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Pressing Challenges in Halide Perovskite Photovoltaics – From the Atomic to the Module Level

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Introduction

There is growing urgency to curb the steady increase in anthropogenic greenhouse gas emissions. This will require increased electrification and accelerating the deployment of renewable sources of energy. Of the spectrum of renewable technologies available, solar photovoltaics (PVs) is one of the most promising, especially since terrestrial solar energy is four orders of magnitude larger than the world's current electrical energy consumption.¹ Despite this, PVs only account for ~2% of total electrical energy production worldwide. It is predicted that achieving a 'high electrification' future by 2050 will require annual PV installations to increase to 1780 GW (compared to 99.1 GW in 2017).²

A rapid expansion in PV manufacturing is required, and this may be fulfilled by a newcomer to the PV scene – lead-halide perovskites. First reported in PVs in 2009, halide perovskites have rapidly outperformed their thin film competitors.³ Remarkably, the most efficient halide perovskites are processed at low temperatures of approximately 100 °C from solution using low-cost, Earth-abundant precursors. The band gap of halide perovskites can also be fine-tuned, and visible-light-absorbing halide perovskite thin film solar cells can be stacked over and work in complement to near-infrared-absorbing crystalline silicon, which is currently the dominant material in the PV industry. Through these tandem solar cells, halide perovskites can boost the efficiencies of silicon without significantly adding to the cost, thus lowering the levelized cost of energy (LCOE). At the end of 2020, the certified efficiency of perovskite-silicon tandems reached 29.52%, exceeding the practical efficiency limit of silicon single-junction devices (~29%). Further reductions in LCOE may be achieved through all-perovskite tandems, in which both sub-cells are manufacturable with low capital-intensity methods. In the meantime, the power conversion efficiency (PCE) of single-junction perovskite solar cells crossed the 25% threshold, and is on the brink of reaching the highest certified PCE of crystalline silicon solar cells (26.7%).^{3,4} Perovskite PV technology is now on the cusp of commercialization, with both Oxford Photovoltaics and Microquanta Semiconductor utilizing mature production lines and poised to deliver the first commercial PV products very soon. Nevertheless, the mostefficient halide perovskite-based devices have all been achieved on lab-scale device areas of approximately 0.1–1 cm², which are comparable to or smaller than a fingernail. Moving forward, key questions now are: i) how halide perovskite PVs can approach their practical limits (30% for single-junction devices; 35% for perovskite-based tandems);⁵ ii) how efficient and stable performance can be preserved in module-scale devices manufactured rapidly with scalable, cost-effective equipment; and iii) how module lifecycles can be managed at a commercial level.

These key questions are the subject of active debate in the halide perovskites community across many venues. The important challenges emerging from these discussions are: i) understanding the nanoscale landscape in halide perovskite thin films, ii) managing interfaces to reduce non-radiative recombination and perovskite degradation, and iii) addressing the speed, stability and toxicity challenges in perovskite manufacturing and deployment. These challenges are discussed herein, highlighting important future directions for the field at this critical juncture as halide perovskite PVs approach the point of breaking into the commercial market.

Nanoscale Performance, Chemical, and Structural Heterogeneities in Halide Perovskite Absorbers

Visualizing Atomic Scale Defects. Atomic resolution imaging is a direct method to experimentally visualize the structural imperfections that influence performance, such as point defects and stacking faults. Such imaging has been challenging in halide perovskites as the materials degrade rapidly in the microscopes capable of achieving the required resolution.

Recently researchers utilized low-dose, low-angle annular dark field imaging performed in a scanning transmission electron microscope to obtain the first atomic resolution images of FAPbI₃ and MAPbI₃ halide perovskites in thin-film form that is technologically relevant for PV.⁶ This atomic-level understanding provides new insight into the mechanisms that underpin the remarkable performance of halide perovskites. For example, the authors observed a coherent, defect-free, low strain interface between remnant precursor PbI₂ and FAPbI₃ grains, helping to explain why small excess amounts of PbI2 may not be detrimental to PV performance. In addition, aligned point defects in the form of vacancies on the Pb-I sublattice in the FAPbI₃ were observed, which provides direct experimental visualization of defects long predicted by theory. At the same time, stacking faults and edge dislocations (Figure 1A,B), relatively underexplored structural defects in perovskites, were also shown to be common, which could have important implications for performance. Examination of FAPbI₃/FAPbI₃ grain boundaries provided further insight: while most triple-point boundaries are crystallographically continuous, some boundaries notably contained amorphous material and aligned point defects (Figure 1C,D). A complete, coherent understanding of the implications of the observed structural defects will require more work, with a focus on atomic resolution imaging combined with photophysical information and/or simulations to determine which defects are most relevant for material stability and performance. A particularly important issue will be reconciling whether (if any) such defects or material in the grain boundaries lead to points of potential failure in operating devices under solar illumination, which would then motivate their selective mitigation. Further important questions relate to how these atomic scale defects differ depending on deposition methods, which will become relevant when scaling different deposition techniques.

Deep Traps. Substantial performance losses due to trap-assisted recombination, in which traps deep in the band gap cause charge-carriers to recombine non-radiatively without usefully contributing to device performance, still persist in halide perovskite absorbers and can be visualized by spatially resolved variations of, for example, photoluminescence. Understanding the origin of deep traps in halide perovskites is a critical step to eventually mitigate them and improve device performance. Recently, researchers combined photoemission electron microscopy and a variety of scanning electron analytical techniques to reveal the distribution of deep traps in $(C_{s_{0.05}}FA_{0.78}MA_{0.17})Pb(I_{0.83}Br_{0.17})_3$ and related halide perovskites.⁵ Rather than a uniform distribution of traps within regions of poor photoluminescence quantum efficiency (PLQE), clusters of traps on the film surfaces were observed (Figure 1E). These trap clusters showed a hole-trapping character and formed almost exclusively at grain boundaries between crystallographically and compositionally distinct entities, illustrating that i) managing structure and composition on the nanoscale is essential to obtain optimal performance in halide perovskite devices and ii) the photovoltaic performance in these absorbers is limited by the halide perovskite grain exterior and not the grain interior. While there is some theoretical evidence that point defects are more stable at grain boundaries,⁷ generally the behavior of grain boundaries in halide perovskites remains poorly understood and the exact nature of the defects that may be causing the trap clusters remains unclear. Future work must focus on understanding these crystallographic phase impurities and identifying how these performance losses also relate to stability losses. A key question will be whether pure phases are essential for eliminating the formation of these trap clusters in order to achieve the highest levels of performance and stability, or whether alloyed compositions - which have mostly led PV efficiency tables to date – can be engineered without these impurity phases. Another concern with multi-cation and multi-halide perovskites is the long-term stability of these compositions, especially those containing volatile MA cations. This has led to a renewal of interest in singlecation, single-halide compositions, such as FAPbI₃. Notably, stabilizing the most desired crystallographic phases in the single cation/halide perovskites remains an area of ongoing research.⁸ Ultimately, correlated atomic resolution studies using the techniques discussed above will provide insight into the specific type of defects in the clusters and how they vary with composition or structure. Such atomic, nano- and micro-scale understanding will be critical for guiding removal of such unwanted inhomogeneities.



Figure 1. Heterogeneity and defects at the atomic and nanoscales. High Resolution Scanning Transmission Electron Microscopy (HR-STEM) images showing (A) stacking faults in the orange rectangles with a stacking fault vector of $\frac{1}{2} <110$ >, (B) edge dislocations in the green rectangles with a Burgers vector of <100>, (C) grain boundary triple junction with no amorphous or intergranular phases, and (D) two triple junctions showing i) amorphization at the intersection on the left and ii) a line of vacancies at the intersection on the right. From Ref. 6. Reprinted with permission from AAAS. In parts A–D, the scale bar is 10 nm. (E) Photoemission electron microscopy images from 4.65 eV pulses (which selectively probe intraband states) showing the location of nanoscale trap clusters (blue) against the intensity

from the 6.2 eV pulse (gray) – probing the valence band edge – that reveals the halide perovskite microstructure. Reprinted with permission from Ref. 5.

Engineering Interfaces to Minimize Recombination and Degradation Essential for Efficient, Stable Performance

Beyond understanding and controlling extended defects in thin films, pushing the efficiency of halide perovskite solar cells toward their radiative limits will also require focus on the design of interfaces to (i) eliminate non-radiative losses, and (ii) achieve efficient, selective charge extraction. This can be done by the addition of interlayers, both of which act as passivating agents and can tune the band alignment between the charge transport layers and the perovskite film.

Challenges at Halide Perovskite Interfaces. Interfaces still limit the open-circuit voltage (V_{oc}), fill factor (FF), and stability of halide perovskite solar cells by introducing additional non-radiative recombination processes and energy barriers, as well as inducing chemical reactions, such as perovskite deprotonation.³ Furthermore, existing defects can favor further defect formation. At high concentrations, charged point defects lead to the production of molecular species that are desorbed from the halide perovskite film. For example, the trapping of holes by I interstitials leads to their oxidation to I₀. An I₀-I₀ pair then produces I₂ which diffuses to the film surfaces.⁹ Defects in halide perovskites can be passivated by molecules able to accept or donate electrons *via* electrostatic interactions.⁹ Treating the top surface of the halide perovskite top surface to a 2D perovskite, depending on the size of the organic cation used.⁹ However, this strategy is difficult to achieve on the bottom surface of the perovskite, since the

solution deposition of the halide perovskite onto a layer of the organic salt or 2D perovskite would redissolve this layer. Recent work has shown that the challenge of passivating the buried perovskite interface next to the substrate can be overcome by using self-assembled monolayers (SAMs).¹⁰ SAMs are comprised of an anchor, a spacer, and a terminal group. The anchoring groups make the SAMs robust to the solution deposition of the halide perovskite film on top. The spacer in SAMs control their self-assembly and conductivity, while the terminal group changes the molecular dipole moment and can passivate defect sites at the halide perovskite surface.¹⁰ The effective use of SAMs played a critical role in achieving the 29.15%-efficient device reported by Albrecht *et al.* that held the highest certified PCE for perovskite-silicon tandems for most of 2020.¹¹ With a thickness <1 nm, the SAMs directly interfaces the halide perovskite layer and electrode to minimize contact resistance, allowing simultaneous improvements in both V_{oc} and FF.¹¹ The halide perovskite film stability is also enhanced because charge accumulation at the electrode interface is reduced, and the perovskite surface defects are passivated by the methyl functional groups of the SAMs (Figure 2A).¹¹

Towards the Radiative Limit. The continuous efforts towards interface passivation have enabled the V_{oc} of halide perovskite PV to reach up to 95.8% of the detailed-balance limit, matching the 95.9% value of GaAs PV (Table S1). On the other hand, the FF and short circuit current density (J_{sc}) of halide perovskites have only reached 93.8% and 93.2% of the detailedbalance limit, respectively, lagging behind the >95% values of Si and GaAs (Table S1). Overcoming these limitations will require: (i) eliminating transport losses across interfaces in halide perovskite solar cells, and (ii) increasing the internal quantum efficiencies of the halide perovskite films towards 100% in order to improve both J_{sc} s and FFs beyond 95% of the detailed-balance limit.¹¹ This is especially important in the wider band gap perovskite compositions (used for top-cells in tandem photovoltaics), which are further from their radiative limits. Thus far, highly efficient halide perovskite PV has only relied on passivating one perovskite interface. The combined use of SAMs and 2D halide perovskites to passivate both the bottom and top interfaces, respectively, has potential to allow the FFs and J_{sc} s to both approach their limits (Figure 2B). But going beyond the current state-of-the-art will also require improved control over the passivating layers, as well as improved understanding of the mechanism of charge extraction through the passivating layers. For the 2D perovskite passivating overlayer, charge-carrier extraction is strongly affected by the 2D film thickness, uniformity and phase-purity, as well as by its band alignment with the 3D perovskite absorber and the carrier-selective contact. Improved control over the thickness and composition of the 2D layer could be achieved with vapor-based deposition routes, including physical and chemical vapor deposition. Charge injection and film uniformity can be monitored using highresolution mapping techniques, such as confocal microscopy to monitor variations in the photoluminescence intensity, peak position and lifetime. For the underlayer, the uniformity of SAMs and the impact of the functional groups on the crystallization of the overlying halide perovskite film needs to be investigated. Only by gaining this understanding will we be able to improve the efficiency of carrier extraction from the halide perovskite to the charge transport layers, whilst maintaining a high V_{oc} .

Furthermore, more thorough reports on the long-term stability of halide perovskites passivated with SAMs and 2D layers are needed. With their sub-nanometer thicknesses, SAMs might provide a weaker barrier to ion diffusion and may increase the likelihood that the halide perovskite film will delaminate from the substrate. On the other hand, the cations from the 2D halide perovskite could diffuse in the 3D bulk, changing the properties of the interface over time. An insight-driven design of the interface passivation layers will be critical to enable stable PV parameters beyond 95% of the detailed-balance limit.



Figure 2. Engineering interfaces for improved efficiency and stability. (A) Evolution of the photoluminescence (PL) over 10 min of a mixed halide perovskite film (Br/I) deposited on ITO/Me-4PACz (SAM) or on ITO/PTAA (top and bottom plots, respectively). The accumulation of photogenerated holes at the PTAA/perovskite interface induces segregation of iodine and bromine in the film, causing the PL peak to shift. From Ref. 11. Reprinted with permission from AAAS. (B) A proposed approach to simultaneously passivate the bottom and top interfaces of the halide perovskite (HP) films. The main advantages and possible limitations at each interface are summarized in the boxes on the right.

Speed, Stability and Toxicity Key Considerations for Perovskite Manufacturing

Speed at scale. Although groups have now succeeded in fabricating >25%-efficient perovskite single-junction solar cells with ~0.1 cm² active areas,¹² achieving perovskite manufacturing at the gigawatt scale will require the deposition of several million square meters of PVs per year.² Not only will it be necessary to develop deposition methods capable of growing uniform and high-quality films at the module level with >100 cm² area, speed is also an essential consideration. Processing speed affects the number of modules that can be processed per manufacturing hour, and increasing processing speed is critical to reducing the capital intensity,

module manufacturing cost and LCOE. Therefore, large-area solution processing methods (e.g., blade coating, inkjet printing, slot-die coating, screen printing, and gravure printing; Figure 3A) have gained attention because of their compatibility with high-throughput roll-toroll processing under ambient conditions.² However, it has been challenging to achieve largegrained, highly-crystalline films when grown with rapid deposition rates. This challenge was recently overcome in blade coating by decoupling film formation and crystallization.² By using a volatile solvent (e.g., acetonitrile), the deposited film rapidly dried after coating, whilst the perovskite precursors remained coordinated to a non-volatile solvent (*e.g.*, dimethylsulfoxide) and could then be fully crystallized to form large grains through post-annealing. As a result, a high processing speed of 5.9 m min⁻¹ was achieved (Figure 3A), with 16.4%-efficient modules (63.7 cm² area) demonstrated (Table S2).² However, the overall throughput is lower than suggested by the 5.9 m min⁻¹ blade coating speed, owing to the post-annealing step, and this is the case for all blade-coated films. Recently, it was shown that a spray deposition method (Rapid Spray Plasma Processing, or RSPP) can overcome this limitation by crystallizing the perovskite film during deposition through thermal (by heating to 140 °C) and plasma energy, with a processing speed of 12 m min⁻¹ demonstrated (Figure 3A; Table S2). Crystalline films that gave 15.2%-efficient modules (5.9 cm² area) were achieved.¹³ Beyond solution-based methods, thermal evaporation and chemical vapor deposition are capable of large-area perovskite manufacturing and are appealing because they can grow perovskite films conformally to front-textured silicon bottom cells, which will be important for tandem devices. However, a disadvantage is that the overall processing rate of many of these vapor-based methods has been estimated to be as low as ~ 0.01 m min⁻¹ owing to the low deposition rate, as well as the added time from pumping down to vacuum.¹³ Recently, this challenge was partially addressed by employing a vapor transport deposition method that could grow perovskite films an order of magnitude faster than thermal evaporation (Figure 3A). Nevertheless, further work

will be needed to improve the film quality in order to achieve efficient PVs with this technique (details in Table S3).



Figure 3. Commercialization of perovskite photovoltaics. (A) Comparison of the linear processing speed of solution-based processing methods (blade coating, inkjet printing and Rapid Spray Plasma Processing or RSPP), as well as the deposition rate of vapor-based processing methods (thermal evaporation and vapor deposition) that are capable of manufacturing large-area modules. Data in Tables S2,S3, including extra data for spray coating, slot-die coating and gravure printing. (B) Effect of the module lifetime (time taken for efficiency to decrease to 80% of the original value) and efficiency (14%, 16%, 18%) on the levelized cost of energy. Adapted with permission from Ref. 13. Copyright 2020 Cell Press. (C) Illustration of the lifecycle of perovskite modules, with key toxicity mitigation steps indicated.

Beyond the perovskite absorber layer, the contact layers in a photovoltaic device also need to be rapidly manufactured at scale. A potentially simpler alternative to sequentially growing several separate layers in a planar device stack is to use the printable triple mesoscopic structure. This is comprised of three screen-printed layers: mesoporous TiO₂ (electron transport layer), mesoporous ZrO₂ (spacer) and carbon anode. The perovskite is subsequently introduced into these mesoporous layers in one step through capillary forces.¹⁴ This structure has the advantages of being fully printable at scale, is recyclable and eliminates the use of high-cost organic charge transport layers and Au/Ag electrodes.¹⁴ However, the parameters discussed above for rapidly growing large-area perovskites may not directly translate to the triple mesoscopic structure owing to the different perovskite crystallization processes. Furthermore, one needs to carefully consider whether the multiple interfaces and grain boundaries inherent in this configuration would ultimately limit the projected performance.

Lifetime of perovskite modules. Currently, the primary focus in the perovskites field is on efficiency. However, the technoeconomic analysis shown in Figure 3B demonstrates that changing the efficiency of a perovskite single-junction PV module from 14–18% makes little difference to the LCOE as compared to the module lifetime, which is here defined as the time taken for the device to degrade to 80% of the original efficiency.¹³ Stability will therefore take center stage in future efforts at commercialization. As such, there have been significant efforts to go beyond thermodynamically unstable MAPbI₃ to develop more stable halide perovskite compositions.³ Beyond the thin films, more efforts are needed to develop packaging materials for perovskite modules, as well as accelerated degradation testing protocols that are specific to perovskites.¹⁵ Currently, the standards from the International Electrotechnical Commission (IEC, especially no. 61215) are used. Although passing the IEC protocols is important to satisfy investors and consumers, these protocols were developed for silicon PV, which likely have different degradation pathways compared to perovskite modules. An emerging concept for identifying critical failure modes is to use machine learning algorithms to predict the decay in perovskite performance (see Table S4 for an overview of recent work). Such efforts will be

bolstered with the creation of databases of perovskite stability data, particularly field testing data, for training the algorithms.

Mitigating toxicity challenges over the lifecycle of perovskite modules. Recent efforts have led to the development of methods to mitigate the risks associated with the toxicity of lead throughout the perovskite lifecycle, as summarized in Figure 3C.¹⁶ For example, ironhydroxyapatite composites have been developed which can adsorb lead from contaminated polar solvents (*e.g.*, freshwater) and be magnetically separated.¹⁶ Lead sequestration is another promising approach for mitigating against lead leaching from modules that have undergone the of a coating (e.g., P,P'-di(2catastrophic damage, and involve use ethylhexyl)methanediphosphonic acid) deposited on the module.¹⁷ Beyond the hazards associated with lead, the solvents used in perovskite manufacturing (e.g., the commonly-used *N*,*N*-dimethylformamide) can be more hazardous than lead itself. Future work should therefore focus on developing large-area manufacturing processes using benign solvents (e.g., dimethylsulfoxide),¹⁸ or solvent-free methods, such as rapid vapor-based deposition techniques.

Future Focus

In summary, the lead-halide perovskite PV field has made astonishing progress in a short span of time. Single-junction polycrystalline perovskite PV are now at the brink of matching the performance of monocrystalline silicon PV. Simultaneously, perovskite PV are now at the cusp of moving from lab to market. Moving forward to the next steps of approaching the radiative limit of perovskite solar cells and commercializing the technology will require developments at the nanoscale, at interfaces, and at the device and module level. In particular, understanding the role of phase impurities and extended defects, as well as developing more effective methods to passivate interfaces, will be critical to push efficiencies toward the radiative limits. For commercialization, it will be important to shift the focus beyond efficiency to rapid manufacturing at scale, as well as improving module lifetime and developing technology to mitigate toxicity risks over the perovskite lifecycle. Overcoming these current bottlenecks could enable halide perovskite solar cells to meet the urgent needs for a rapid acceleration in photovoltaic deployment.

SUPPLEMENTAL INFORMATION

Supporting tables and plots can be found online at https://doi.org/XXXX

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AUTHOR CONTRIBUTIONS

R. L. Z. H. and J.-P. C.-B. conceived the idea for writing this article. R. L. Z. H. led in writing the introduction and section on commercialization and upscaling. T. A. S. D. and S. D. S. wrote

the section on nanoscale defects. C. P. and J.-P. C.-B. wrote the section on interfaces. All authors discussed and edited the entire manuscript.

DECLARATION OF INTERESTS

SDS is a co-founder of Swift Solar Inc.

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Table S1. Comparison of the photovoltaic parameters of top-performing lead-halide perovskite, GaAs and Si solar cells. The percentage of the performance metrics achieved relative to the maximum values expected from the detailed-balance limit is shown in parentheses. Reported halide perovskite compositions are approximated from the precursor solution stoichiometry. $FA = CH(NH_2)_2^+$, $MA = CH_3NH_3^+$, $DMA = CH_2(NH_3)_2^{2+}$.

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Semiconductor (approximate composition)	Eg (eV)	$V_{ m oc}$ (V)	$J_{\rm sc}$ (mA cm ⁻²)	FF (%)	PCE (%)	Defect Passivation Strategy	Ref.
$Cs_{0.015}FA_{0.97}DMA_{0.015}PbI_3$	1.48	1.162 (95.84)	26.17 (88.17)	80.1 (89.15)	24.2 (75.47)	Strain management	1
FA0.92MA0.08PbBr0.24I2.76	1.53	1.179 (93.64)	25.2 (90.02)	78.4 (86.97)	23.32 (73.4)	Thin organic film	2
FA0.95MA0.05PbBr0.15I2.85	1.55	1.185 (92.74)	24.71 (90.63)	83.9 (92.97)	24.59 (78.21)	2D LHP	3
$FA_{0.73}MA_{0.27}Pb(Br_{0.008}I_{0.992})_3$	1.56	1.181 ^{<i>a</i>} (91.75)	25.08 (93.21)	84.7 (93.79)	25.4 (81.22)	Thin organic film	4
$Cs_{0.05}FA_{0.73}MA_{0.22}PbBr_{0.66}I_{2.33}$	1.68	1.151 (82.25)	20.31 (88.07)	84.0 (92.40)	20.00 (68.17)	SAM	5
Si	1.11	(85.1)	(96.70)	(97.7)	(80.36)		6
GaAs	1.44	(95.9)	(95.3)	(96.77)	(88.48)		6

^{*a*} The unmasked device reached a V_{OC} of 1.225 V, corresponding to 95.17% of the detailed-balance limit.



Figure S1. Photovoltaic parameters of the best performing halide perovskite solar cells (colored squares) and of Si and GaAs solar cells (gray squares) with respect to the detailedbalance limit (black line). The number in the figure follows the reference number in Table S1.

Table S2. Comparison of the linear processing speed of large-area solution-based deposition methods for fabricating perovskite thin films, along with the performance and size of the active area of the resulting photovoltaic devices. For modules, the module V_{OC} is given, whereas the J_{SC} is the per-cell value, unless otherwise noted

50	1	,							
No.	Method	Device	Speed	Area (am^2)	$V_{\rm OC}$ (V)	$J_{\rm SC}$ (mA cm ⁻²)	FF	PCE	Ref
1		Lab-scale	(111111)	0.1^a	1 048	23.40	(%)	19.47	7
1		Lab-scale	0.5	0.08	1.040	23.40	81.8	21.3	,
2		Module	5.9	63 7	18.936	1 15 ^b	75.5	16.4	8
		Lab-scale		0.12	1 097	22.53	~75	18 55	
3		Module	0.8	11.09	4.396	20.5	59	13.3	9
4		Lab-scale	0.3	0.1	1.10	20.58	72.4	16.8	10
5		Lab-scale	0.6	0.09	1.04	21.36	75	16.71	11
6	Blade	Lab-scale	0.45	0.08	1.10	22.7	80.9	20.2	12
_	coating	Lab-scale	0.0	0.12	1.10	22.4	78	19.4	10
1	C	Module	0.3	10.36	4.35	20	74	16.3	13
		Lab-scale		0.1	1.0	18.9	70.5	13.3	
8		Module	2.4	10.1	4.11	17.17	58.14	10.4	14
		Module		100	9.61	7.48	53.79	4.30	
9		Lab-scale	0.42	0.1	0.95	19.89	53.67	10.14	15
10		Lab-scale	1.2	0.1	0.89	16.85	73	11.04	16
11		Lab-scale	1.2	0.034	0.91	18.38	73	12.21	17
12		Lab-scale	0.2	0.064	1.028	19.35	71	14.11	18
		Lab-scale		0.04	1.08	22.71	69.58	17.04	
12	Inkiat	Lab-scale	0.3	1	1.04	22.45	66.39	15.50	10
15	printing	Lab-scale	0.5	2	1.04	21.31	66.22	14.67	19
	printing	Lab-scale		4	1.04	20.40	62.57	13.27	
14		Lab-scale ^d	0.2	0.16	0.861	16.6	66.8	9.54	20
15		Lab-scale	0.2	0.09	1.00	18.4	56	11.3	21
16		Lab-scale	~1	0.2	1.05	21.8	69	15.7	22
10	R S D D ^c	Module		2.4	~0.95	~22	~64	13.4	22
17	K511	Lab-scale	12	0.2	0.99	22.6	~80	~18	23
17		Module	12	5.9	18.05	20.7	69	15.2	25
18	<mark>Spray</mark>	Lab-scale	0.6	<mark>0.096</mark>	1.15	<mark>18.08</mark>	<mark>81</mark>	<mark>16.81</mark>	24
10	<u>coating</u>	Module	0.0	<u>112</u>	<mark>7.64</mark>	<mark>2.51</mark>	<mark>72</mark>	<mark>13.82</mark>	<u></u>
<u>19</u>	<mark>Slot-die</mark>	Lab-scale	<mark>0.1</mark>	0.09	<mark>0.89</mark>	18.33	<mark>73</mark>	<mark>11.7</mark>	<mark>25</mark>
<mark>20</mark>	coating	Lab-scale	0.18	<mark></mark>	1.10	<u>17.21</u>	<mark>67</mark>	12.7	<mark>26</mark>
<mark>21</mark>	Gravure printing	Lab-scale	<mark>4^e</mark>	<mark>0.052</mark>	<mark>0.89</mark>	<mark>17.2</mark>	<mark>63</mark>	<mark>9.7</mark>	<mark>27</mark>

^{*a*} Technique demonstrated to deposit perovskite films over 72 cm² area.⁷

^b Sub-cell area not given, so current divided by total module area of 63.7 cm²

^c RSPP = Rapid Spray Plasma Processing

^d This device used a screen-printed triple mesoscopic device structure²⁰

^e This processing speed is only for the deposition of the PbI₂-DMSO layer, which is

subsequently immersed in an MAI bath for 3 min, followed by 10 min annealing at 100 °C



Figure S2. Comparison of the linear processing rate of solution-based perovskite deposition methods compatible with large-area manufacturing. Values next to data points correspond to the numbers in the first column of Table S2.

Table S3. Comparison of the deposition rate of vapor-based deposition methods in fabricating the perovskite thin film, along with the performance and size of the active area of the resulting photovoltaic devices. All techniques shown here grow the perovskite film in one step

No.	Method	Device type	Deposition rate (nm min ⁻¹)	Area (cm ²)	$V_{\rm OC}$ (V)	$J_{ m SC}~(m mA~cm^{-2})$	FF (%)	PCE (%)	Ref
1	Thormal	Lab-scale	~5	0.16	1.06	23.0	74.6	18.1	28
2		Lab-scale	3.6	0.09	1.37	7.79	81	8.65	29
3	evaporation	Lab-scale	~6	0.25	1.046	18.4	59.6	11.51 ^a	30
4	Vapor	Lab-scale	$5-10^{b}$	_	0.97	18	64	11.1	31
5	deposition	Lab-scale	78 ^c	0.20	1.01	14.2	48	6.9	32

^{*a*} Semi-transparent solar cell

^{*b*} 500 nm thick films of CH₃NH₃PbI_{3-*x*}Cl_{*x*} grown after precursor vaporized for a total of 100 min, with the hold time at the maximum temperature of 360 °C for 46 min.³¹

^{*c*} Deposition rate measured for PbI₂ growth. CH₃NH₃PbI₃ grown through sequential deposition of PbI₂ and CH₃NH₃I. Approximately 250 nm thick CH₃NH₃PbI₃ films are grown after 12 min of PbI₂ and CH₃NH₃I exposure, implying that the averaged growth rate of the perovskite film is lower than 78 nm min⁻¹. However, simulations showed that significantly higher growth rates are possible³²



Figure S3. Comparison of the deposition rate of vapor-based perovskite deposition methods compatible with large-area manufacturing. Values next to data points correspond to the numbers in the first column of Table S3.

		ЪC
Machine learning method	Outcome	Ref.
Linear regression with	Model capable of predicting the time take for the	33
greedy feature selection	diffusion length of MAPbI ₃ films to decay to 85% of the	
algorithm	initial value with a prediction accuracy of 12.8%	
Echo state networks	Prediction of the decay in the PL of MAPbI ₃ and	34
	MAPbBr ₃ films under ambient conditions	
Physics-constrained	Identified optimal composition of triple-cation	35
Bayesian optimisation	perovskites with improved stability	
framework		
Random forest regression	Identified that alkylammonium cations with a low	36
algorithm and	number of hydrogen-bonding donors and small	
importance ranking using	topological polar surface area give rise to improved	
Shapley value concept	stability of MAPbI ₃ films	
Association rule mining	Identified features that led to improved device stability.	37
and decision trees	Beneficial film processing features: mixed cation	
applied to 404 halide	perovskites, multi-spin spin coating, the use of a mixture	
perovskite photovoltaics	of <i>N</i> , <i>N</i> -dimethylformamide and dimethylsulfoxide, and	
from 181 papers	the use of chlorobenzene antisolvent	
	Beneficial device features: SnO ₂ and PCBM electron	
	transport layers, inorganic or hole-transport-layer-free	
	devices, carbon back contacts	

Table S4.	Selection of	recent efforts	to couple machin	ne learning v	with predicting	and
improving	g the stability	of perovskite	solar absorbers a	and photovo	ltaics	

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				- /	= (*/= :	
Semiconductor (approximate composition)	Eg (eV)	Voc (V)	$J_{ m sc}$ (mA cm ⁻²)	FF (%)	PCE (%)	Defect Passivation Strategy	Ref.
Cs0.015FA0.97DMA0.015PbI3	1.48	1.162 (95.84)	26.17 (88.17)	80.1 (89.15)	24.2 (75.47)	Strain management	1
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FA0.95MA0.05PbBr0.15I2.85	1.55	1.185 (92.74)	24.71 (90.63)	83.9 (92.97)	24.59 (78.21)	2D LHP	3
FA0.73MA0.27Pb(Br0.008I0.992)3	1.56	1.181^a (91.75)	25.08 (93.21)	84.7 (93.79)	25.4 (81.22)	Thin organic film	4
Cs0.05FA0.73MA0.22PbBr0.66I2.33	1.68	1.151 (82.25)	20.31 (88.07)	84.0 (92.40)	20.00 (68.17)	SAM	5
Si	1.11	(85.1)	(96.70)	(97.7)	(80.36)		6
GaAs	1.44	(95.9)	(95.3)	(96.77)	(88.48)		6

^{*a*} The unmasked device reached a V_{OC} of 1.225 V, corresponding to 95.17% of the detailedbalance limit.



Figure S1. Photovoltaic parameters of the best performing halide perovskite solar cells (colored squares) and of Si and GaAs solar cells (gray squares) with respect to the detailedbalance limit (black line). The number in the figure follows the reference number in Table S1.

Table S2. Comparison of the linear processing speed of large-area solution-based deposition methods for fabricating perovskite thin films, along with the performance and size of the active area of the resulting photovoltaic devices. For modules, the module $V_{\rm OC}$ is given, whereas the $J_{\rm SC}$ is the per-cell value, unless otherwise noted

- 50)							
No.	Method	Device	Speed	Area	$V_{\rm OC}$ (V)	$J_{\rm SC}$ (mA cm ⁻²)	FF	PCE	Ref
1		type	$(m m m^{-1})$	(cm^2)	1.0.40	22.40	(%)	(%)	
1		Lab-scale	0.3	0.1^{a}	1.048	23.40	79.38	19.47	1
2		Lab-scale	5.9	0.08	1.13	23.0	81.8	21.3	8
		Module		63.7	18.936	1.15 %	75.5	16.4	
3		Lab-scale	0.8	0.12	1.097	22.53	~75	18.55	9
-		Module	0.0	11.09	4.396	20.5	59	13.3	-
4		Lab-scale	0.3	0.1	1.10	20.58	72.4	16.8	10
5		Lab-scale	0.6	0.09	1.04	21.36	75	16.71	11
6	Blade	Lab-scale	0.45	0.08	1.10	22.7	80.9	20.2	12
7	coating	Lab-scale	0.3	0.12	1.10	22.4	78	19.4	13
/		Module	0.5	10.36	4.35	20	74	16.3	15
		Lab-scale		0.1	1.0	18.9	70.5	13.3	
8		Module	2.4	10.1	4.11	17.17	58.14	10.4	14
		Module		100	9.61	7.48	53.79	4.30	
9		Lab-scale	0.42	0.1	0.95	19.89	53.67	10.14	15
10		Lab-scale	1.2	0.1	0.89	16.85	73	11.04	16
11		Lab-scale	1.2	0.034	0.91	18.38	73	12.21	17
12		Lab-scale	0.2	0.064	1.028	19.35	71	14.11	18
		Lab-scale		0.04	1.08	22.71	69.58	17.04	
10	.	Lab-scale		1	1.04	22.45	66.39	15.50	1.0
13	Inkjet	Lab-scale	0.3	2	1.04	21.31	66.22	14.67	19
	printing	Lab-scale		4	1.04	20.40	62.57	13.27	
14		Lab-scale ^d	0.2	0.16	0.861	16.6	66.8	9.54	20
15		Lab-scale	0.2	0.09	1.00	18.4	56	11.3	21
		Lab-scale		0.2	1.05	21.8	69	15.7	
16		Module	>4	2.4	~0.95	~22	~64	13.4	22
	RSPP ^c	Lab-scale		0.2	0.99	22.6	~80	~18	
17		Module	12	5.9	18.05	20.7	69	15.2	23
	Spray	Lab-scale		0.096	1.15	18.08	81	16.81	
18	coating	Module	0.6	112	7.64	2.51	72	13.82	24
19	Slot-die	Lab-scale	0.1	0.09	0.89	18.33	73	11.7	25
20	coating	Lab-scale	0.18	-	1 10	17.21	67	12.7	26
21	Gravure	Lab-scale	4 ^e	0.052	0.89	17.2	63	9.7	27

^{*a*} Technique demonstrated to deposit perovskite films over 72 cm² area.⁷

^b Sub-cell area not given, so current divided by total module area of 63.7 cm²

^c RSPP = Rapid Spray Plasma Processing

^d This device used a screen-printed triple mesoscopic device structure²⁰

^{*e*} This processing speed is only for the deposition of the PbI₂-DMSO layer, which is subsequently immersed in an MAI bath for 3 min, followed by 10 min annealing at 100 °C



Figure S2. Comparison of the linear processing rate of solution-based perovskite deposition methods compatible with large-area manufacturing. Values next to data points correspond to the numbers in the first column of Table S2.

Table S3. Comparison of the deposition rate of vapor-based deposition methods in fabricating the perovskite thin film, along with the performance and size of the active area of the resulting photovoltaic devices. All techniques shown here grow the perovskite film in one step

No.	Method	Device type	Deposition rate (nm min ⁻¹)	Area (cm ²)	Voc (V)	$J_{\rm SC}$ (mA cm ⁻²)	FF (%)	PCE (%)	Ref
1	Thomas	Lab-scale	~5	0.16	1.06	23.0	74.6	18.1	28
2		Lab-scale	3.6	0.09	1.37	7.79	81	8.65	29
3	evaporation	Lab-scale	~6	0.25	1.046	18.4	59.6	11.51 ^a	30
4	Vapor	Lab-scale	$5-10^{b}$	_	0.97	18	64	11.1	31
5	deposition	Lab-scale	78^{c}	0.20	1.01	14.2	48	6.9	32

^a Semi-transparent solar cell

^{*b*} 500 nm thick films of CH₃NH₃PbI_{3-*x*}Cl_{*x*} grown after precursor vaporized for a total of 100 min, with the hold time at the maximum temperature of 360 °C for 46 min.³¹

^{*c*} Deposition rate measured for PbI₂ growth. CH₃NH₃PbI₃ grown through sequential deposition of PbI₂ and CH₃NH₃I. Approximately 250 nm thick CH₃NH₃PbI₃ films are grown after 12 min of PbI₂ and CH₃NH₃I exposure, implying that the averaged growth rate of the perovskite film is lower than 78 nm min⁻¹. However, simulations showed that significantly higher growth rates are possible³²



Figure S3. Comparison of the deposition rate of vapor-based perovskite deposition methods compatible with large-area manufacturing. Values next to data points correspond to the numbers in the first column of Table S3.

mproving the stability of pe	sovskite solar absorbers and photovortales	
Machine learning method	Outcome	Ref.
Linear regression with	Model capable of predicting the time take for the	33
greedy feature selection	diffusion length of MAPbI ₃ films to decay to 85% of the	
algorithm	initial value with a prediction accuracy of 12.8%	
Echo state networks	Prediction of the decay in the PL of MAPbI ₃ and	34
	MAPbBr ₃ films under ambient conditions	
Physics-constrained	Identified optimal composition of triple-cation	35
Bayesian optimisation	perovskites with improved stability	
framework		
Random forest regression	Identified that alkylammonium cations with a low	36
algorithm and	number of hydrogen-bonding donors and small	
importance ranking using	topological polar surface area give rise to improved	
Shapley value concept	stability of MAPbI ₃ films	
Association rule mining	Identified features that led to improved device stability.	37
and decision trees	Beneficial film processing features: mixed cation	
applied to 404 halide	perovskites, multi-spin spin coating, the use of a mixture	
perovskite photovoltaics	of <i>N</i> , <i>N</i> -dimethylformamide and dimethylsulfoxide, and	
from 181 papers	the use of chlorobenzene antisolvent	
	Beneficial device features: SnO ₂ and PCBM electron	
	transport layers, inorganic or hole-transport-layer-free	
	devices, carbon back contacts	

Table S4.	Selection of	f recent effor	rts to coupl	e machine l	earning w	with predicting	and
improving	g the stability	of perovski	te solar ab	sorbers and	photovol	taics	

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