Eco-Friendly Spray Deposition of Perovskite Films on Macroscale Textured Surfaces

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An innovative sequential eco-friendly spray coating (SEF-SC) technique is developed to uniformly deposit metal halide perovskite films on macroscale textured surfaces, such as textured crystalline-silicon wafers. Contrasting with previous work on spray-coated perovskite solar cells, the method presented in this work completely avoids the use of toxic and dangerous solvents. Both MAPbI₃ and CsFAMAPbI_{3-x}Br_x perovskite films deposited by SEF-SC show excellent optoelectronic properties and no phase segregation, even when synthesized in ambient conditions. Uniform perovskite coatings are obtained on textured-silicon heterojunction solar cells underlining the promise of this method, which holds the potential for scalable wet processing of perovskites on rough substrates, such as for low-cost perovskite/silicon tandem solar cell fabrication.

In the last decade, metal halide perovskites found successful application as photovoltaic absorber layer in solar cells, nowadays resulting in power conversion efficiencies (PCEs) above 25% for lab-scale devices.^[1] Moreover, the recent coupling of perovskite solar cells with silicon solar cell technology enabled already the realization of monolithic tandem devices with PCEs above 28%,^[1] promising a high-end entry of perovskite technology into the mainstream photovoltaics (PV) market.

In the monolithic tandem configuration, also referred as two-terminal (2T) tandem, the perovskite solar cells (PSCs)

are directly realized on top of a silicon bottom cell. Utilizing commercial crystalline silicon (c-Si) wafers brings a technological challenge since the perovskite device needs then to be fabricated on wafers that feature micron-scale randomly distributed pyramidal texture, an imperative characteristic for industrial c-Si solar cells for minimizing reflection losses. The PSCs owe their present prominence to their high PCE obtained via solution-deposition techniques, which is arguably cheaper and simpler compared to conventional vacuum-based deposition for device fabrication. From this perspective, it is required to make solution-based processing of perovskite solar cells compatible with the use of micron-scale textured substrates. Among solution processing techniques, spin coating is widespread due to its process simplicity, ease of access, and because high-quality polycrystalline perovskite films can be obtained. However, this technique is not suitable for upscaling toward industrialization. Also, considering suggestions for large-scale applications in which spin coating is translated into blade coating, the application of this technique usually results in high material consumption, which is undesirable for a sustainable low-cost production. Moreover, spin coating the perovskite layer on textured silicon bottom cells represents a challenge by itself which, to date, reportedly led to poor coverage of the films resulting in low-performing tandems.^[2,3]

At present, 2T tandems are mainly realized following two approaches. In the first case, the c-Si bottom cell features a mirror-polished flat front surface to accommodate spin-coated perovskite films. However, this causes reflection losses in the device, which hamper the overall PCE and require additional antireflective coatings or foils.^[4] In the second case, the perovskite is deposited on textured c-Si via hybrid conversion, where the perovskite precursors, lead(II) iodide (PbI₂) and cesium bromide (CsBr), are thermally evaporated on the c-Si bottom cell and then converted into perovskite by spin coating the organic ammonium salts (formamidinium iodide/bromide, FAI, and FABr, respectively).^[2] In this case, the limiting factor is represented by fine-tuning the conversion process. Overall, both techniques strongly rely on spin coating as a deposition/conversion method, which still represents a roadblock toward scaling-up for commercialization. Indeed, for successful PV

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market entry, the 2T tandems arguably need to meet the contemporary standard size of commercial cells (and modules), which for high-efficiency c-Si solar cells are at present based on 6 in. (pseudo-) squared c-Si wafers.^[5] In this communication, we present an innovative method to deposition metal halide perovskite thin films on microscale textured surfaces by using a sequential eco-friendly spray coating (SEF-SC) technique. Contrasting with previously reported studies on spray-coated perovskite solar cells,^[6–9] our approach completely avoids the use of hazardous solvents. Spray coating is already an established scalable technique which can be easily adopted for various applications.^[10] Here, we adapt the technique for the deposition of both methylammonium lead triiodide (MAPbI₃) and mixed-cation lead mixed-halide (CsFAMAPbI_{3–x}Br_x) perovskites, demonstrating the versatility of the technique and its suitability for the realization of perovskite films on 2T tandem devices through bandgap tuning. First, we prepare an eco-friendly ink of PbI₂ nanocrystals (NCs) via laser ablation synthesis in solution (LASiS)^[11–16] and, after adding CsBr to the colloidal solution, the PbI₂–CsBr ink is deposited via spray coating on textured-silicon bottom cells. Finally, we converted the inorganic precursor layer into mixed-cation lead mixed-halide perovskite with another spray coating step, now of the organic precursors (FAI, FABr, and methylammonium bromide (MABr)). The same two-step spray coating method was adopted in the case of MAPbI₃, by spraying first the PbI₂ NC ink and then MAI solution. With this protocol, the limiting factors of spin coating are avoided,

without losing the benefits of the solution processing or relying on costly vacuum deposition equipment. This technique is compatible with current industrial PV manufacturing standards, paving the way to a scalable low-cost process required for tandem commercialization.

As a test platform for the SEF-SC technique, we first fabricated silicon heterojunction (SHJ) solar cells from float zone n-type c-Si wafers (**Figure 1a**). Our SHJ process starts with immersing the raw, as-cut c-Si wafers into an alkaline solution to obtain 7–10 micrometric randomly distributed pyramids as texture at the front and back surfaces. **Figure 1b** shows the cross-section scanning electron microscopy (SEM) image of the textured surface of the c-Si wafer. We then deposited the intrinsic and doped silicon amorphous layers via plasma-enhanced chemical vapor deposition (PECVD) and later indium tin oxide (ITO) by sputtering to form the passivating heterojunction contacts at front and back, as well as the recombination junction, needed to electrically couple the sub cells in the tandem.^[17] To accommodate the 2T design, we fabricated the SHJ in a so-called rear-junction configuration (i.e., electrons are collected at the illuminated side of the device).^[18] We then sputtered a layer of nickel oxide (NiO_x) as hole transport layer (HTL) for the inverted (p–i–n) perovskite top cell onto the sunward ITO layer of the bottom cell, acting as recombination junction.^[19] More details about the SHJ fabrication are reported in the experimental session. To fully cover the textured surface of the NiO_x/SHJ bottom cell with perovskite precursors, we

Figure 1. a) Schematic representation (not in scale) of the SHJ bottom cell. b) Cross-sectional SEM image of the textured surface of the randomly distributed silicon pyramids. c) UV-vis absorption spectra of the PbI₂ NC ink in IPA and the PbI₂–CsBr thin film on glass. d) TEM image of the PbI₂ NCs obtained by LASiS in IPA.

produced PbI_2 NC inks by laser ablation in solution (LASiS). The main advantages of our LASiS approach are the environmental-friendly solvents used in the process, such as alcohols, and absence of ligands or surfactants to stabilize nanoparticles. Indeed, conventional spray coating of perovskite precursors in high-boiling polar solvents, such as dimethylformamide (DMF) and dimethylsulfoxide (DMSO), often hinder the potential of the technique due to the toxicity and hazards related to these solvents. Contrasting with this, we are able to synthesize PbI_2 NC inks in low-boiling alcoholic solutions, such as isopropanol (IPA), via laser ablation. The inks are stable over days, requiring only a sonication treatment before spray depositions when stored for long time (Figure S1, Supporting Information). Moreover, the absence of stabilizers in the inks avoids any secondary post-treatment processes, simplifying overall the deposition and cost-efficiency of the process. We refer to the supporting information (Figure S2, Supporting Information) for the experimental setup of LASiS technique and ablation details. Figure 1c shows the ultraviolet–visible (UV–vis) absorption spectra of the PbI_2 NC ink and PbI_2 -CsBr thin film deposited on glass. The typical absorption spectrum of PbI_2 NC ink is also preserved, once spray-coated over a substrate, with the typical optical absorption edge at 500 nm. A scattering contribution to the spectrum can be observed for the colloidal solution in the near infrared region since the average dimensions of the PbI_2 NCs are several tens of nm (Figure S3, Supporting Information). The scattering contribution further increases once the PbI_2 NCs are spray coated onto a substrate, since larger structures are formed. Figure 1d depicts the transmission electron microscopy (TEM) image of the ablated PbI_2 NCs. The ablated NCs appear in the typical hexagonal shape of PbI_2 crystals,^[20] testifying their crystallinity after synthesis by laser ablation in solution. An average nanocrystals diameter of 51 ± 9 nm was estimated from TEM images, in line with the value of 64 ± 11 nm obtained from dynamic light scattering (DLS) measurements (Figure S3, Supporting Information). To form

a compact thin film, we first spray coated PbI_2 NCs and PbI_2 -CsBr inks on top of the textured surface of SHJ bottom cells, respectively. Then they were respectively converted into MAPbI_3 and $\text{CsFAMAPbI}_{3-x}\text{Br}_x$ perovskite films by spray coating the solution of the organic precursors, as reported in the experimental section. Figure 2a,b respectively shows the top-view and cross-sectional SEM images of the spray-coated PbI_2 NC ink with optimized volume over the textured c-Si surfaces, which reveals conformal coverage of the c-Si pyramids. Both the tips and the valleys of the pyramids are well covered by spraying 2.0 mL of PbI_2 NC ink with a concentration of 0.3 mg mL^{-1} in IPA. Lower solution-loading amounts result in uncovered areas, in particular on the tip of the pyramids (Figure S4, Supporting Information). On the contrary, higher solution-loading films lead to the formation of micrometric-thick bridges between the pyramids (Figure S5, Supporting Information), which complicate subsequent perovskite conversion and could hamper tandem device performance. Similar results were obtained for the PbI_2 -CsBr ink deposition (Figure S6, Supporting Information), where 2.0 mL solution was confirmed as the best ink volume to spray for obtaining a good conversion and uniform coating of the perovskite film over the textured c-Si surface. As a source of Cs^+ for the mixed-cation lead mixed-halide perovskite, the inorganic precursor ink was prepared by adding an aqueous solution of CsBr to the PbI_2 NC ink, prepared by laser ablation in IPA. To get fully converted MAPbI_3 and $\text{CsFAMAPbI}_{3-x}\text{Br}_x$ perovskites from PbI_2 and PbI_2 -CsBr layers, we prepared two different types of organic precursor solutions containing MAI and a mixture of FAI:FABr:MABr in ethylacetate (EA), respectively. For the conversion process, all the samples were annealed at 100°C for 10 min under inert conditions (Ar flux). Images of the spray coating conversion and of our home-made setup can be found in the Supporting Information (Figures S7 and S8, Supporting Information). The SEM micrographs of the best MAPbI_3 and $\text{CsFAMAPbI}_{3-x}\text{Br}_x$ samples are reported in Figure 2c,d and e,f,

Figure 2. Top-view and cross-section SEM images of the spray-coated films onto the textured silicon bottom cell. a–d) PbI_2 NC ink, b–e) MAPbI_3 perovskite, and c–f) $\text{CsFAMAPbI}_{3-x}\text{Br}_x$ mixed perovskite films after spray conversion.

respectively. Both samples show a conformal perovskite layer with well-defined crystals; the conformal coating mimics the texturing of the SHJ bottom cell. To find the optimal conversion conditions, we changed both the concentration and the volume of the organic precursor solutions sprayed over the $\text{PbI}_2/\text{PbI}_2\text{-CsBr}$ thin films. The volume seemed not to be a relevant parameter by itself. What turned out to be more critical was to calibrate the ink flow of the spray coater to guarantee that the spray deposition process was complete in just one cycle. One-cycle spraying is important to avoid dissolution and recrystallization of the perovskite crystals, which would otherwise lead to a non-conformal coating on the textured substrate. As expected, at a fixed volume, organic solutions with low concentrations lead to an unconverted $\text{PbI}_2/\text{PbI}_2\text{-CsBr}$ layer at the perovskite/ NiO_x interface of the top cell in the 2T tandem device structure (Figure S9b, Supporting Information). On the contrary, those solutions with higher concentrations resulted in crystallization of the organic precursors onto the perovskite films. Moreover, we found that the concentration of MAI solutions plays a key role in determining the quality of the final perovskite film in the case of MAPbI_3 . In particular, we synthesized MAPbI_3 with bigger grains (up to 700 nm) by spraying an over-stoichiometric quantity of MAI over the PbI_2 NCs (Figures S9 and S10, Supporting Information). Despite this, the best MAPbI_3 film (Figure 2b–e) was obtained in stoichiometric conditions to get a uniform coating on the textured c-Si substrate without MAI accumulations. For this, a 1:1 molar ratio between PbI_2 and MAI was used, by spraying 2.0 mL of 0.3 mg mL⁻¹ PbI_2 NC ink in IPA and then converting into perovskite by spraying 1.0 mL of 0.2 mg mL⁻¹ MAI solution in EA. In the case of $\text{CsFAMAPbI}_{3-x}\text{Br}_x$ perovskites, good conversion was only obtained in stoichiometric conditions between inorganic and organic precursors. The best mixed-cation lead mixed-halide perovskite film (Figure 2c–f) was obtained by spraying 2.0 mL of 0.3 mg mL⁻¹ $\text{PbI}_2\text{-CsBr}$ ink and then converting it by spraying 1.0 mL of 5.6 mg mL⁻¹ FAI-FABr-MABr (10:6:3 molar ratio) solution in IPA diluted 1:50 (v:v) in EA. Samples of the spray-cast, mixed perovskite with increasing thickness are reported in the supporting information (Figure S11, Supporting

Information). All of the spray-coated perovskite films show smaller crystal grains than those reported in literature.^[6,8] We ascribe this to the PbI_2 NC precursor layer, which provides a large amount of perovskite nucleation centers. Moreover, the dissolution and the recrystallization of precursors and perovskite, respectively, are highly hindered using low-boiling volatile solvents for the whole spray coating deposition process. For further structural analysis, we performed X-ray diffraction (XRD) measurements as shown in Figure 3a. Both MAPbI_3 and $\text{CsFAMAPbI}_{3-x}\text{Br}_x$ films do not present any residual reflections of the PbI_2 precursor, suggesting complete conversion into perovskite. To investigate the optical properties of the spray-coated perovskite films, we prepared a specific set of samples on textured silicon wafers covered by 300 nm of silicon nitride (SiN_x) deposited via PECVD. The dielectric SiN_x layer is required to isolate the perovskite films from possible electronic interaction with the c-Si wafers. On these substrates, we performed time-resolved photoluminescence (TRPL) spectroscopy with a streak camera to collect the spectral shape and time evolution of the PL at once for MAPbI_3 and the $\text{CsFAMAPbI}_{3-x}\text{Br}_x$ perovskite films. Figure S12 (Supporting Information) shows the 2D pseudocolor graphs for each sample. Additionally, we used a MAPbI_3 film spin coated on quartz substrate as a reference sample. Figure 3b shows the normalized PL spectra of MAPbI_3 (blue), $\text{CsFAMAPbI}_{3-x}\text{Br}_x$ (orange), and reference spin-coated MAPbI_3 (black). Both the spray- and spin-coated MAPbI_3 films exhibit emission centered at 770 nm, which is indicative of a bandgap of around 1.61 eV, in agreement with MAPbI_3 polycrystalline films.^[21,22] The mixed perovskite shows a broader and blueshifted emission, centered at 736 nm, indicative of a higher bandgap around 1.68 eV. This corresponds to a Br^- ratio of about 25% with respect to I^- .^[23] Moreover, the emission is stable even after keeping the $\text{CsFAMAPbI}_{3-x}\text{Br}_x$ perovskite sample in ambient conditions for many hours, without evidences of dominant phase segregation (Figure S13, Supporting Information). This is in agreement with previous results from mixed halide perovskites obtained via LASiS.^[15,24] Figure 3c shows the PL lifetime of the three samples obtained with a laser excitation at 532 nm (further details are reported in

Figure 3. a) XRD diffraction pattern of the $\text{CsFAMAPbI}_{3-x}\text{Br}_x$ (orange), MAPbI_3 (blue), and spray-coated PbI_2 (black) films. The reflection peaks at 33° is from the silicon substrate. b) Normalized PL spectra and c) transient PL decay of spin-coated MAPbI_3 (black), spray-coated MAPbI_3 (blue), and spray-coated $\text{CsFAMAPbI}_{3-x}\text{Br}_x$ (orange) perovskite films on textured silicon. The spin-coated MAPbI_3 (black) on quartz substrate is shown as reference. The samples were excited at 532 nm with a fluence of $0.5 \mu\text{J cm}^{-2}$.

the experimental session). We used a biexponential fit to extrapolate the average PL lifetime (τ_{avg}) from the decay transients. The MAPbI₃ films shows a similar transient at later times; on the other hand, the films have PL lifetimes of 21 and 33 ns for the spray-casted and spin-coated films, respectively. For the CsFAMAPbI_{3-x}Br_x sample, the PL lifetime is slightly reduced, with a τ_{avg} of 17 ns. Although, the mixed cations stabilize the structure and enhances the PL lifetime of the perovskite, increasing the Br ratio in the structure (wider bandgap) reduces the PL lifetime. This has been attributed mainly to halide segregation under illumination.^[25,26] In our case, we did not observe notable halide segregation during measurement for optimized samples. Additionally, we conducted the TRPL measurements for the samples prepared with different volume of precursor solution as discussed before. Parallel to SEM micrographs, mixed-cation lead mixed-halide perovskite made from 1:2 molar ratio between inorganic–organic precursors resulted in a longer lifetime which also proves the better conversion yielding and higher quality of the mixed perovskite film (Figure S14, Supporting Information).

An innovative method is presented to deposit metal halide perovskite thin films on textured surfaces by using a sequential eco-friendly spray coating (SEF-SC) technique. The SEF-SC protocol, avoids the usage of toxic and dangerous solvents, solving an important step of perovskite solar cell technology. Starting from a PbI₂ NC ink made by laser ablation in alcohol, we demonstrate its deposition on textured silicon substrates by spray coating and its conversion into the desired perovskite layer by a second spray step of the organic precursors for obtaining MAPbI₃ and CsFAMAPbI_{3-x}Br_x. SEM investigation allowed to optimize the deposition conditions for obtaining a conformal coating of the textured SHJ bottom solar cells. Good perovskite coverage was obtained, with smaller crystal grains than those reported in literature. This result is related to the PbI₂ NC precursor layer and the low-boiling volatile solvents used for the spray coating process. Different conversion conditions and/or perovskite post-treatments could be evaluated to improve the morphology of the films, to decrease the amount of grain boundaries and increase the grain size.^[27–32] XRD patterns, testified a complete conversion of precursors into perovskite phases. PL measurements showed a bandgap change for Br incorporation into CsFAMAPbI_{3-x}Br_x film, which is important for perovskite-silicon tandem application. The presented new deposition protocol well suits industrial standards and will be interesting for future large-scale tandem fabrication by optimizing also the spray coating of the layers needed for a complete cell.

Experimental Section

Sequential Eco-Friendly Spray Coating: A sketch of the sequential eco-friendly spray coating (SEF-SC) approach presented in this work for deposition of perovskite thin films over NiO_x/ITO/textured silicon substrates for silicon-perovskite 2T tandem solar cells application is depicted in Figure S8 (Supporting Information). The process was performed by using a home-made spray coating system operating with a nitrogen flow at 3 bar and with an output temperature of 45 °C. The airbrush was controlled by stepper motors regulating the horizontal and vertical steps, with a speed of 0.4 cm s⁻¹. The tip (0.25 mm nozzle

diameter) was located 3 cm far from the substrates, which were heated at 100 °C by a hot plate integrated into the spray coater. The optimized ink flow for the first (Figure 2a) and the second step (Figure S8b, Supporting Information) was equal to 0.2 and 0.4 mL min⁻¹ respectively. All the perovskite films were deposited under extractor hood (50% humidity) with an area of 1.5 × 1.5 cm². Finally, all the samples underwent thermal annealing for 10 min at 100 °C under inert atmosphere (Ar flow).

PbI₂ NC–CsBr Thin Film on Soda-Lime Glass: The precursor thin film reported in Figure 1c was obtained by spray coating 2.0 mL of PbI₂ NC ink in IPA (0.3 mg mL⁻¹) mixed with 20 µL of CsBr aqueous solution (0.7 mg mL⁻¹) over soda-lime glass (1 × 1 cm²) substrate, heated at 100 °C by a hot plate. The PbI₂ NC–CsBr ink was sonicated for 5 min before spraying. The spray deposition was performed under extractor hood in ambient condition, with a constant ink flow of 0.3 mL min⁻¹.

Steady-State Photoluminescence (SS-PL): SS-PL measurements were performed using a Renishaw InVia micro-Raman instrument, equipped with a CCD detector (100 µm slits) and a piezoelectric xyz scanning stage. A 633 nm line of He-Ne laser (Renishaw RL63, 13 mW) excitation beam with an output power of 1 µW was focused on the sample using a 50× objective. A reference of crystalline silicon was used before and after each measurement to account for small (less than 5%) intensity fluctuations of the laser output. All the measurements were performed in ambient conditions.

Time-Resolved Photoluminescence (TRPL) Spectroscopy: TRPL measurements were conducted using a high-resolution streak camera system (Hamamatsu, C10910). The excitation beam at 532 nm (HELIOS 532-4-125, Coherent Inc.) was focused to pump the perovskite, mounted inside the sealed nitrogen chamber to prevent any changes due to exposure to oxygen and humidity. The associated PL emission was spectrally and temporally resolved using a spectrograph and streak camera system. The data were acquired in photon counting mode using the Streak Camera software (HPDTA) and exported to Origin Pro 2015 for further analysis. All measurements were done at room temperature.

Silicon Bottom Cell Fabrication: SHJ solar cells are realized on float-zone double-side-textured four inches wafers (thickness 250–280 µm) as defined in the previous study.^[33] The wafers are processed in alkaline solution to obtain randomly distributed pyramidal texturing and cleaned in RCA1 and RCA2 solution. Amorphous intrinsic and doped silicon layers are deposited via plasma-enhanced chemical vapor deposition (PECVD, Indeotec Octopus 2). The back contact of the SHJ is realized by sputtering sequentially ITO and Ag (150 and 250 nm, respectively) in the PVD part of the Octopus 2 cluster. To mimic the tandem configuration, an ITO sputtered layer (25 nm) covered by a sputtered layer of NiO_x (17 nm) are deposited as the recombination junction and the perovskite hole transport layer (Angstrom EvoVac).

Supporting Information

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

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Conflict of Interest

The authors declare no conflict of interest.

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