

Navigating the Kinetic and Manufacturing Boundaries of Plasma-Engineered Perovskite Heterojunctions

Jingbi You^(✉)1,2

1 State Key Laboratory of Semiconductor Physics and Chip Technologies, Institute of Semiconductors, Chinese Academy of Sciences, Beijing 100083, China

2 Center of Materials Science and Optoelectronics Engineering, University of Chinese Academy of Sciences, Beijing 100049, China

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E-mail: jyou@semi.ac.cn (You J.).

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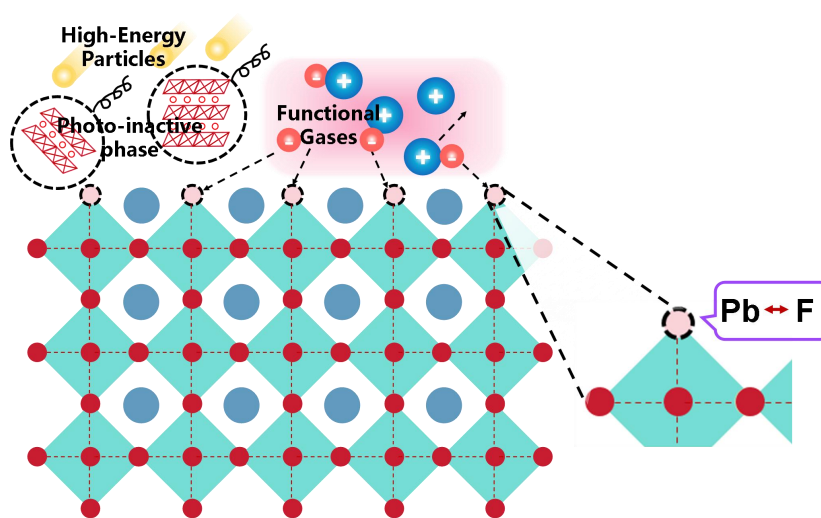
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GRAPHICAL ABSTRACT



Controlled plasma etching and in situ passivation of the perovskite surface enable the formation of a continuous and compact interfacial heterostructure.

HIGHLIGHT

- Solvent-free Ar/CF₄ plasma treatment converts defect-rich perovskite surfaces into continuous, strongly bonded 4–7 nm PbF₂ heterostructures.
- Passivating the heat-affected zones enables a certified efficiency of 23.5% for 100 cm² modules.
- This process shows considerable application potential in perovskite/silicon tandem solar cells, PeLEDs, photodetectors, and non-planar optoelectronic devices.

KEYWORDS Plasma; Passivation; Perovskite solar cells; Interface engineering; Device design

The transition of metal halide perovskite photovoltaics from laboratory-scale small cells to commercially viable large-area solar modules hinges on resolving multiscale interfacial instabilities and localized degradation at scribing interconnects [1,2]. The recent report by Fan et al. (2026) introduces an industry-compatible, gas-phase plasma passivation methodology that replaces conventional wet-chemical treatments [3]. By combining radio-frequency argon (Ar) physical sputtering with reactive fluorocarbon (CF₄) fluorination, the authors demonstrate an *in situ* chemical transformation of defect-rich perovskite surfaces into a continuous, strongly bonded lead fluoride (PbF₂) heterostructure (4–7 nm thick). Crucially, this plasma-assisted process is extended to passivate heat-affected zones (HAZs) within laser-scribed interconnects (such as the P2 series-interconnection and P3 top-electrode isolation scribe regions), yielding a certified efficiency of 23.5% on 100 cm² modules alongside operation under continuous illumination and thermal stress. While gas-phase plasma processing eliminates solvent-induced surface reconstruction and concentration fluctuations inherent to spin-coating or blade-coating, several fundamental physical-chemical mechanisms and engineering constraints warrant deeper scrutiny. This commentary evaluates three key aspects arising from this plasma surface engineering framework: (1) spatial uniformity and precise kinetic control across industrial large-area substrates; (2) interfacial robustness under severe multi-factor aging conditions; and (3) application potential across diverse optoelectronic device architectures.

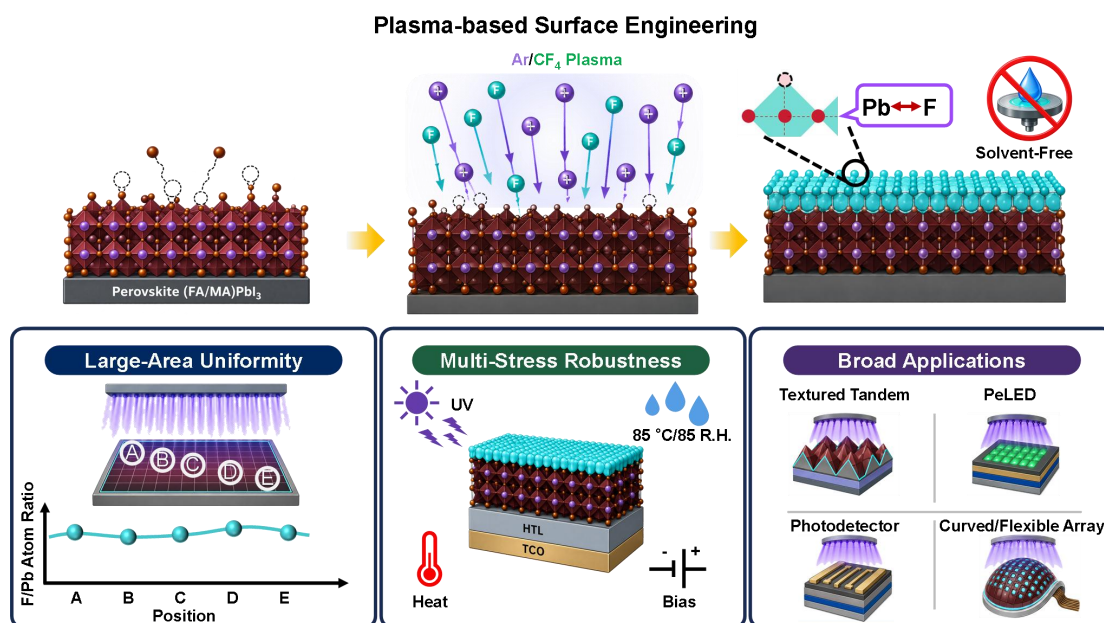


Fig. 1 A schematic drawing for the plasma-based surface engineering.

1 Spatial Uniformity and Precise Kinetic Control in Industrial Large-Area Manufacturing

Conventional wet-chemical passivation methods (e.g., spin-coating or blade-coating of organic ammonium salts) are inherently constrained by solvent evaporation kinetics, Marangoni convection, and hydrodynamic boundary layer variations over large areas. These factors frequently lead to local passivation concentration gradients, phase separation, or pinhole formation when scaling up to substrates exceeding 100 cm² or commercial sizes (> 1 m²) [4]. Other solvent-free passivation routes, including atomic layer deposition of metal oxides and vacuum evaporation of organic ammonium salts, serve as important benchmarks for comparison. ALD offers conformal coverage and cycle-controlled deposition, whereas evaporation delivers molecular passivates without solvent exposure. The distinguishing feature of the route reported by Fan et al. (2026) is the combination of Ar-assisted surface removal with *in situ* fluorination of the existing perovskite surface to form a PbF₂ heterostructure, rather than relying primarily on deposition of an externally supplied passivation layer. Its extension to laser-scribing heat-affected zones further highlights this surface-remediation capability. This distinction does not establish universal superiority over other dry routes; comparative evaluation should consider substrate damage, charge extraction, throughput, and process compatibility. For this coupled surface-removal and conversion process, a central scale-up question is whether the balance between ion bombardment and reactive radical exposure can be maintained uniformly across the substrate. Moving from laboratory-scale batch chambers to industrial high-throughput manufacturing therefore requires quantitative control of spatial power coupling, reactive-species transport, and surface-reaction kinetics. Fan et al. demonstrated spatial consistency through fluorine contents of 9.4%–10.5% at five sampled positions and performance mapping of 25 subcells from a 10 cm × 10 cm substrate. Extending this consistency to meter-scale substrates nevertheless requires reactor-specific validation. For example, Lim et al. reported that increasing RF power from 1 to 10 kW reduced the ion-current non-uniformity metric from 18.1% to 11.4% over a

2300 mm × 2000 mm substrate in a large-area inductively coupled plasma source [5]. Although this metric cannot be directly equated with PbF₂ thickness variation, it illustrates the sensitivity of large-area plasma uniformity to power coupling and wall losses. Achieving sub-nanometer thickness homogeneity across meter-scale modules demands highly uniform radio-frequency (RF) or microwave power distribution, precise control over sheath electric fields, and spatial stabilization of plasma density across large-area vacuum or atmospheric chambers. Minor fluctuations in local discharge impedance or gas distribution could cause spatial variance in the etching-to-conversion kinetics, potentially altering the target 4–7 nm PbF₂ heterojunction thickness across the module. Mechanistically, local fluorine-radical dose, ion fluence, and ion-energy distribution can affect the balance between surface removal and fluoride formation. The optimized treatment reported by Fan et al., namely 2 s of Ar exposure followed by 3 s of Ar/CF₄ exposure, also motivates assessing discharge stabilization and gas-replacement times relative to these short processing intervals. Whether spatial exposure variations translate into proportional conversion-depth variations, or are attenuated by reaction saturation, remains an important question for scale-up. Real-time diagnostic integration, such as optical emission spectroscopy combined with closed-loop process control, will be critical to maintain sub-nanometer layer depth uniformity and repeatability during continuous production [6]. The same plasma-surface interactions that enable defect removal and fluorination may also cause damage outside the optimized process window. Excessive ion bombardment, plasma-generated UV exposure, or overly aggressive fluorination could induce halide depletion, lattice disorder, or excessive surface conversion, potentially compromising charge extraction. These are process-dependent risks rather than demonstrated failures of the reported treatment; defining the window between beneficial passivation and plasma-induced damage is therefore important for manufacturing transfer.

Beyond thickness uniformity, the electronic role of the 4–7 nm PbF₂ interlayer warrants consideration. A potential extraction barrier would depend on its band offsets and electronic structure, and efficient direct tunneling cannot be inferred from nanometer-scale thickness alone. Fan et al. report a 0.07 eV upward shift of the surface Fermi level and an increase in fill factor from 83.5% to 85.2%, supporting a beneficial net effect of the optimized treatment. However, the reported surface energetics do not by themselves establish both band offsets across the perovskite/PbF₂/C₆₀ stack or distinguish direct tunneling from other transport pathways. Thickness-dependent measurements of contact resistance and charge extraction, combined with interface-sensitive band-alignment measurements, would help determine whether further fluoride growth introduces a trade-off between defect passivation and transport losses, reflected in series resistance and fill factor.

Industrial implementation also requires consideration of the environmental footprint and process safety of CF₄, a persistent greenhouse gas with high global-warming potential. High-throughput processing should quantify gas utilization and residual emissions per unit substrate area, and incorporate point-of-use abatement with experimentally verified destruction or removal efficiency. Safe gas delivery and exhaust handling, including management of potentially hazardous fluorinated reaction and abatement by-products, are also important. Alternative fluorine sources, including NF₃ or solid-source fluorination, merit investigation, but should be compared in terms of net emissions,

abatement energy demand, process safety, and compatibility with the perovskite. In particular, NF_3 is itself a potent greenhouse gas, so substitution alone does not establish a sustainability advantage.

2 Interfacial Robustness Under Severe Multi-Factor Aging Conditions

Real-world photovoltaic deployment subjects solar modules to complex, coupled stress factors far beyond standard single-variable testing, including damp heat (85 °C/85% R.H.), dynamic thermal cycling (−40–85 °C), high UV flux, and reverse-bias stress caused by partial shading [7]. Fan et al. (2026) demonstrate that *in situ* plasma fluorination replaces relatively weak Pb-I bonds with robust, Pb-F bonds, forming an inorganic barrier shell that suppresses defect formation and volatility. Despite these energetic advantages, the long-term thermomechanical and electrochemical fatigue of the ultrathin PbF_2 /perovskite heterojunction under extreme environments requires thorough investigation. The mismatch in thermal expansion coefficients between the rigid inorganic PbF_2 nanolayer and the softer hybrid perovskite lattice may generate interfacial shear stresses during rapid, repeated thermal shock. Furthermore, in string modules operating at high system voltages, localized reverse bias can generate very high electric fields [8]. Whether fluorine-containing species redistribute toward adjacent charge-transport layers under sustained electrical stress remains an open question rather than an established degradation mechanism. Depth-resolved ToF-SIMS before and after controlled bias-temperature aging, with unbiased controls, could test for changes in fluorine distribution across the interface. Bias-induced photoluminescence mapping could reveal associated spatial changes in recombination, while temperature-dependent admittance spectroscopy could probe thermally activated electrical relaxation. Because neither optical nor electrical signatures alone identify the migrating species, their correlation with compositional profiles would be needed to assess possible field-assisted fluorine redistribution.

3 Broad Application Horizon Across Emerging Optoelectronic Platforms

Beyond single-junction p-i-n planar solar cells, the solvent-free, non-contact, and gas-phase nature of plasma surface engineering unlocks immense potential for a wide spectrum of optoelectronic architectures. In monolithic perovskite/silicon tandem solar cells, solution-processed passivating agents tend to pool inside the valleys of textured silicon pyramids due to capillary forces, resulting in non-uniform passivation thickness. Gas-phase plasma radicals provide an isotropic, conformal exposure across complex 3D microstructures, offering a viable route to passivate wide-bandgap top absorbers without disrupting light trapping texturing [9]. Moreover, this gas-phase protocol can be extended to perovskite light-emitting diodes (PeLEDs), photodetectors, and non-planar/curved optoelectronic devices. In PeLEDs, surface traps dominate non-radiative recombination and efficiency roll-off; gentle plasma fluorination can eliminate uncoordinated Pb^{2+} defects while avoiding the formation of bulky, electrically insulating organic layers that hinder carrier injection [10]. Crucially, for advanced architectures such as hemispherical artificial eyes or flexible sensor

arrays, where liquid coating techniques are physically infeasible due to geometric constraints, omnidirectional gas-phase plasma modification provides an indispensable processing tool for precise interfacial engineering [11].

4 Conclusions

Gas-phase plasma surface engineering represents a transformative shift from solvent-dependent passivation to precise, deterministic interfacial chemical modification in perovskite solar modules. Realizing the full industrial potential of this methodology requires quantifying spatial plasma kinetics across meter-scale modules, validating thermomechanical interface fatigue under severe multi-stress conditions, and extending solvent-free radical passivation to textured tandems, PeLEDs, and non-planar optoelectronic architectures. Within the broader manufacturing landscape, the industrial value of this route will depend on whether its interfacial benefits can be retained at production scale with reproducible process windows, competitive throughput, and controlled environmental costs. Crossing these manufacturing boundaries would position plasma-induced surface conversion as a complementary option alongside established deposition-based passivation methods, particularly where surface remediation and treatment of laser-scribed interconnects are required.

Data availability No datasets were generated or analyzed for this work.

Acknowledgment The authors declare that no generative artificial intelligence (AI) or AI-assisted technologies were used in the preparation, analysis, or writing of this manuscript.

Competing interests The authors declare no conflicts of interest.

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