimal results the samples were left in solution for 24 to 48 hours. The substrates were then rinsed with isopropanol, dried under a stream of N_2, and annealed for 10 minutes at 105°C on a hotplate. For the vapor-phase functionalization, the plasma treated substrates were placed in an evacuated desiccator with 500 µl of liquid silane allowed to evaporate from an open container. The best quality of functionalization was obtained when the samples were kept in the low-pressure desiccator environment for 48 hours or longer. The perovskites had to be deposited within 3-5 hours after silanization, before the quality of functionalization began to deteriorate.

Preparation of precursor solutions

Non-saturated solutions

Two main types of non-saturated bromide perovskite precursor solutions were used in this study: 1M stoichiometric precursors in N,N-Dimethylformamide (DMF) and 2M stoichiometric precursors in Dimethyl sulfoxide (DMSO). Both were also used with the addition of 48% hydrobromic acid (HBr) in H_2O. To make the solutions, $PbBr_2$ and CH_3NH_3Br were mixed at the desired molarity to form $CH_3NH_3PbBr_3$ in DMF or DMSO, shaken to break up the larger pieces of the precursors or pre-formed perovskite, and then sonicated for approximately 10 minutes until the precursors were dissolved completely. HBr was added only immediately before spincoating at a 5:1 or 10:1 ratio in a smaller vial, which was shaken before use.

Saturated solutions

For saturated solutions the same procedure as described in the previous section was followed, except the amounts of the stoichiometric precursors added were now such that they would yield 2M and 4.5M solutions if dissolved in DMF and DMSO respectively, and the resulting mixtures were sonicated for 30 minutes to reach maximum saturation. However, since the solutions were intentionally made supersaturated, not all precursors dissolved during sonication and some residual pre-crystallized perovskite powder remained in the vials. Consequently, the solutions were subsequently centrifuged at 10 000 rpm for 5 minutes for DMF and 10 minutes for DMSO. If HBr was used in saturated solutions, it was added already at the precursor mixing stage at a 10:1 or 5:1 ratio to the polar solvent so that the final solution was still saturated.

Deposition of $CH_3NH_3PbBr_3$

The bromide perovskite films were deposited by spincoating the precursor solution on the substrates, in all cases followed by annealing for 5 minutes at 100°C. The speed of spincoating for the samples discussed in the report is indicated in the corresponding figure captions.

Sample Characterization

The most prominent morphological characteristics of each sample were first determined and imaged using an optical microscope. Overall morphology was characterized with bright field imaging, and roughness was checked qualitatively from the amount of scattering using dark field imaging. For morphological features of sub-micron scale a scanning electron microscope (SEM) was used. An atomic force microscope (AFM) in tapping mode was used for surface roughness characterization. Lastly, an x-ray diffractometer (XRD) was used to determine the material composition and crystallinity of the resulting perovskite films.

RESULTS AND DISCUSSION

Improved nucleation with addition of HBr

Here the possibility of using a $CH_3NH_3PbBr_3$ precursor solution in DMF with added HBr on substrates thiol-functionalized with MPTS is demonstrated to be an effective tool for improving perovskite nucleation and crystal faceting. Panels a) and b) in figure 1 show the resulting perovskite crystallites on O_2 plasma treated and thiol-functionalized glass substrates, when deposited from a 1M precursor solution in DMF. A slight change in morphology could be observed when a functionalized

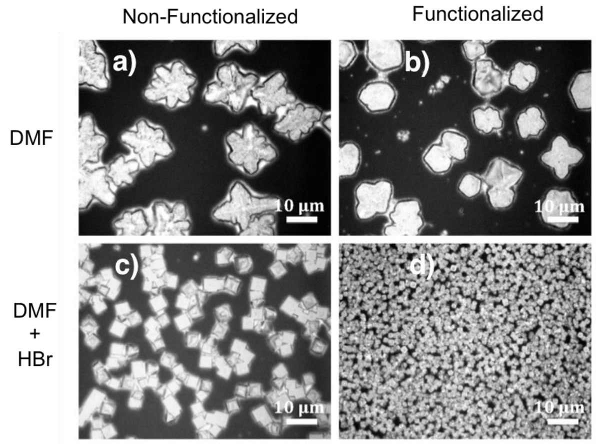

Figure 1 - Bright-field optical microscope images of $CH_3NH_3PbBr_3$ spincoated on a,c) O_2 plasma treated and b,d) thiol-functionalized smooth glass substrates. Top panels show crystallites deposited from a precursor solution in DMF. The bottom panels show crystallites spun from the same precursor solution mixed with HBr at a 10:1 ratio. All samples were deposited at 3000 rpm.

substrate was used, but the crystals remained poorly faceted and with relatively low nucleation density - far from the desired smooth and continuous films. The addition of hydrobromic acid (HBr) to the perovskite precursor solution, however, was found to significantly increase the nucleation density and faceting of the resulting crystals.

Generally, better nucleation with added HBr was not surprising, since it increases the solubility of the precursors and thus the supersaturation concentration, lowering the free energy barrier for nucleation, as already demonstrated by Heo et al. [9]. However, the density of nucleation was improved significantly more on the functionalized substrates as can be seen by comparing panels c) and d) of figure 1. Thus the addition of hydrobromic acid to the precursor solution was facilitating better thiol-perovskite interaction, which had apparently lowered the surface energy of the substrate-crystal interface, making smaller and denser crystallites energetically more favorable than larger crystals that are more sparsely distributed despite their more favorable bulk free energies. Nevertheless, the films were still not continuous, indicating that the bulk free energy term still dominated the lowered surface energy term at the substrate-perovskite interface. Thus the formation of small dense crystallites was a purely kinetic process. This was further demonstrated by increasing spin speed, which yielded even denser nucleation, and smaller crystallites, but not to the extent that a continuous film could be achieved, due to maximum speed limitations of the spincoater.

The increase in faceting of the perovskite crystallites after the addition of HBr, however, cannot be explained only by increased supersaturation concentration, particularly at high spin speeds, where the rate of crystallization is increased, and should thus result in less well defined structures. There is some evidence that the addition of hydrobromic acid to the precursor solution could result in the formation of an intermediate complex. First of all, large transparent crystals could be observed to crystallize out of saturated perovskite solutions in DMF and HBr at a 5:1 ratio after dropcasting on a substrate and leaving overnight. XRD scans of these crystals showed the presence of peaks not corresponding to the perovskite or either of the precursors used, indicating the presence of a new, previously unreported, material, possibly an intermediate complex, formed during the drying of the film. Wang et al. report that combining lead iodide (PbI_2) and hydroiodic acid (HI) in DMF can result in the formation of ($HPbI_x$) [10]. They suggest that this compound is responsible for the observed reduced crystallization rate of the perovskite, ultimately leading to highly crystalline films. Their rationale is that for the perovskite to form the organic precursor ions would need to intercalate the intermediate PbI_6 octahedral framework to replace the hydrogen bonded H^+ ions, which is a relatively slow process. The results of Wang et al. could thus lead to speculation that the observed intermediate crystals could be $HPbBr_x$ precipitated out of the saturated solutions, but further investigation is needed to confirm this hypothesis.

Continuous films with addition of non-solvent

In the previous section it was stated that with increasing the spincoating speed the kinetic barrier for nucleation on functionalized substrates could be significantly reduced; however, full surface coverage could not be obtained due to the maximum spin speed limitations of the spincoater. To reduce the kinetic barrier further a miscible non-solvent was dripped on the substrate during the spincoating step to force the perovskite to precipitate out of the precursor solution. The method was first described by Xiao et al. using chlorobenzene dripping for iodide perovskite deposition on dense TiO_2, yielding highly uniform surface coverage [17].

Figure 2 shows the resulting perovskite films when toluene was dripped during spincoating of the perovskite precursor solution on thiol-functionalized substrates. To achieve completely continuous films the non-solvent had to be added at the point of highest saturation before crystallization, to achieve maximum supersaturation upon contact, leading to rapid nucleation [17]. This point could be pre-determined by first spinning a test sample and observing the point in time at which the film changes color, indicating nucleation. Panel a) of figure 2 shows the resulting film when a 1M precursor solution was used, while panel b) shows the perovskite layer obtained using a saturated precursor solution. The latter shows a significant improvement in smoothness, since individual crystallites can no longer be discerned. Atomic force microscope measurements of the resulting surface show peak-to-valley roughness of ~150 nm, which is still slightly too high to avoid measurement artifacts during optical characterization; however, it should be possible to optimize the processing conditions to yield films of roughness small enough to facilitate these measurements.

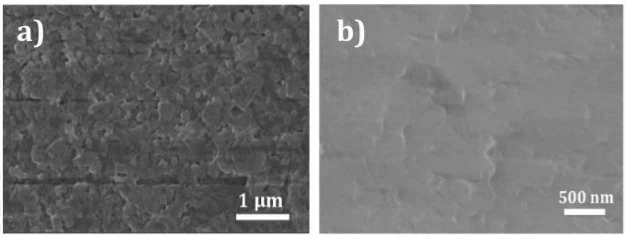

Figure 2 - SEM images of $CH_3NH_3PbBr_3$ films spincoated at 10 000 rpm on thiol-functionalized substrates from a) a 1M and b) a saturated precursor solution in DMF mixed with HBr at a 10:1 ratio with toluene non-solvent dripping at point of highest saturation.

Controllable crystal size with sequential deposition

Alternatively to non-solvent dripping full surface coverage could also be achieved by utilizing a sequential deposition method, with the added benefit of controllable crystal size. Here a saturated precursor solution was dynamically dripped on an already deposited film during a second spincoating step. This yielded continuous films with a morphology resembling that of the starting "seed" layer, but with larger crystallites. It was, however, crucial for the solution to be fully saturated, as it would dissolve the underlying layer even with concentrations just slightly below saturation.

Figure 3 shows the importance of the "seed" layer density and crystal size for the final film morphology. As can be seen by comparing panels a) and c) to b) and d), fewer and larger crystals in the initial layer would result in larger crystallites in the resulting film as well, which is what would be expected, if the decrease in free energy associated with island growth of the perovskite was larger than for layered growth, since more new material would be grown on each individual crystal. It was also found that the crystallite size in the perovskite film could be controlled by changing the spin speed during the second deposition step, as well as by using a different solvent for the saturated solution. In particular, a DMSO precursor solution would yield significantly larger crystals.

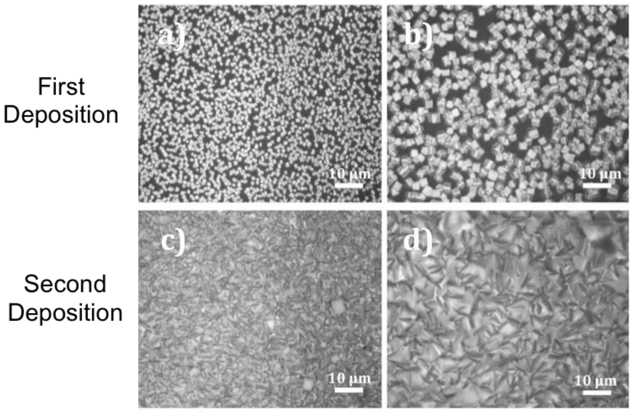

Figure 3 - Bright-field optical microscope images of $CH_3NH_3PbBr_3$ films from sequential deposition on different perovskite “seed” layers. Top row: optical images of $CH_3NH_3PbBr_3$ films deposited at 10 000 rpm for on amino-functionalized substrates from a) a 1M precursor solution in DMF mixed with HBr at a 10:1 ratio and b) a saturated precursor solution in DMF mixed with HBr at a 10:1 ratio. Bottom row: optical images of saturated $CH_3NH_3PbBr_3$ precursor solutions in DMF with HBr at a 10:1 ratio dynamically deposited on the corresponding substrates in the top row during sequential spincoating at 2000 rpm.

CONCLUSION AND OUTLOOK

It has been demonstrated that continuous films of organic-inorganic lead bromide perovskite on planar substrates can be achieved using surface silane functionalization and employing the appropriate processing conditions. Adding hydrobromic acid to the precursor solution was shown to improve the density of nucleation and oriented crystallinity of the film. With the addition of hydrogen bromide to a precursor solution in DMF it was also shown that thin continuous films with low surface roughness could be obtained by introducing a non-solvent during the spincoating process. Alternatively, sequential deposition of a saturated precursor solution during a second spincoating step of a perovskite “seed” layer was used to obtain continuous films of controlled crystal size and thickness.

Following up on these results, optoelectronic characterization of the different perovskite films obtained in this study should be performed to determine the fundamental properties of these materials, and their potential for device integration. In particular, the smooth thin films obtained with the non-solvent dripping method could be useful for more reliable determination of the material’s optical constants with minimal measurement artifacts from surface inhomogeneities. If the visible improvements in film quality are accompanied by improvements in optoelectronic properties, bromide perovskites could be used to produce efficient tandem solar cells with silicon, which would be an important step towards low-cost, high-efficiency photovoltaics.

ROLE OF THE STUDENT

Haralds Āboliņš was an undergraduate student working under the supervision of Dr. Sarah Brittman (AMOLF), Dr. Forrest Bradbury (AUC) and Dr. Erik Garnett (AMOLF) when the research in this report was performed. The idea for surface functionalization was proposed by Dr. Brittman and Dr. Garnett. The subsequent series of experiments were decided on and carried out, the (over 300) samples were analyzed and this paper was written by the student in consultation with all supervisors. Haralds Āboliņš will continue working on research building on the results presented in this report throughout the next academic year as part of the Nanoscale Solar Cells group at AMOLF.

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