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Luis K. Ono,† Matthew R. Leyden,† Shenghao Wang and Yabing Qi*

Organometal halide perovskites (OHPs) are currently under the spotlight as promising materials for new generation low-cost, high-efficiency solar cell technology. Within a few years of intensive research, the solar energy-to-electricity power conversion efficiency (PCE) based on OHP materials has rapidly increased to a level that is on par with that of even the best crystalline silicon solar cells. However, there is plenty of room for further improvements. In particular, the development of protocols to make such a technology applicable to industry is of paramount importance. Vapor based methods show particular potential in fabricating uniform semitransparent perovskite films across large areas. In this article, we review the recent progress of OHP thin-film fabrication based on vapor based deposition techniques. We discuss the instrumentation and specific features of each vapor-based method as well as its corresponding device performance. In the outlook, we outline the vapor deposition related topics that warrant further investigation.

1. Introduction

Organometal halide perovskite (OHP) solar cells have emerged as the most promising candidate for the next generation high efficiency solar cell technology that is compatible with low-cost, low-temperature processing, flexible substrates, and large-area fabrication using e.g. ultrasonic spray-coating,† printing,‡ roll-to-roll,§ and vapor deposition techniques.‖ Laborat...
the space formed by the eight adjacent octahedra (Fig. 1). The larger cation A (A being larger than B) can be Cs, methylammonium (CH3NH3+, MA+), ethylammonium (CH3CH2NH3+, EA+), formamidinium (NH2CH═NH2+, FA+), or mixed CH3NH3 and 5-aminovaleric acid (5-AVA) cations ([5-AVA],(-CH3NH2)6). The crystallographic stability and probable structure are estimated by considering the Goldschmidt tolerance factor and the octahedral factor. Nevertheless, the determination of chemical and thermal stability of the resultant perovskite structure requires more detailed analysis. CH3NH3PbI3, the most commonly employed material in OHP solar cells, was reported to have a high absorption coefficient (direct bandgap of ~1.55 eV) and high mobilities for electrons (7.5 cm2 V−1 s−1) and holes (12.5–66 cm2 V−1 s−1), i.e., ambipolar nature, resulting in long carrier diffusion lengths (100 nm to 1 μm). Although the amount and role of incorporated Cl are still under debate, mixed methylammonium-lead halide CH3NH3PbI3−xClx is another type of halide perovskite reported with an even higher charge-carrier mobility (~33 cm2 V−1 s−1), resulting in carrier diffusion lengths of up to 3 μm. Theoretical studies have shown that most point defects in OHP form shallow defect states. In addition, grain boundaries were shown that they do not generate gap states, which makes the electronic property behavior of polycrystalline halide perovskite similar to that of a thin-film single crystal. In a recent work by deQuilettes et al., the existence of large spatial variations in photoluminescence (PL) intensity and carrier recombination lifetimes were probed using a confocal PL microscope. In particular, higher contrasts were observed at the grain boundaries in comparison to the bulk of the material within the individual grains of CH3NH3PbI3−xClx perovskite. Differences in PL intensities were attributed to the variations in radiative and nonradiative recombination dynamics. The question whether the perovskite solar cell system is excitonic, similar to an organic solar cell, which requires a heterojunction interface to separate electron-hole pairs, or instead photoexcitations spontaneously dissociate into free carriers in the bulk, similar to inorganic solar cells, has not been completely settled. On the other hand, a number of studies suggest that exciton binding energies (BEs) in perovskites are in the range of ~2–50 meV, and ultrafast interfacial charge-transfer dynamics take place; collectively, the majority of these observations imply that perovskite solar cells are predominantly non-excitonic similar to inorganic solar cells showing relatively low exciton BEs, e.g., Si (15.0 meV), GaAs (4.2 meV), and CdTe (10.5 meV).

In the 1990s, Mitzi and co-workers studied OHPs and discovered desirable physico-chemical properties of these materials mainly for electronic applications. Almost in parallel, Grätzel and co-workers developed a new class of photovoltaic technology, dye-sensitized solar cells (DSSCs or Grätzel cell) and solid-state DSSCs (ssDSSCs) shown in Fig. 2. Miyasaka and co-workers were the first to apply perovskites in DSSCs in 2009. The dye was replaced by methylammonium lead triiodide/tribromide (CH3NH3PbI3 and CH3NH3PbBr3) perovskites in DSSC configuration obtaining a PCE of ~3.8% and ~3.1%, respectively, using the iodine/ triiodide redox liquid electrolyte as the hole-transport material. Due to the high instabilities of the perovskite materials in the electrolytes, ruthenium-based dyes were still the preferable choice. In 2012, Park and co-workers fabricated all solid-state perovskite (CH3NH3PbI3) solar cells and achieved a PCE of ~9.7% and much better durability. The key advance was made possible by replacing the liquid electrolyte with a solid hole transporting layer (HTL) material, Fig. 2. Since then, a myriad of reports have been published exploring the different perovskite materials, various device architectures, and fabrication methods. Both the dye and CH3NH3PbI3 assume the function of a sensitizer in which light absorption induces subsequent electron injection into the conduction band of the mesoporous TiO2 scaffold (electron transport layer, ETL) accompanied by hole injection from the oxidized sensitizer to the highest-occupied molecular orbital (HOMO) of the HTL.

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Further charge transport of electron and hole through the external circuit completes the photovoltaic operation. The use of TiO₂ and HTL as selective contacts ensures that photoexcited charge carriers (electrons and holes) are transported in opposite directions. In a separate experiment, Lee et al. showed that a mesoporous (mp-) scaffold made of Al₂O₃ instead of TiO₂ generated a similar PCE even though Al₂O₃ is an insulating material. This paradigm has been rationalized by suggesting that perovskite itself is a good electron conductor; if so, no mp-TiO₂ scaffold is necessary at all. This led to a much simpler device architecture, Fig. 2, and first confirmed by Liu et al., who showed efficient (PCE ~ 15.4%) CH₃NH₃PbI₃–Cl based perovskite solar cells without employing any mesoporous metal oxide layer. Etgar et al. had demonstrated that CH₃NH₃PbI₃ could also act as an efficient hole conductor, which could even eliminate the need for employing the additional HTL layer. However, generally both electron and hole selective contacts contribute to the enhancement of the cell fill factor (FF). In particular, the hole selective contact tends to enhance the open-circuit voltage (V_{oc}) by minimizing interfacial charge recombination processes, i.e. the HTL performs both functions of blocking electrons as well as transporting holes efficiently.

The film morphology, thickness, stoichiometry, crystallinity as well as material purity have significant impact on the overall solar cell performance. A variety of solution- and vapor-based OHP deposition techniques have been reported including one-step spin-coating, two-step deposition techniques, solvent–solvent extraction, vapor-assisted solution processes, dual-source vacuum deposition, hybrid deposition, hybrid chemical vapor deposition, sequential vapor deposition, flash evaporation, etc. One-step spin-coating is one of the widely used methods because of its simplicity and low-cost. However, the films prepared by this method often have a poor morphology (incomplete coverage) especially in the case of planar architecture, which results in decreased solar cell performance. In the two-step process, a layer of metal halide is deposited by spin-coating followed by dipping the film into the organic salt solution and perovskite formed by a chemical reaction. However, due to the high reaction rates of perovskite formation, it is challenging to optimize the processing conditions with sufficient reproducibility. Despite the fact that laboratory record efficiencies have been obtained by solution processing, it is observed that the reaction kinetics need to be rigorously controlled to maintain consistent device performance and minimize batch-to-batch variations. Yang and co-workers introduced a CH₃NH₃I vapor-based approach for the deposition of a perovskite layer called vapor-assisted solution process (VASP). In their process, PbI₂ films were annealed in MAI vapor at 150 °C in an N₂ environment for 2 h, Fig. 3a. Perovskite films exhibited high crystallinity, uniform surface coverage and large grain sizes up to 1 micron, Fig. 3b–d. The high quality films of CH₃NH₃PbI₃ enabled enhanced solar cell parameters of short-circuit current (J_{sc}), V_{oc}, FF, and PCE: 19.8 mA cm⁻², 0.924 V, 0.663, 12.1%, respectively, in a planar architecture, Fig. 3e. The surface roughness of the films was measured by atomic force microscopy (AFM) (5 × 5 μm², Fig. 3f) and calculated to be 23.2 nm. In a recent publication, the authors state that it is still unclear why the efficiency of perovskite solar cells based on VASP is slightly lower than that of devices derived from an optimized solution process. In this review, we focus on the difference vapor-based methods to deposit perovskite films, which in many cases show properties different from their counterparts prepared by solution-based methods.

2. Vapor deposition by dual-source

2.1. Vapor deposition system description

Vapor deposition techniques are widely used in the semiconductor industry aiming at large scale production in optoelectronic applications. The viability of OHP material synthesis by physical vapor deposition techniques has also been demonstrated. Such techniques offer unique advantages such as (1) it is feasible to fabricate films with high-
In 2013, Liu et al.\textsuperscript{4} reported the synthesis of three-dimensional CH$_3$NH$_3$PbI$_{3-x}$Cl$_x$ by using the dual-source vapor deposition technique with PbCl$_2$ and CH$_3$NH$_3$I as precursors leading to high efficiency photovoltaic devices (PCE \textasciitilde 15.4\%, Table 1). Similarly, Malinkiewicz et al. deposited a pure CH$_3$NH$_3$PbI$_3$ perovskite by using PbI$_2$ and CH$_3$NH$_3$I sources showing uniform film formation with a root mean square (RMS) roughness of 5 nm measured by AFM.\textsuperscript{5} In addition, the films showed uniform grainy structures with an average grain size of 150 nm.\textsuperscript{7} The schematic illustration of the dual-source vacuum deposition process is shown in Fig. 4.\textsuperscript{7,73} PbX$_2$ (X = I, Cl) and CH$_3$NH$_3$I precursor materials contained in crucibles are heated (co-evaporation) to their corresponding sublimation temperatures. CH$_3$NH$_3$PbI$_{3-x}$Cl$_x$ and CH$_3$NH$_3$PbI$_3$ perovskite layers are formed on the substrate that is fixed at a distance of \textasciitilde 20 cm above the crucibles.\textsuperscript{2} Typical base pressures of 10$^{-5}$ to 10$^{-6}$ Torr are reached after loading the precursor materials.\textsuperscript{4,6} The stoichiometry (chemical composition) and film thickness are monitored with the aid of piezo-electric sensors\textsuperscript{4,5} mounted inside the vacuum chamber (or a quartz crystal microbalance, QCM). Because perovskites are formed by the co-evaporation process, it requires the initial calibration as precise as possible for the thicknesses of individual evaporated PbX$_2$ and CH$_3$NH$_3$I films. Material density ($\rho$), acoustic impedance (or Z-ratio), and geometric (or tooling factor) are parameters that need to be determined for the calibration of evaporation rate of the material being sublimated. Often it is difficult to find those parameters especially for organic compounds. For example, Liu et al. assumed the density and Z-ratio of CH$_3$NH$_3$I to be 1 g cm$^{-3}$ and 1, respectively, because its precise density is unknown.\textsuperscript{4} The density for CH$_3$NH$_3$Cl of 1.1 g cm$^{-3}$ was previously reported.\textsuperscript{4} More recently, the density value of 2.224 g cm$^{-3}$ for CH$_3$NH$_3$I has been reported.\textsuperscript{66} In addition, the tetragonal CH$_3$NH$_3$PbI$_3$ perovskite phase was calculated to have a density of 4.149 g cm$^{-3}$.\textsuperscript{88}
The densities of PbCl₂ and PbI₂ can be found in the literature with typical values of 5.85 g cm⁻³ and 6.16 g cm⁻³, respectively. As the source-to-substrate distance generally differs from the source-to-QCM distance, it is often a common practice to perform some initial tests to determine the tooling factor. A certain amount of material is deposited on a flat substrate recording the nominal thickness measured by the QCM with a preset tooling factor value. This nominal thickness value is then compared to the thickness value determined using another technique (e.g., AFM or surface profilometry). The linear relationship provides the new tooling factor of the evaporation system. As it will be discussed in more detail in the next section (3. Hybrid deposition method), the calibration procedure for the CH₃NH₃I was reported to be difficult due to the formation of a non-uniform layer dominated by the Volmer–Weber or Stranski–Krasanov growth mode and the volatile nature of the organic film.³⁷–⁷⁹ Alternatively Malinkiewicz et al.⁵,⁷¹ kept the evaporation temperature for the CH₃NH₃I crucible constant (at 70 °C) and varied the CH₃NH₃I : PbI₂ ratio by changing only the evaporation temperature of the PbI₂ crucible (250–260 °C). The optimum conditions were determined by analyzing the evaporated perovskite films by grazing incident X-ray diffraction (GIXRD). Once the optimum PbI₂ crucible temperature (250 °C) for generating the stoichiometric perovskite is determined, perovskite films with similar properties can be prepared reproducibly indicating the robustness of the protocol.⁵,⁷¹

The substrate holder is maintained at near room-temperature during perovskite deposition for the processes described above.⁵,⁷¹ Because of low-temperature processing, it is highlighted that the technique is of particular interest for the deposition of perovskite films onto flexible substrates. Liu et al.⁴ provide side-by-side comparison on the morphology of the CH₃NH₃PbI₃₋ₓClₓ perovskite films prepared by the solution and dual-source vacuum evaporated films. For example, the top- and side-views of scanning electron microscopy (SEM) highlight that vacuum-deposited films show full coverage and are extremely uniform with crystalline features on the size scale of hundreds of nanometers, Fig. 5a and b. Large-area cross-sectional SEM images, Fig. 5c and d, reveal that solution-processed films exhibit large variations in film thickness (50 to 410 nm) over the sample area, whilst vacuum-evaporated films have a constant film thickness of ~330 nm. X-ray diffraction (XRD) patterns for both solution- and vacuum-processed show the main diffraction peak positions to be identical indicating that both techniques generate similar mixed-halide perovskite, Fig. 5e. The observed diffraction peaks at 14.12°, 28.44°, and 43.23° are assigned to the (110), (220), and (330) planes of the orthorhombic crystal structure.⁴⁷ The small peak at 12.65° is assigned to the (110) diffraction peak of the remaining PbI₂ compound. The best solar cell device based on the planar heterojunction architecture of FTO/c.l.-TiO₂/CH₃NH₃PbI₃₋ₓClₓ/spiro-MeOTAD/Ag generates solar cell parameters of Jsc, Voc, FF, and PCE: 21.5 mA cm⁻², 1.05 V, 0.67, 15.4%, respectively, Fig. 5f. More recently, Lin et al.⁷² reported the use of vacuum-processing CH₃NH₃PbI₃-perovskite planar structures with optimized ultrathin n- and p-type organic interlayers of PCBM and PCPDTBT, respectively, which serve to modify the electrode work functions. Enhanced solar cell parameters were obtained: Jsc = 21.9 mA cm⁻², Voc = 1.05 V, FF = 0.72, and PCE = 16.5%. The complete devices (ITO/PEDOT:PSS/PCPDTBT/CH₃NH₃PbI₂/PCBM/LiF/Ag) had an active area of 0.2 cm².

### 2.2. Large-area solar cell

The first attempt for the fabrication of a larger-area solar cell (0.95 cm²) was reported by Malinkiewicz et al. in an inverted device architecture [ITO/PEDOT:PSS/polyTPD/CH₃NH₃PbI₂/PCBM/3TPYMB/Au], Fig. 6. In most reports the active area sizes of the cells are smaller than 0.1 cm², Table 1. Despite the general trend of lower FF as the active area increased, the authors observed that the high Voc was maintained and attributed to negligible surface and sub-bandgap trap states in vacuum-deposited perovskite films.⁵ The industrial-scale manufacturing of perovskite solar cells urgently calls for methods that are suitable to coat high-quality perovskite films over a large area (e.g. 1 cm² or larger).⁵
### Solar cell architecture and Perovskite solar cell parameters

<table>
<thead>
<tr>
<th>Solar cell architecture</th>
<th>Perovskite thickness (nm)</th>
<th>Electrode active area (cm²)</th>
<th>$J_{sc}$ (mA cm⁻²)</th>
<th>$V_{oc}$ (V)</th>
<th>FF</th>
<th>PCE (%)</th>
<th>Norm. PCE/thickness (%/100 nm)</th>
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<td>FTO/c.l.-TiO₂/CH₃NH₃PbI₃, Cl, spiro/Ag (co-evaporation)</td>
<td>330</td>
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<td>16.12</td>
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<td>0.67-0.68</td>
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<td>0.06</td>
<td>18.8</td>
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<td>0.63</td>
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<td>4.5</td>
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<td>0.72</td>
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<td>4.5</td>
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<td>0.98</td>
<td>0.68</td>
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</table>

**Notes:**
- Abbreviations: FTO = fluorine doped tin oxide; c.l.-TiO₂ = compact layered TiO₂; spiro = 2,7’-7’,7”-tetrakis N,N-di-p-methoxyphenylamine)-9,9’-spirobi fluorene; ITO = indium tin oxide; PEDOT-PSS = poly(3,4-ethylenedioxy-thiophene):poly(styrene sulfonate); poly(TPD) = poly(N,N’-bis[4-butylnaphthyl]-N,N’-bis[4-butylnaphthyl]-1,1’-diphenyl)-4,4’-diamine; PCBM = (6,6)-phenyl C₆₁-butyric acid methyl ester; Bphen = bathophenanthroline; NPB = N,N’-di(1-naphthyl)-N,N’-diphenyl-[1,1’-biphenyl]-4,4’-diamine; BCP = bathocuproine; 3TPYMB = triis[2,4,6-trimethyl-3-(pyridine-3-yl)phenyl]borane; F6-TCNNQ = 2,2’-perfluoronaaptalenol-2,6-diyldilime; spiro-MeO-TPD = 2,7’-bis[N,N’-bis[4-methoxy-phenyl]aminol]-9,9’-spirobi fluorene; PCDTBT = poly(N,N’-heptadecanyl-1,2,7-carbazole-alt-5,5-(4,7’-di(thien-2-yl)-2,1’,3’:6’,4’-terthiophene)); b Not provided.

Table 1: Summary of perovskite solar cells in a planar configuration with perovskite thin-films synthesized by the different vapor-based techniques. Perovskite thicknesses, electrode active areas, solar cell parameters of short-circuit current ($J_{sc}$), open-circuit voltage ($V_{oc}$), fill factor (FF), and power conversion efficiency (PCE), and normalized PCE by film thickness are indicated.
2.3. Vacuum deposition of HTL

The top selective contacts (either ETL or HTL) in perovskite-based solar cells can be influenced by the doping and environmental conditions (air, humidity, temperature, and light-soaking) in which the cell is being operated.\textsuperscript{106–109} Efforts have been made to find ETL/HTL materials that are less influenced by environmental conditions, which is expected to help minimize batch-to-batch variations.\textsuperscript{76,72–74} For example, Momblona \textit{et al.}\textsuperscript{70} fabricated the inverted structure solar cell (ITO/
PEDOT:PSS/polyTPD/CH$_3$NH$_3$PbI$_3$/PCBM/Au) by varying the perovskite layer thicknesses from 200 nm to 900 nm. $J_{sc}$ was observed to increase as the perovskite layer thickness increased, and the rate of $J_{sc}$ increase was faster at the beginning up to 300 nm and slower for devices with thicker active layers. The devices with thicker perovskite layers were observed to have lower FF reducing the overall PCE. The cell with a 900 nm perovskite film thickness was still able to generate respectable solar parameters of $J_{sc}$, $V_{oc}$, FF, and PCE: 19.8 mA cm$^{-2}$, 0.92 V, 0.4, 7.2%, respectively. Interestingly, the authors observed that replacing the pristine polyTPD with a slightly p-doped version of polyTPD (0.05% oxidized) in the cell with a 900 nm perovskite layer led to the significant improvement of the FF and PCE ($J_{sc} = 19.5$ mA cm$^{-2}$, $V_{oc} = 0.94$ V, FF = 0.65, and PCE = 12%). This work showed that with an appropriate HTL, solar cell PCEs had only a weak dependence on the perovskite film thickness. In addition, it demonstrated the properties of long diffusion lengths for electrons and holes in vacuum-processed perovskite films.

Perovskite solar cells using inorganic hole conductors (such as NiO, CuI, and CuSCN) as HTLs have received attention because of their better stability than HTLs using spiro-MeOTAD.72,101,111 Subbiah et al.72 reported the initial attempts of vacuum-deposited CH$_3$NH$_3$PbI$_3$–xCl$_x$ perovskite employing NiO and CuSCN, Table 1. Although the reported PCEs were much lower compared to those employing organic HTLs, it represents a promising step toward stability.

Schulz et al.115 identified that $V_{oc}$ losses of up to 0.4 eV could arise from an ionization energy (IE) mismatch between the spiro-MeOTAD HTL (IE = 5.0 eV) and CH$_3$NH$_3$PbI$_3$–xCl$_x$ perovskite (IE = 5.4 eV). Polander et al.74 reported fully vacuum-processed planar heterojunction CH$_3$NH$_3$PbI$_3$–xCl$_x$ perovskite solar cells using various p-doped HTLs with different IE values ranging from 5.0 to 5.6 eV and C$_{so}$ as the ETL. The authors studied the influences of the energy level mismatch between the valence band maximum (VBM) of CH$_3$NH$_3$PbI$_3$–xCl$_x$ (IE = 5.4 eV) perovskite and the different HTLs on the solar cell performance. It has been shown that the IE of the HTL correlates with the $V_{oc}$ of solar cell devices. Devices employing HTLs with IEs of up to 5.3 eV yielded a high $V_{oc}$ and PCE. In contrast, with IEs beyond 5.3 eV, a substantial decrease in both $J_{sc}$ and $V_{oc}$ was observed, which was attributed to the absence of driving force for hole extraction. Optimized solar cells employing spiro-MeOT/TPD in a planar cell configuration of ITO/F6-TCNQ/spiro-MeOT/TPD/CH$_3$NH$_3$PbI$_3$–xCl$_x$/C$_{so}$/Ag generated $J_{sc} = 16$ mA cm$^{-2}$, $V_{oc} = 1.03$ V, FF = 0.66, and PCE = 10.9%. In another study of fully vacuum-processed planar heterojunction performed by Kim et al.,73 the employment of HTL (MoO$_3$/NPB) and ETL (C$_{so}$/BCP) with a double-layer structure was observed to show improved energy level alignments at the interfacial contact resulting in higher $V_{oc}$. The solar cell with ITO/MoO$_3$/NPB/CH$_3$NH$_3$PbI$_3$/C$_{so}$/BCP/Al planar heterojunction architecture showed best solar cell parameters of $J_{sc} = 18.1$ mA cm$^{-2}$, $V_{oc} = 1.12$ V, FF = 0.68, and PCE = 13.7%.

3. Hybrid deposition method

Despite the aforementioned advantages of vacuum-based fabrication of perovskite layers and solar cells, difficulties in calibrating the QCM parameters for CH$_3$NH$_3$I materials were mentioned in almost all of these studies as a key challenge to achieve reproducible, uniform and stoichiometry controllable perovskite films.5,37,71,74,75 The evaporation rate of CH$_3$NH$_3$I is difficult to control and because of its relatively high vapor pressure. In addition, CH$_3$NH$_3$I is observed to deposit everywhere on the cold surfaces inside the chamber. For instance, the CH$_3$NH$_3$I layer was detected (XRD and AFM) on the top surface of a substrate that is facing the opposite direction of the CH$_3$NH$_3$I source.74 In contrast, lead halides were observed to deposit mainly along the line-of-sight direction from the source. The high vapor pressure of CH$_3$NH$_3$I also leads to cross-talking to the reading of the QCM that is used to monitor the evaporation rate of lead halides. To solve such a challenge, Qi and co-workers developed a new methodology (the hybrid deposition method) where the perovskite stoichiometry is ensured by controlling the CH$_3$NH$_3$I vapor partial pressure inside the vacuum chamber.76–79 The optimized homemade instrumentation is illustrated in Fig. 7a.79 A more detailed study on the hybrid deposition method was reported by Wang et al.79 and is discussed later in this section. The main vacuum chamber (Part #1 in Fig. 7a) is evacuated by using a pumping system consisting of a turbo molecular pump (HiPace 300, Pfeiffer) and a manual gate-valve (10840-CE01, VAT). The substrate holder stage (Part #3) allows stable cooling and heating in the temperature range from −190 °C up to 200 °C and can accommodate a wide range of substrate (Part #4) sizes up to 5 × 5 cm$^2$. A substrate shutter (Part #5) is mounted just below the substrate. The evaporation rates are monitored by two QCMs (Parts #6 and #7). The first QCM (Part #6) facing downward monitors the PbCl$_2$ evaporation rate while the second QCM (Part #7) facing upward is used to monitor the CH$_3$NH$_3$I vapor and avoids the cross-talk from the metal halide source. Two evaporation sources are used for the sublimation of the precursor materials. CH$_3$NH$_3$I vapor was produced by a Knudsen cell (Part #8) type source to fill the chamber. It is emphasized that a permanent shutter in front of the Knudsen cell was mounted for avoiding the high flux of CH$_3$NH$_3$I reaching directly the substrate, which may cause the non-uniform composition of the film. To achieve a high level of film uniformity in thickness and composition as well as to provide large scale uniform evaporation (5 × 5 cm$^2$), the PbCl$_2$ is resistively heated from a large dish-shaped crucible (Part #9) with ~3 cm in diameter. The heating element (Part #10) consists of a tungsten wire (ϕ = 0.25 mm) wound into a spiral shape and connected to a power supply through electric feedthroughs (Part #11). The halide shutter (Part #12) allows de-convolution and extrapolation of the lead halide evaporation rate after subtracting the CH$_3$NH$_3$I evaporation rate entering in the first QCM (Part #6). The total pressure inside the chamber is monitored by using a full-range (~10$^{-5}$ to 10$^{-2}$ Pa) pressure gauge (Part #13).

The initial CH$_3$NH$_3$I calibration and the determination of the optimized CH$_3$NH$_3$I : PbCl$_2$ ratio procedure are similar to the method described by Malinkiewicz et al. (see Section 2).5,73 However, in the hybrid deposition, because the CH$_3$NH$_3$I QCM faces upwards, the QCM parameters are set to values in such a way that the signal-to-noise ratio was reasonable to monitor the CH$_3$NH$_3$I during evaporation. The optimized parameters
were \( \rho = 0.2 \text{ g cm}^{-2} \), Z-factor = 0.2, and tooling factor = 100. The absolute amount of CH\(_3\)NH\(_3\)I inside the chamber cannot be quantified. Therefore, the perovskite deposition conditions (PbCl\(_2\):CH\(_3\)NH\(_3\)I ratio) were optimized by depositing several batches of perovskite films with varied CH\(_3\)NH\(_3\)I nominal rates to identify the evaporation conditions that led to strong XRD peaks measured on perovskite films. In this way, large-area uniformity of the perovskite films (~135 nm) was demonstrated by measuring XRD patterns at 12 different points on the 5 × 5 cm\(^2\) deposited film, Fig. 7b. The hybrid-deposited films with ~50 nm and ~135 nm perovskite films were observed to show a uniform semi-transparent light-orange color with a highly reflective (shiny) surface, distinctively different from the black or dark brownish color commonly observed for solution processed samples. Based on AFM measurements the surface roughness values of ~4.6 nm (Fig. 7c) and ~9 nm were determined for the ~50 nm and ~135 nm perovskite films, respectively.

The centimeter-scale uniform semi-transparent nature of the perovskite films grown by the hybrid deposition method is particularly suitable for large-scale window photovoltaic applications where good transparency and reasonable efficiency are prerequisites.\(^{13,14}\) The best performing device for the ~50 nm
perovskite film (Fig. 7d, blue curve) under standard AM1.5G illumination achieved $J_{sc} = 10.5 \text{ mA cm}^{-2}$, $V_{oc} = 1.06 \text{ V}$, FF = 0.566, and PCE = 6.33%. On the thicker perovskite film (~135 nm), the measured $J-V$ curve under illumination produced $J_{sc}$, $V_{oc}$, FF, and PCE of 17 mA cm$^{-2}$, 1.09 V, 0.535, and 9.9%, respectively (Fig. 7d, red curve).

Wang et al. performed detailed systematic studies on the perovskite formation using the hybrid deposition method by varying the (i) evaporation source materials (PbCl$_2$ : CH$_3$NH$_3$I versus PbI$_2$ : CH$_3$NH$_3$I), (ii) substrate temperature, and (iii) post-annealing conditions. The instrumentation was slightly modified to position the CH$_3$NH$_3$I QCM facing downwards and right above the CH$_3$NH$_3$I evaporation rate detector for CH$_3$NH$_3$I. A shutter was placed between the CH$_3$NH$_3$I QCM and evaporation source. With this new geometry, the authors were able to better control the CH$_3$NH$_3$I rate by the QCM over a long deposition period (~1 h). This shows that the evaporation of CH$_3$NH$_3$I cannot be treated as standard line-of-sight evaporation (e.g., PbI$_2$ or PbCl$_2$) and significant optimization in the system is needed for the better control of the CH$_3$NH$_3$I vapor inside the chamber during perovskite formation. Based on the PbCl$_2$ : CH$_3$NH$_3$I versus PbI$_2$ : CH$_3$NH$_3$I studies, the following reaction steps are proposed to take place for the perovskite film formation under the vacuum conditions:

\[
\begin{align*}
PbCl_2 + 2CH_3NH_3I & \rightarrow 2CH_3NH_3Cl + PbI_2 \quad \text{(R1)} \\
PbCl_2 + CH_3NH_3Cl & \rightarrow CH_3NH_3PbCl_3 \quad \text{(R2)} \\
PbI_2 + CH_3NH_3I & \rightarrow CH_3NH_3PbI_3 \quad \text{(R3)}
\end{align*}
\]

In the PbCl$_2$ : CH$_3$NH$_3$I deposition case when excessive PbCl$_2$ is present, reactions (R1) and (R2) occur, forming a pure CH$_3$NH$_3$PbCl$_3$ phase. As the ratio of PbCl$_2$ : CH$_3$NH$_3$I reduces, the films are composed of phase segregated CH$_3$NH$_3$PbCl$_3$ and CH$_3$NH$_3$PbI$_3$ perovskites via reactions (R1), (R2), and (R3). When the PbCl$_2$ : CH$_3$NH$_3$I ratio was further decreased matching stoichiometry, only the pure CH$_3$NH$_3$PbI$_3$ perovskite phase was observed to form and corroborated by XRD and X-ray photoelectron spectroscopy (XPS). This is also consistent with the solution-processed perovskite films where no XPS Cl 2p signal was found in the bulk perovskite film and only 1% Cl could be detected at the bottom 20 nm of the film. Therefore, the chemical formula of “CH$_3$NH$_3$PbI$_3$” was more precise to be represented than “CH$_3$NH$_3$PbI$_{1-x}$$\cdot$$x$Cl$$_x$$” in the perovskite films formed from PbCl$_2$ + CH$_3$NH$_3$I precursors. In the PbI$_2$ : CH$_3$NH$_3$I deposition case, only reaction (R3) takes place. The excess of PbI$_2$ is readily detected in XRD with a characteristic 12.6° peak, which corresponds to the PbI$_2$. On the other hand, excess of CH$_3$NH$_3$I was observed to generate the characteristic peaks at 9.7°, 19.6°, and 29.6°. An additional peak at 11.4° was observed to evolve as a function of air exposure time and associated with the H$_2$O-incorporated perovskite (complex formation). No significant morphology differences were observed in the optimized perovskite films deposited from PbCl$_2$ : CH$_3$NH$_3$I and PbI$_2$ : CH$_3$NH$_3$I cases showing surface roughnesses of 24.5 nm and 26.5 nm, respectively, measured by AFM. It is interesting to note that in the PbCl$_2$ : CH$_3$NH$_3$I case, stronger preferred orientation along the (110) plane of CH$_3$NH$_3$PbI$_3$ was observed to form compared to that of the PbI$_2$ : CH$_3$NH$_3$I case. It has been proposed that the additional intermediate CH$_3$NH$_3$Cl species formed (R1) from the PbCl$_2$ : CH$_3$NH$_3$I evaporation help slow down the reaction kinetics for the final CH$_3$NH$_3$PbI$_3$ formation.\[20\] In the recent work by Teuscher et al., a proportional-integral-derivative (PID) driven thermal evaporator was developed in their vacuum chamber allowing a more precise control of the PbI$_2$ : CH$_3$NH$_3$I stoichiometric ratio as well as improving reproducibility. The composition of the deposited materials was quantitatively analyzed using inductively coupled plasma mass spectrometry (ICP-MS) and the PbI$_2$ : CH$_3$NH$_3$I ratio of 1 : 0.96 resulted in the best performing solar cell devices (device structure: FTO/TiO$_2$ compact layer/perovskite/spiro-MeOTAD/Au): $J_{sc} \approx 18 \text{ mA cm}^{-2}$, $V_{oc} > 1.1 \text{ V}$, FF > 0.7, and PCE > 12%.

The growth of the perovskite film was highly dependent on the substrate temperature during deposition, mainly influenced by the sticking coefficient of CH$_3$NH$_3$I vapor. The low substrate temperature (~50 °C) led to a high sticking coefficient, but a poor quality perovskite film with partial coverage. At higher temperatures (>80 °C), films with excess PbI$_2$ and intermediate phases were observed and associated with the lower sticking coefficient of CH$_3$NH$_3$I vapor. The optimum substrate temperature was 20 °C, which generated growth of perovskite films with high crystallinity and full coverage.

Solution-processed perovskite films generally require the post-annealing treatment (80–120 °C) for efficient conversion from the precursors to perovskite and to ensure vaporization of the solvent and subsequent crystallization.\[4\] On the other hand, Malinkiewicz et al.\[79\] have shown that post-annealing is not required in vacuum-processed perovskite films, yet attain high solar cell efficiencies. Wang et al.\[79\] performed detailed post-annealing studies on non-stoichiometric and stoichiometric perovskite films formed by the hybrid-deposition method. It is shown that post-annealing is beneficial for the perovskite films with excessive CH$_3$NH$_3$I. Gentle annealing in an N$_2$ environment at 110–120 °C helps desorb the undesirable H$_2$O-incorporated complex. High temperatures (~130 °C) decompose the CH$_3$NH$_3$PbI$_4$ to PbI$_2$. The post-annealing at 120 °C for 1 h in an N$_2$ environment on a perovskite film with stoichiometric composition was observed to have a negligible effect on the crystallinity and morphology of the film probed by XRD and AFM. This is in good agreement with the device performance that shows nearly the same PCE compared to that of the identically prepared cells (same deposition batch), but one with and the other without the post-annealing treatment. In this work, the solar cells based on optimized perovskite films as thin as ~170 nm generated $J_{sc}$, $V_{oc}$, FF, and PCE of 19.92 mA cm$^{-2}$, 1.098 V, 0.524, and 11.48%.\[79\] The high $V_{oc}$ (over 1 V) typically achieved by the hybrid deposition is well aligned with the reported values using vacuum-deposition methods: 1.07 V in the work of Liu et al.\[4\] and 1.05 V in the work of Malinkiewicz et al.\[79\] On the other hand, solution processed ones have generally substantially lower $V_{oc}$ possibly due to the large...
variations of the film morphology.\textsuperscript{4} The pin-hole free uniform perovskite layer prevents shunting pathways effectively, leading to a lower recombination rate.\textsuperscript{52,118,117} In a recent work by Zhao \textit{et al.},\textsuperscript{41} vacuum-processed perovskite solar cells with an ultrathin metal-oxide free and annealing-free C\textsubscript{60} or C\textsubscript{70} as the ETL was demonstrated to generate high PCEs (Table 1).

4. Hybrid chemical vapor deposition

Chemical Vapor Deposition (CVD) is a scalable technology that uses batch processing to generate throughput sufficient for industrial applications, and is used for a wide variety of material deposition. CVD is often performed with a tube furnace, where the temperature, gas environment, and flow rate can be well controlled. Perovskite film growth by a CVD process was first demonstrated in 2014,\textsuperscript{65} and can be differentiated from other vapor deposition processes that are more direction dependent and require higher vacuum conditions. CVD relies more on thermally driven diffusion, which can transport material to substrates regardless of substrate orientation. Typically perovskite growth by CVD uses an inert carrier gas such as nitrogen or argon to provide an oxygen and water free environment, but has been demonstrated using air as well.

Ambient pressure thermal diffusion driven perovskite film growth was first demonstrated using VASP with the PCE up to 12.1%.\textsuperscript{65} In this system lead iodide was first deposited onto substrates, which were then loaded into a heated (150 °C), closed container with CH\textsubscript{3}NH\textsubscript{2}I. The time required for complete conversion was approximately 2 h. This is essentially a 2-step CVD process with nitrogen gas at atmospheric pressure. A similar ambient pressure perovskite growth was reported, but used a CVD tube furnace (145 °C) and ambient air, which demonstrated maximum PCE of 12.2%.\textsuperscript{65} This process also required 2 h for complete conversion.

Lower pressures increase the rate of diffusion and the rate of sublimation of organic halide, therefore low pressures allow for greater uniformity, faster deposition rates or the use of lower temperatures. Low pressure CVD growth was demonstrated to generate high PCEs (Table 1).

at a slightly lower substrate temperature (140 °C) to achieve a PCE of 12.7%.\textsuperscript{45} However, the pressure was not specified. The highest performing reported solar cell fabricated by CVD (15.1%) used a low vacuum (100 Pa) and single zone furnace (140 °C) with 2–3 h deposition time.\textsuperscript{118} Low pressures can be used to reduce the required reaction temperature, because the sublimation temperature of organic halide is reduced at lower pressures. High performing cells were fabricated at ~0.3 Pa and 82 °C reaching a PCE of 14.7%.\textsuperscript{119} However, a long reaction time of 3 h was required for complete conversion at low temperatures.

It was consistently observed that longer deposition times could be detrimental to solar cell performance, even in cases when XRD crystallinity was enhanced.\textsuperscript{83,118} There are several possible reasons for the decrease in performance. It is possible that longer deposition times produce an excess of organic halide, which then can act as insulating contaminant in the solar cell, or can lead to more hygroscopic surfaces causing rapid decay of the cell from water absorption. In the case of chlorine-containing perovskite, longer deposition times can cause depletion of chlorine, which is believed to cause shorter carrier lifetimes and lower PCE.\textsuperscript{83} In the case of formamidinium perovskite, the excess organic component is easily absorbed in the perovskite thin film, creating a different crystal structure. The excess can be desorbed by annealing, but the modification of the crystal structure was observed to negatively impact the grain size and reduce performance.\textsuperscript{85}

Most processes for perovskite solar cell fabrication used a 2 step process for perovskite growth. There is a significant difference in temperature between the evaporation temperature of metal halide and organic halide, and therefore it is difficult to uniformly deposit both layers at the same step. Most reports that deposited both layers by CVD formed discontinuous films. This is not ideal for solar cells, but can be useful for optoelectronics devices. For instance, perovskite nano-platelets,\textsuperscript{120,121} and nanowires\textsuperscript{122} can be used for laser applications. Another type of single step CVD process used aerosol-assisted chemical vapor deposition for the formation of discontinuous perovskite thin films.\textsuperscript{123,124} One work fabricated solar cells by single step CVD and produced efficiencies up to 11.1%.\textsuperscript{125} The advantage of using a single step approach is clear as long as uniformity is sufficient across a batch.

Solar cells prepared by a CVD process typically had reasonably high stability compared to some solution processed methods.\textsuperscript{82,83,118,119} Solution processed samples can decay even in an inert, dark environment,\textsuperscript{80} but CVD cells kept under similar conditions were reported to be stable and even improved in efficiency over time. As the solar cell aged the \(V_{oc}\) increased, while the \(J_{sc}\) decreased resulting in a small net gain for the PCE.\textsuperscript{82,83,116,117} However, it is possible that this behavior is specific to cells using spiro-MeOTAD as the hole transport medium. When kept in air, CVD solar cells were reported to decay from 14.7% to 12.1% over the course of 30 days.\textsuperscript{119} This prolonged stability is possibly due to high temperatures during perovskite formation (less chemical and/or phase impurities) or the absence of solvent usage (e.g. DMF, DMSO) that can get incorporated into solution processed perovskite films. However, few papers directly addressed stability under operational conditions, but it is mentioned that solar cells under continuous irradiation decay faster than cell with periodic measurements.\textsuperscript{118}
5. Vacuum sequential deposition

General difficulties in co-evaporation methods are often associated with the need for careful and simultaneous control of evaporation rates of both precursors (lead halides and methylammonium halides) to achieve uniform stoichiometry in the deposited films. In this sense, the one-material-at-a-time deposition method has a big advantage for easy control of the evaporation rates of the individual sources. Chen et al. reported planar structured perovskite solar cells by the sequential layer-by-layer vacuum deposition method attaining a PCE as high as 15.4%, Table 1. Their devices were prepared using indium-doped tin oxide (ITO) spin-coated coated with PEDOT:PSS. Subsequently, the substrates were loaded into a high vacuum chamber (base pressure $< 1 \times 10^{-6}$ Torr) to evaporate PbCl$_2$, CH$_3$NH$_3$I, C$_{60}$, bathophenanthroline (Bphen), Ca, and Ag. Except for the CH$_3$NH$_3$I deposition, the substrate temperature was maintained at room temperature during deposition of all other layers (PbCl$_2$, C$_{60}$, Bphen, Ca, Ag), Fig. 8a. The substrate temperature while sublimating CH$_3$NH$_3$I was found to be crucial for the photovoltaic performance, Fig. 8b and c. Photovoltaic performance was the highest when the substrate was heated to 75 °C and compared to those where the substrate temperature was maintained at 65 °C and 85 °C during CH$_3$NH$_3$I deposition, Fig. 8d. The thickness of the perovskite film was determined to be proportional to the initial thickness of the PbCl$_2$ layer. The film thickness expansion ratio of $\sim 1:2.9$ was reported when PbCl$_2$ is converted to CH$_3$NH$_3$PbI$_3$-Cl$_x$. All the optimized films (thickness $\sim 430$ nm) were reported to have smooth surfaces with surface RMS roughness of 24.1 nm, 22.7 nm, and 23.3 nm for substrate temperatures of 65 °C, 75 °C, and 85 °C, respectively. The smoothness of the perovskite films for all temperatures was attributed to the typical ultra-smooth nature of the starting PbCl$_2$ film (RMS roughness $\sim 7.8$ nm). When CH$_3$NH$_3$I was deposited on the PbCl$_2$ coated substrate kept at room temperature, the CH$_3$NH$_3$I diffusion depth was limited to less than 25 nm leaving the bottom PbCl$_2$ layer unreacted leading to decreased PCEs.

Ng et al. have employed the deposition of both PbI$_2$ and CH$_3$NH$_3$I at room temperature by decreasing the thickness of both precursor layers. However, an additional subsequent thermal annealing step was necessary for the full conversion to CH$_3$NH$_3$PbI$_3$ perovskite. A multilayered structure consisting of seven alternating depositions of PbI$_2$ (50 nm)/CH$_3$NH$_3$I (50 nm) pairs with subsequent annealing in N$_2$ gas (90 °C, 1 h) generating a CH$_3$NH$_3$PbI$_3$ perovskite film with $\sim 473$ nm thickness and surface roughness of $\sim 20$ nm exhibited the highest average solar cell parameters: $J_{sc} = 20.0 \pm 0.8$ mA cm$^{-2}$, $V_{oc} = 1.00 \pm 0.03$ V, FF = 0.57 $\pm$ 0.02, and PCE = 11.4 $\pm$ 0.5%. Planar structured perovskite solar cells were composed of glass/FTO/c.l.-TiO$_2$/CH$_3$NH$_3$PbI$_3$/spiro-MeOTAD/MoO$_3$/Al layers. The same group of authors investigated the impact of dry-O$_2$ annealing$^{117}$ of the thermally evaporated CH$_3$NH$_3$PbI$_3$-based solar cells. The results suggested that O$_2$-treatment enhanced the solar cell performance. Under the optimized conditions, the champion device exhibited: $J_{sc} = 21.8$ mA cm$^{-2}$, $V_{oc} = 0.96$ V, FF = 0.60, and PCE = 12.5%. Low-temperature (max. of 100 °C) fabrication of hole-conductor-free planar perovskite solar cells consisting of only a CH$_3$NH$_3$PbI$_3$/C$_{60}$ bilayer structure was reported by Hu et al.$^{118}$ to generate a PCE of 5.4%. Abbas et al.$^{119}$ have fabricated CH$_3$NH$_3$PbI$_3$ perovskites through sequential deposition of PbI$_2$ in vacuum and subsequently to CH$_3$NH$_3$I after transferring the samples to a graphite vessel. The solar cell devices with FTO/c.l.-TiO$_2$/CH$_3$NH$_3$PbI$_3$/P3HT/Au structure and after optimization of the P3HT layer (thickness $\sim 30$ nm and polymer concentration $\sim 12$ mg ml$^{-1}$) have generated high solar cell parameters: $J_{sc} = 21.76$ mA cm$^{-2}$, $V_{oc} = 0.96$ V, FF = 0.653,
and PCE = 13.7%. More recently, Yang et al.\textsuperscript{92} have demonstrated solar cell devices with large active areas of 1 cm\textsuperscript{2} that exhibit a high PCE of 13.84%, by the alternating layer-by-layer (PbCl\textsubscript{2}/CH\textsubscript{3}NH\textsubscript{3}I) vacuum deposition technique. Atomic layer deposition (ALD) can be another suitable technique for automatizing the sequential deposition of alternating layers of precursors. ALD is a low-vacuum and low-temperature deposition technique capable of uniform, conformal growth of films over large area with atomic thickness precision. Although, at present, there are no direct processes for the growth of OHPs fully by ALD, alternative protocols have been proposed by Sutherland \textit{et al.}, who showed enhanced optoelectronic properties of ALD processed OHP layers.\textsuperscript{128,129}

6. Flash evaporation or single-source thermal ablation technique

The concept of flash evaporation was first described by Harris and Siegel in 1948 demonstrating the evaporation of metal alloys with controlled stoichiometry.\textsuperscript{130} Later on, the method was applied for the evaporation of inorganic semiconductor alloys\textsuperscript{111} as well as oxide-based perovskite materials.\textsuperscript{115} In 1999, Mitzi \textit{et al.}\textsuperscript{97,133} demonstrated that the same technique could be applied for the fabrication of OHP films (named as single source thermal ablation technique). Briefly, the OHP material is initially synthesized by solution processing and spread on a metal heater (e.g. tantalum or molybdenum), Fig. 9a. The dried OHP and heater are loaded into a vacuum chamber. After the system is pumped to vacuum, a large current is passed through the heater causing the OHP material to rapidly evaporate and condense onto a substrate. The desired OHP films are formed when the material is heated rapidly and at high enough temperatures, causing sublimation of the entire compound without thermal decomposition of the organic constituents, Fig. 9a.\textsuperscript{93,97,133–136} Longo \textit{et al.}\textsuperscript{93} have synthesized CH\textsubscript{3}NH\textsubscript{3}PbI\textsubscript{3} perovskite films by using the flash evaporation technique and showed that smooth surface morphology was obtained with a surface RMS roughness of ~17.6 nm, Fig. 9b. GIXRD measurements confirmed the formation of stoichiometric CH\textsubscript{3}NH\textsubscript{3}PbI\textsubscript{3} and revealed high degree of crystallinity, Fig. 9c. Solar cell devices with ITO/PEDOT:PSS/CH\textsubscript{3}NH\textsubscript{3}PbI\textsubscript{3}/polyTPD/PCBM/Ba/Ag layers in a planar heterojunction structure showed respectful solar cell parameters of J\textsubscript{sc} = 18 mA cm\textsuperscript{-2}, V\textsubscript{oc} = 1.067 V, FF = 68.04 %, and PCE = 12.2%.\textsuperscript{93}

7. Fundamental understanding of OHP films prepared by vacuum processing

In parallel to several studies focusing on improving the device performance, equal effort has also been made to address the fundamental aspects of the device physics and chemistry. This
section is intended to summarize the fundamental understanding earned from the vapor-processed OHPs and solar cells and describe the remaining open questions in this field.

The majority of the fundamental aspects of perovskites come from reports on solution-processed perovskites.26,34,112,137–150 Vapor-based systems used for the OHP film synthesis offer unique advantages, i.e., they are compatible with surface science analytical tools and in situ studies. In situ monitoring allows the investigation of events taking place in the OHP films, e.g., during formation or degradation, without altering its pristine conditions that can be influenced by the environmental conditions (e.g. H2O, O2, temperature, light, etc.). In addition, it allows systematic investigation of the influences of controlled environmental conditions (e.g. humidity, O2, temperature, light, etc.) on the material system under study. Pistor et al.151,152 have used a dedicated vacuum chamber system where perovskite film crystalline phase formation from the co-evaporation of PbCl2 and CH3NH3I sources could be monitored in situ and real-time by a built-in XRD setup, Fig. 10a. The PbCl2 : CH3NH3I flux ratio was observed as a key parameter for the formation of perovskite films with distinct crystalline phases, Fig. 10b. The CH3NH3I (MAI) source was heated at a constant temperature of 110 °C. The temperature ramp of the PbCl2 source (Tpbcl2) was increased steadily from 350 °C to 465 °C. Under low PbCl2 flux conditions, marked with a dotted line (1) in Fig. 10b, the formation of a dark gray/brown CH3NH3PbI3-yCl_y perovskite film with diffraction peaks at 14.046°, 28.332°, and 31.69°, phase (A), was characteristic. Additional energy dispersive X-ray spectroscopy (EDX) and optical transmission/reflection measurements revealed films with low chloride content (y = ~0.02–0.05) and a bandgap of ~1.6 eV. At higher PbCl2 flux, dotted line (2) in Fig. 10b, XRD revealed formation of a second crystalline phase (B) with peaks at 15.40°, 19.71°, 21.89°, and 35.05°. A chloride-rich phase was identified (y ~ 1) by EDX with films appearing greenish and transparent. A further increase in temperature of the PbCl2 crucible generates films with pure PbCl2 composition, dotted line (3) in Fig. 10b. In contrast to the Br− mixed perovskites (CH3NH3PbI3-yCl_yBr_y) where the formation of solid solution over the whole range (0 < z < 1) was reported,151 the authors of this study concluded that mixed CH3NH3PbI3-yCl_yBr_y perovskites are not stable for all mixtures between CH3NH3PbI and CH3NH3PbCl3. The authors estimated this miscibility gap to be in the range of 0.02 < y < 0.5 and explained it by the increasing difference in the I−Br−Cl− ionic radii and was demonstrated by Mosconi et al.154 using first-principle calculations. Ng et al.78 have also studied the formation chemistry of mixed CH3NH3PbI3-yCl_y perovskites by in situ XPS. PbCl2 was evaporated layer by layer with an increasing total thickness on top of a CH3NH3I film (15 nm) pre-deposited on ITO and XPS Pb 4f, Cl 2p, C 1s, and N 1s core levels were monitored as a function of the PbCl2 thickness. During the initial deposition (0.2 nm to 0.5 nm) the Pb signal was detected, but no Cl signal was observed taking into account the detection limit of the XPS measurement (~±0.1 atm%). The Cl signal is only observed for a PbCl2 film thickness above 1 nm indicating that PbCl2 can be included when away from the CH3NH3I/PbCl2 interface. The absence of Cl at the CH3NH3I/PbCl2 interface (PbCl2 thickness below 0.5 nm) was attributed as a result of the interaction between PbCl2 and CH3NH3I where Cl− is energetically unfavorable because of the abrupt difference in the ionic radii of Cl− and I− ions.154 These results are also consistent with the low content of chloride identified in solution processed CH3NH3PbI3-yCl_y perovskite films.16,155,156

The formation mechanism of pure CH3NH3PbI3 perovskite was studied by Liu et al.177 using in situ XPS on successive depositions of thermally evaporated CH3NH3I on a pre-formed
PbI$_2$ film with focus on the double C 1s feature observed, while only one N 1s species was present. The peaks observed at 286.6 eV and 402.7 eV in the BE scale were assigned to the photo-electrons originated from C and N elements in CH$_3$NH$_3$PbI$_3$ perovskite. The low-BE feature at 285.3 eV in C 1s was assigned to CH$_3$I from the dissociation of CH$_3$NH$_3$I to CH$_3$I and NH$_3$. In fact, the assignment of the low-BE feature is still under debate. Ng et al.\textsuperscript{158} and Li et al.\textsuperscript{159,160} have also identified more than one peak in the C 1s region and assigned the low BE feature to amorphous carbon (C–C).

Li et al.\textsuperscript{160} performed in situ XPS and investigated the degradation of co-evaporated CH$_3$NH$_3$PbI$_3$ perovskite films under a controlled environment of dry-O$_2$, and H$_2$O exposures conducted in the vacuum chamber by the aid of high-precision leak-valves. CH$_3$NH$_3$PbI$_3$ was reported to be not sensitive to O$_2$ even at higher exposures of 10$^{13}$ Langmuir (L, 1 L $= 10^{-6}$ Torr s). However, a reaction threshold of $\sim 2 \times 10^{10}$ L was found for H$_2$O exposure proposing decomposition of CH$_3$NH$_3$PbI$_3$ to NH$_3$, HI, and PbI$_2$ in agreement with previous reports.\textsuperscript{161,162}

One important requirement for attaining high-efficiency OHP solar cells is to match the electronic energy levels of OHP absorber and the adjacent selective contacts (ETL and HTL) for minimal energy loss and reduced charge recombination.\textsuperscript{121,142,146} A large collection of energy levels with respect to (w.r.t.) the vacuum level ($E_{\text{vac}}$) for the different materials commonly employed in OHP-based solar cells is shown in Fig. 11. The indicated bandgap values for OHPs in Fig. 11 correspond to optical bandgaps (that differs from the transport gap) and all of studies were reported on solution-processed OHPs.\textsuperscript{164} Few studies exist on the determination of energy levels on vacuum-process perovskites measured by UPS.\textsuperscript{157,159,160} The flat band assumption widely considered can still provide a rational judgement when choosing functional layers to be coupled with the OHP layer. However, careful determination of band bending, interfacial states, and interfacial dipoles is important when considering the band alignments of OHP layers with adjacent functional layers.\textsuperscript{113,142,146,147} In this sense, film deposition by vacuum-methods is suitable for studying the energy alignments because step-wise deposition with controlled incremental amounts of film thickness can be conducted as well as it is directly compatible with UPS and IPES systems. Energy level diagrams at interfaces were determined for the following material systems: CH$_3$NH$_3$PbX/spiro-MeOTAD (X = I$_3$, I$_3$–Cl$_x$, Br$_2$),\textsuperscript{113} CH$_3$NH$_3$PbI$_3$/C$_{60}$,\textsuperscript{139} CH$_3$NH$_3$PbI$_3$/Au,\textsuperscript{139,145} CH$_3$NH$_3$PbI$_3$/MoO$_x$,\textsuperscript{142,144} CH$_3$NH$_3$PbI$_3$/copper phthalocyanine (CuPc),\textsuperscript{147} CH$_3$NH$_3$PbBr$_3$/spiro-MeOTAD,\textsuperscript{142} CH$_3$NH$_3$PbBr$_3$/N,N’-diphenyl-N,N’-dibenzyl-naphthalene-1-yl-N,N’-diphenylbenzidine (NPB),\textsuperscript{142} CH$_3$NH$_3$PbI$_3$/copper-hexadecafluorophthalocyanine (F$_{16}$CuPc),\textsuperscript{142} and CH$_3$NH$_3$PbI$_3$/Au,\textsuperscript{4,5,6,8,11}hexaazatriphenylene hexacarbonitrile (HAT-CN).\textsuperscript{142}

Hysteresis appears as a manifestation in the J–V curves, where its shape is strongly influenced by the scan direction (forward versus reverse), scan rate, scan history, pre-illumination, and pre-biasing conditions.\textsuperscript{165–170} It is pointed out that hysteresis in OHP-based solar cells will lead to inaccurate reporting of PCEs, leading to inaccuracies when comparing the different reported PCEs among different laboratories. Stabilized power output under working conditions has been suggested as a useful parameter.\textsuperscript{165} Efforts have been made on determining the origins of the hysteresis phenomena. Recently, several studies have enforced to ion migration as the main phenomena in determining charge transport in OHP materials.\textsuperscript{165,170–175} Few studies reported on the hysteresis-free J–V characteristics in vapor-processed OHP solar cells.\textsuperscript{71,85,90,91,93,177} However, its origin is difficult to be understood from the reported studies as systematic studies are lacking.

8. Conclusions and outlook

The identification of new properties in novel materials is key for generating new technologies. The introduction of well-established inorganic or organic materials led to dramatic improvements in the history of technology. Inorganic silicon-based technology enabled unprecedented development of advanced electronic devices (e.g. laptops, smart phones, digital cameras, Si solar cells, etc.). Organic semiconductors on the other hand have received attention in light-weight, flexible, flat-panel-display and organic light emitting diode applications. The past few years have witnessed a rapid evolution of hybrid organic–inorganic OHP-based solar cells. OHP materials effectively combine the properties of the inorganic framework and the intercalated organic species. As has been reviewed previously,
OHP materials show several desirable properties for photovoltaic and other optoelectronic technologies, high absorption coefficients, long carrier diffusion lengths, ambipolar transport, shallow defect levels, emission efficiency, and low concentration of defects. Although the operation of vapor based methods often require a certain level of vacuum that is generally perceived as high cost processing, they have been widely employed in the semiconductor industry demonstrating high throughput and reliability. Therefore, a detailed factual cost analysis would be required for evaluating various fabrication methods taking into account the cost-effectiveness in a mass production scenario.

When transferring solar cell technology from laboratory scale fabrication know-how to industry-scale production, fabrication cost, efficiency, and lifetime are the three major factors, which are associated together with functionality (e.g. transparency, flexibility, easy integration in tandem cells, etc.). At this stage, despite the superior quality of films prepared by the vapor-deposition method (e.g. uniform and full coverage), best efficiencies achieved for OHP solar cells based on vapor-based methods (a PCE of 16.5% with an active area of 0.2 cm²), (Table 1) are still somewhat lower than that of the solution-processed cells (a certified PCE of 20.1%). The efficiencies of vapor deposition based perovskite solar cells are still lagging behind their counterpart prepared by solution based methods. On the other hand, we regard this more as a strong motivation to invite more research effort on vapor based methods, rather than an intrinsic disadvantage associated with vapor based methods. Since the ground-breaking work by the groups of Prof. Snaith and Prof. Bolink in 2013 on vapor deposition prepared perovskite solar cells, more and more research groups became interested and have been making contributions to this topic. For example, at this stage it has been demonstrated by a number of groups that vapor based methods provide another viable route to fabricate perovskite solar cells leading to promising efficiencies using both regular and inverted structures (see Table 1 and Fig. 12). Efficiencies as high as 16.5% have been reported so far and the trend of efficiency increase is very clear as shown in Fig. 12. Further improvements on the performance of vapor deposition based perovskite solar cells may come from the following strategies. First of all, multiple reports have indicated that the properties of vapor deposition based perovskite are distinctively different from those prepared by solution processing. Therefore, it is necessary to carry out more in-depth investigations on vapor deposition based perovskite films. Secondly, due to the property difference, the optimal fabrication conditions for vapor deposition based perovskite solar cells are most likely not the same as those for solution prepared ones. A complete set of optimization processes hopefully will provide further efficiency growth of vapor deposition based perovskite solar cells. Thirdly, vapor deposition based perovskite films have some specific advantages, e.g. high degree of uniformity (even at relatively thin film thicknesses) and semitransparency, which may provide the vapor based methods with unique features beyond the pure efficiency considerations. Note that none of the PCE values reported in Table 1 has been certified, which to some degree also underscores the need to further explore these vapor-based methods. In general, caution should be practiced when comparing the cell performance reported by different laboratories as PCE values in OHP solar cells are shown to strongly depend on measurement conditions, such as the voltage-scan polarity (forward versus reverse) and rate, light-soaking, pre-biasing, and cell temperature. OHP films deposited by vapor-based methods generally show low XRD intensity, but the corresponding solar cells still show relatively high efficiencies. No direct correlation has been reported between XRD peak intensity (generally considered as a measure of crystallinity) and the corresponding solar cell efficiency. In addition, the crystallinity, perovskite composition, and film morphology are strongly dependent on the choice of the substrate (e.g. FTO, TiO₂, SiO₂/Si, etc.), which is expected to become critical when designing tandem cell architecture: the optimized evaporation conditions may differ according to the substrate on which OHP films are being deposited. With regard to vacuum systems that are usually needed for vapor based processing, special care is required for pumps (especially turbo molecular pumps).

For commercialization to take off, large area modules will be required. A few attempts were made on large area (1 cm²) fabrication based on vacuum- and CVD processes, Table 1, showing a promising PCE as high as 13.84%. Because uniform, high-quality, and full-coverage OHP films are achievable, vacuum- and CVD processes are expected to have unique advantages in the fabrication of large-area OHP solar modules.

The OHP materials are hygroscopic in nature, and are susceptible to degradation upon the intake of moisture. Therefore, for protecting the core material in the OHP-based solar cells it requires stringent encapsulation. In addition to extrinsic degradation factors by moisture, the intrinsic stability of perovskites remains a major issue. The chemical reactions between moisture and perovskite need be carefully studied to...
unravel the reaction pathways, which provide insight for the development of methods (e.g. chemical composition engineering\(^{2,153,193}\)) for stabilizing perovskites. The negative standard Gibbs free energy for iodide perovskite degradation was also reported in the absence of moisture.\(^{161,192,194}\) The majority of stability tests reported in the literature, provides the lifetime profiles of OHP solar cells under the storage conditions (in N\(_2\) or in ambient air). Only limited data exist for stability profiles under real operating conditions for vacuum- or CVD processed OHP solar cells.\(^{199}\)

A major drawback of high efficient OHP solar cells is the use of Pb\(^{2+}\), the material toxicity of which has been emphasized.\(^{184,190,195}\) Efforts have been made to find alternatives such as Sn\(^{2+}\). However, the instability of Sn\(^{2+}\) to form Sn\(^{4+}\) leads to a metal-like behavior and lowers the photovoltaic performance.\(^{196}\) Many other elements in the periodic table (e.g. Co\(^{2+}\), Fe\(^{3+}\), Mn\(^{2+}\), Pd\(^{2+}\), and Ge\(^{2+}\)) were suggested as alternatives for Pb\(^{2+}\). Through comparison with the amount of lead used in lead acid batteries, a much lesser amount of lead is estimated to be required to produce 1000 GW per year from CH\(_3\)NH\(_3\)PbI\(_3\) perovskite solar cells.\(^{197}\) Therefore, tracking and minimizing the amounts of lead salt as well as quantifying solar cell efficiency normalized by the perovskite amount (e.g. PCE/thickness parameter calculated in Table 1) are proposed as important parameters to evaluate the toxicity at the times of disposal, recycling, and of eventual accidents.\(^{184,190,195}\)

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## Notes and references