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Silicon-Based Tandem Solar Cells

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Lead Iodide by APCVD for Silicon-Perovskite Tandem Solar Cell Production

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Abstract. Recent advancements in silicon-perovskite tandem devices have shown potential to surpass the Shockley-Queisser efficiency limit for an ideal single junction solar cell. However, high-throughput deposition of perovskite on large areas remains challenging. A promising method for scalable perovskite thin film formation is the two-step deposition process, in which a PbI_2 thin film is deposited and converted by exposition to an organic halide source like formamidinium iodide (FAI). The approach in particular addresses the rate limitation for the organic components. Thus, a high-rate deposition of inorganic components such as PbI_2 remains the missing piece. One promising high throughput deposition technique is atmospheric pressure chemical vapor deposition (APCVD), that was already successfully demonstrated for the deposition of n- and p-type amorphous silicon as well as transparent conductive oxides. This work demonstrates for the first time the application of an industrial APCVD tool for producing PbI_2 thin films. Stationary deposition shows a Gaussian injector slit deposition profile, while for in-line deposition a PbI_2 thin film of 365 nm thickness with a maximum rate of 81.2 ± 12.5 nm/min is achieved. High crystallinity is confirmed through X-ray diffraction (XRD), and subsequent wet chemical conversion with a FAI solution yields >500 nm thick perovskite thin films with a maximum implied open circuit voltage (iV_{oc}) of 1.133 V.

Keywords: Lead Iodide, Perovskite, APCVD

1. Introduction

In recent years, tandem silicon-perovskite devices have shown significant potential in enhancing photovoltaic conversion efficiency, with recent advances surpassing the Shockley-Queisser efficiency limit of 33.7% for ideal single-junction cells [1]. High efficiencies have also been achieved using co-evaporation on textured surfaces for large-area applications, indicating the feasibility of these tandem devices for scalable production [2]. A widely used approach for high-quality perovskite thin film formation is the two-step deposition method, initially introduced by Burschka et al. [3]. This technique involves first depositing PbI_2 thin films, followed by exposure to an organic halide source, such as FAI, to complete the perovskite formation [4].

APCVD represents a promising alternative for the efficient, solvent-free deposition of perovskite films. APCVD operates under ambient pressure, potentially lowering production costs and facilitating integration with existing silicon cell manufacturing processes. While the deposition of n- and p-type amorphous silicon was already demonstrated [5] as well as the deposition of transparent conductive oxides [6], the deposition of PbI2 is the missing piece for the production of silicon-perovskite tandem solar cells.

Therefore, for the first time a successful deposition of lead PbI2 thin films via an industrial APCVD tool is presented here. Furthermore, we demonstrate a successful wet chemical conversion of these films into perovskite thin films.

2. Experimental

Indium tin oxide (ITO)–coated square glass substrates (Luminescence Technologies, 15 Ω/sq., 13.8 mm per side) were cleaned in an ultrasonic bath for 15 min each in detergent, acetone, and isopropanol (IPA) and are then UV–ozone treated for 15 min (Ossila Type F) to enhance surface reactivity. The substrates were transferred to a nitrogen glovebox, where a 0.168 mg mL^{-1} ethanol solution of the self-assembling monolayer MeO-2PACz as the hole-selective layer (HSL) was spin-coated at 4000 rpm (acceleration: 1000 rpm s^{-1}) after a 20 s dwell, followed by annealing at 100 °C for 10 min. For further deposition, the samples were sealed in a nitrogen container and transported to an industrial APCVD tool from Gebr. Schmid GmbH (five tracks), with one track modified to include a sublimation chamber and a novel injector for PbI_2 deposition. The APCVD process was performed either in stationary deposition or cyclically by repeatedly passing the substrates beneath the injector. A chamber temperature of 400°C was set to heat the PbI_2 in a metal crucible. The evaporated PbI_2 is then led to the injector with the carrier gas nitrogen at a flow of 8 lpm. The substrate is only heated by the carrier gas. The temperature of the substrate is unknown. Subsequently, the samples returned in the nitrogen container to University of Konstanz. There, under nitrogen in a glovebox, perovskite films were formed by spin-coating a solution of FAI (60 mg mL^{-1}), MABr (6 mg mL^{-1}), and MACl (6 mg mL^{-1}) in IPA at 4000 rpm (acceleration: 1000 rpm s^{-1}) for 30 s atop the PbI_2 layer, followed by annealing at 150 °C to convert PbI_2 into the perovskite phase. In case of FAI concentration variation, all contents were varied with the same factor.

Experiments involving the thickness measurement using a 3D microscope, ITO coated glass substrates without HSL were used. XRD measurements were performed using a Bruker D8 Advance (Z10) system with a Cu source ($\lambda = 1.5418$ Å). The instrument was calibrated prior to each measurement. All measurements used identical settings: Increment of 0.0225°, integration time of 0.3 s, and a 2.5° tilted multilayer polarizer. Layer structures were imaged using a high-resolution scanning electron microscope (SEM), Zeiss Neon 40 EsB, at 5 kV acceleration voltage and varying magnifications. Cross-sections were prepared by focused ion beam (FIB). Photoluminescence quantum yield (PLQY) was quantified using an integrating sphere setup (LuQY Pro, Quantum Yield Berlin) with laser excitation at 433 nm. Spectra were analyzed by spectrometer to determine iVoc values according to Ross and Unold [7,8].

3. Results

3.1 Stationary deposition

For the investigation on the stationary APCVD deposition, PbI_2 was grown on purchased and cleaned glass substrates coated with ITO. The substrates were stopped underneath the injector for a 30 min deposition. Afterwards the samples were characterized by 3D microscopy to determine the deposition profile of the injector. Therefore, the thickness was determined at different sites perpendicular to the injector slit. The profile is shown in Figure 1. A Gaussian fit was applied to determine the profile's width, yielding an FWHM of 5.5 ± 0.7 mm. The maximum thickness at the center of the injector slit is 287.3 ± 13.9 nm. This results in a deposition rate for stationary deposition of 9.6 ± 0.5 nm/min.

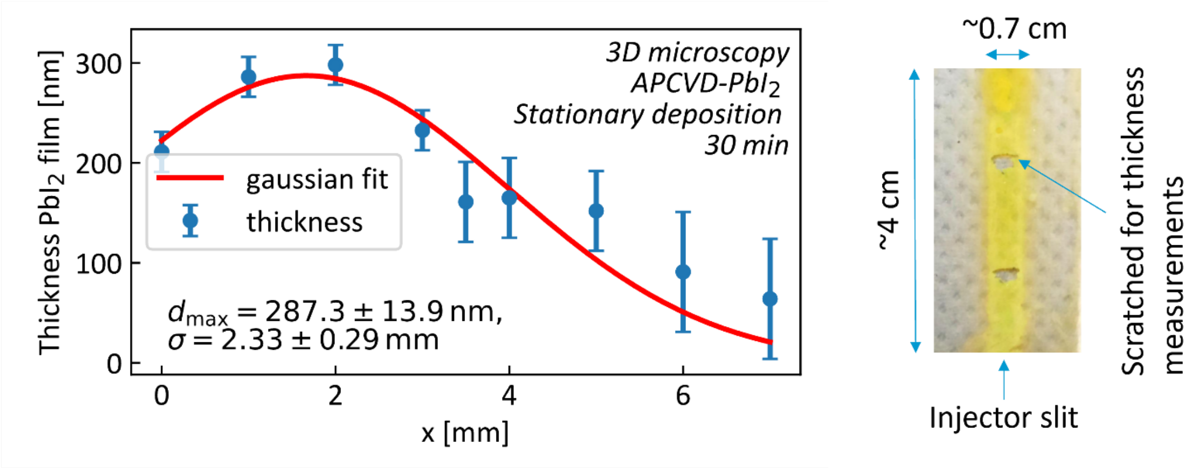

Figure 1. *Deposition thickness profile perpendicular to the injector slit determined by 3D microscopy at stationary deposition for 30 min. The whiskers define the measurement uncertainty (1σ)*

3.2 In-line deposition

For the morphological investigation of the growth behaviour of in-line deposition, the PbI_2 was deposited on glass substrates coated with ITO and the hole-selective layer (HSL) [2-(3,6-dimethoxy-9H-carbazol-9-yl)ethyll]phosphonic acid (MeO-2PACz), which was spin-coated on top of the ITO. To keep the PbI_2 thin film homogeneous and to be able to control the thickness of the deposited film, the substrates were driven underneath the injector multiple cycles. A chamber temperature of 400°C was set to heat the PbI_2 in a ceramic crucible. The evaporated PbI_2 is then led to the injector with the carrier gas nitrogen at a flow of 8 lpm.

First, the growth behaviour of APCVD-PbI2 is be investigated by SEM imaging. In Figure 2, SEM images of APCVD-PbI2 after different numbers of cycles through the injector are shown. In the beginning the ITO substrate is still visible. After 3 cycles, small PbI2 crystals are created and become visible. First, they increase in number, then in size and finally grow together after appr. 10 cycles. In Figure 3(a), a tilted SEM image of a cross section of a PbI2 thin film after 60 cycles is shown. At this point, the substrate is completely covered, crystals have reached µm-size and the hexagonal shape of PbI2 crystals becomes visible. XRD measurements (see Figure 3(b)) confirm the highly crystalline phase of the PbI2 thin film.

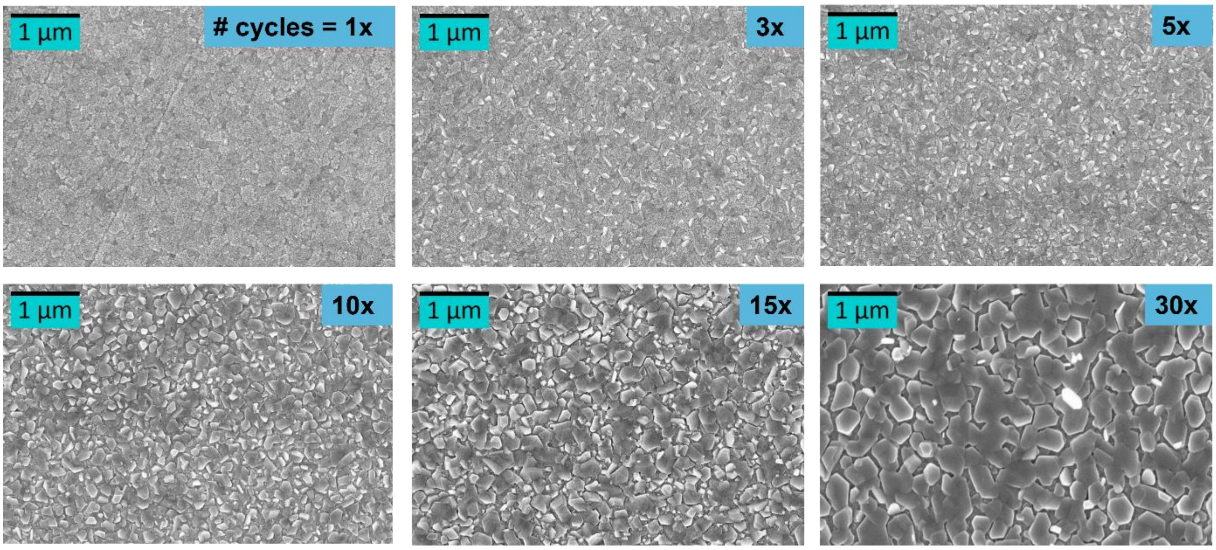

Figure 2. *SEM images of APCVD PbI_2 after different numbers of deposition cycles*

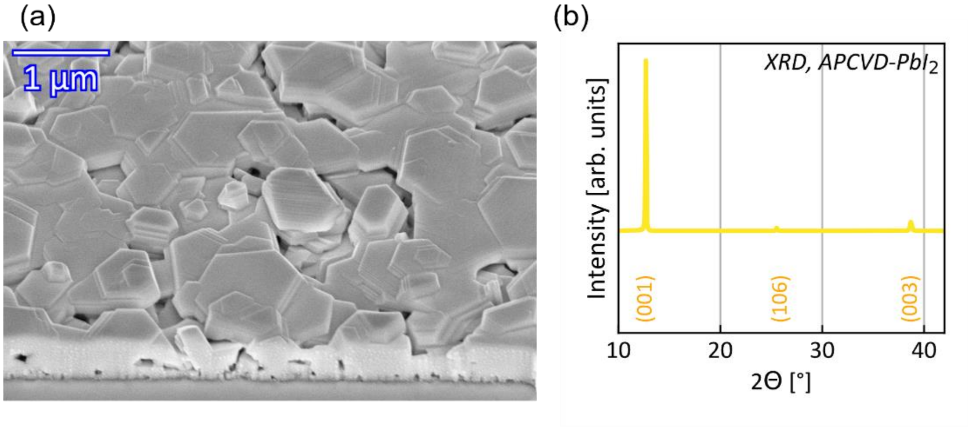

Figure 3. *(a) Cross section SEM image of an APCVD-PbI_2 thin film after 60 cycles. (b) XRD pattern of a PbI_2 thin film deposited by APCVD*

To measure the thickness and determine the deposition rate for in-line deposition, PbI2 was deposited by APCVD on purchased glass substrates with ITO on top, without HSL. The thin films were examined with a 3D microscope in order to measure their thicknesses after different number of cycles. The results are shown in Figure 4. The deposition exhibits an approximately linear increase in thickness with the number of cycles up to 40 cycles. Here, the deposition rate fluctuates around 55 nm/min with a maximum of 81.2 ± 12.5 nm/min. Afterwards a decrease in rate is observed. After 60 cycles the thin films exhibit a thickness of 365 nm. Overall, for the in-line process an average deposition rate of 55.5 ± 2.3 nm/min is achieved. This rate lies among the highest of vapor phase deposition approaches [9].

In comparison, the in-line process enables a more than 5 times higher deposition rate than the stationary deposition. This is expected to be caused by the lower effective substrate temperature during deposition. The substrate cools down between the passages under the injector in case of the in-line deposition. In contrast, for stationary deposition, the substrate stays heated due to the carrier gas flowing from the injector onto the substrate during the entire process. Therefore, a cooling system of the substrate is expected to further enhance the deposition rate. Other methods to further increase the deposition rate would be the optimization of the injector design and the usage of a larger crucible leading to expanded surface area of PbI2 in the sublimation chamber and therefore higher sublimation rates.

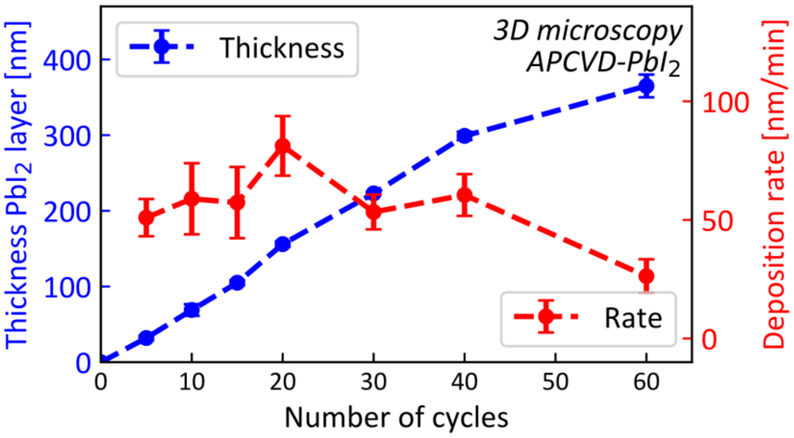

Figure 4. *Thickness of in-line APCVD deposited PbI_2 thin films as a function of the numbers of cycles through the injector. In red the corresponding actual deposition rate is given. The whiskers define the measurement uncertainty (1σ)*

3.3 Conversion to perovskite

APCVD-PbI_2 thin films were successfully converted into perovskite thin films by a wet chemical approach. An FAI solution, also including methylammonium chloride (MACl) and methylammonium bromide (MABr), was spin-coated on top of the PbI_2. The sample was subsequently annealed on a hotplate at 150°C to complete the conversion. Perovskite thin films with sufficiently large thicknesses of above 500 nm have been created. To achieve a complete conversion, an appropriate concentration of the FAI-solution seems important (see Figure 5). At least 60 mg/ml FAI concentration was needed to fully convert the precursor film. The perovskite film with the highest iV_{oc} exhibits a bandgap value of 1.617 eV and an iV_{oc} of 1.133 V, both values determined by PLQY measurements. For this film, a short conversion annealing duration of 1 min was applied. This is a first promising value for the potential as absorber layers in single or multijunction solar cell devices.

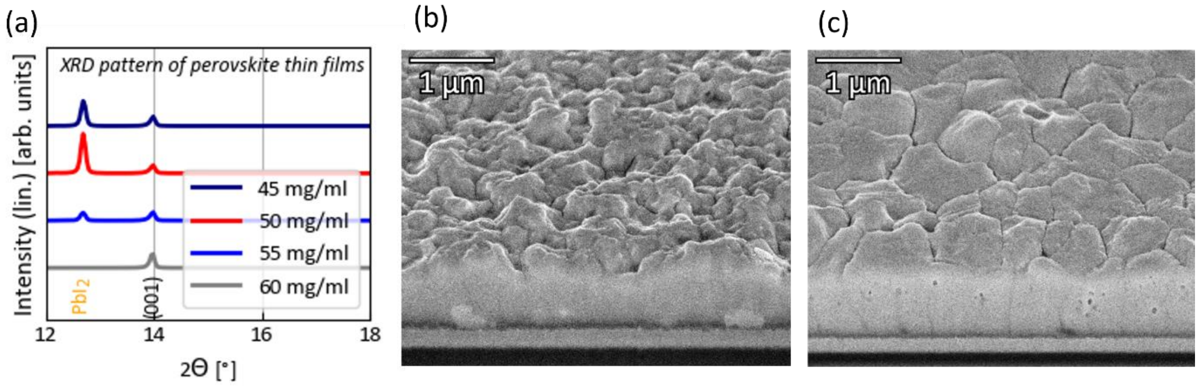

Figure 5. *(a) XRD patterns of perovskite thin films converted from PbI_2 thin films deposited by APCVD for FAI-concentrations between 45 mg/ml and 60 mg/ml. The PbI_2 (001) XRD peak at 12.6° is marked as well as the (001) $FAPbI_3$ perovskite peak at 13.9°. (b) and (c) Tilted SEM cross section images of perovskite thin films created using an FAI concentration of (b) 40 mg/ml and (c) 60 mg/ml. The concentration of the FAI in the second step solution is varied, but the solution volume is kept constant. The concentration of the MACl and MABr contents in the FAI-solution were scaled accordingly (see Experimental section)*

4. Summary

In this work, the first PbI_2 thin films deposited by an industrial APCVD tool are presented. It is shown that µm-sized PbI_2 crystals are created. XRD measurements confirm a high crystallinity. A 365 nm thick PbI_2 thin film is deposited at a maximum rate of 81.2 ± 12.5 nm/min. It is shown that a lower substrate temperature has a beneficial influence on the deposition rate. Furthermore, a successful wet chemical conversion into perovskite thin film is shown, with complete conversion for 60 mg/ml FAI concentration. The perovskite thin films annealed for 1 min reached a maximum iV_{oc} value of 1.133 V.

Data availability statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Author contributions

Tom Burgard[1]: Conceptualization, Supervision, Investigation, Visualization, Writing – Original Draft. Christian Ebert[2]: Project administration, Conceptualization, Investigation.

Heiko Plagwitz[1]: Project administration, Supervision, Conceptualization, Writing – review & editing. Alexander Pippert[1]: Investigation. Sven Seren[2]: Project administration. Giso Hahn[1]: Resources, Writing – review & editing. Barbara Terheiden[1]: Project administration, Funding acquisition, Supervision, Conceptualization, Writing – review & editing

Competing interests

The authors declare no conflict of interest.

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