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Rapid, stable and self-powered perovskite detectors *via* a fast chemical vapor deposition process†

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Organometal halide perovskite materials are outstanding candidates not only for solar cells but also for photo-detection. In this work, we develop a well-controlled lower temperature (<120 °C) and fast chemical vapor deposition process (LFCVD) to fabricate photovoltaic detectors with a high speed response ($\tau_{\text{rise}}/\tau_{\text{fall}} \sim 460$ ns/940 ns) and a 3 dB-bandwidth above 0.9 MHz, which are the highest among those with a large active area (>0.1 cm²) without external power supply. Remarkably, the perovskite photovoltaic detectors demonstrate an excellent air-exposure stability for more than two months without particular encapsulation. These excellent performances are attributed to a well-controlled expansive gas–solid reaction and formation of perovskite crystallites that collide and pinch off the pinhole leakage paths at the grain boundaries. More importantly, the accumulated strain at the colliding grain boundaries leads to a selective evaporation of MAI during post-growth annealing, and thus passivate the local defects by the remnant PbI₂ layer. These results highlight the potential of LFCVD perovskite materials in developing ultra-fast and self-driven photovoltaic detectors with outstanding stability and scalability.

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Introduction

Organometal trihalide perovskites (CH₃NH₃PbX₃, where X = Cl, Br, I, or a mix halide) are emerging new hybrid semiconductors that have enabled a series of exciting optoelectronic applications, including high performance photovoltaics (PV),^{1–4} light-emission,^{5,6} lasing^{7,8} and sensing.^{9–13} Thanks to a strong broad spectral absorption, a long carrier lifetime and a very high carrier mobility (≈ 10 cm² V⁻¹ s⁻¹), the power conversion efficiency of the perovskite solar cells has reached a new record of 20.8%,^{14–16} and 22.1% very recently.¹⁷ In parallel, perovskite materials are promising candidates for rapid photodetections, operating in the visible and near infrared (NIR) spectrum range. For example, Hu Xin and Xie Yi *et al.* first reported a flexible organic-halide photodetector by one-step solution deposition and exhibited excellent flexibility and reasonable sensitivity.⁹ Yang Yang *et al.* demonstrated perovskite photodetectors working at low or even zero bias, with a fast response ($\tau_{\text{rise}}/\tau_{\text{fall}} \sim 0.97$ μs/1.1 μs), a large dynamic linear response up to 100 dB

and a detectivity approaching 10¹² Jones.¹⁰ Meanwhile, a high gain (nearly 500) perovskite detector has been achieved by Huang's group at a low driving or bias voltage of -1 V.¹²

Seeking a low-cost, scalable and reliable fabrication of the perovskite solar cells has been crucial to establishing large-scale photovoltaic and detector applications.^{18–20} All solution-based one-step or two-step spin-coating^{21–24} deposition are convenient strategies, but usually experience a radical reaction that is hard to control over large area. Alternatively, perovskite thin film can be deposited *via* sequential^{25,26} or concurrent^{15,27} thermal evaporations in expensive high vacuum system, where a precise and readily controllable deposition has been achieved. Recently, a vapor-assisted solution process (VASP),^{28–30} low pressure VASP (LPVASP),^{19,31} hybrid chemical vapor deposition (HCVD)^{32,33} and hybrid physical–chemical vapor deposition (HPCVD)³⁴ have been proposed to combine the solution-based fabrication with a low vacuum deposition and obtained a high performance in perovskite solar cells.

In this work, we explore a well-controlled lower temperature and fast chemical vapour deposition (LF-CVD) process within 20 min to prepare high quality compact perovskite films, and employ them in a vertical photodetector structure of FTO/c-TiO₂/CH₃NH₃PbI₃/Spiro-OMeTAD/Ag that exhibits very high speed detection with a response time of $\tau_{\text{rise}}/\tau_{\text{fall}} \sim 460$ ns/940 ns, a responsivity of 0.55 A W⁻¹ and a 3 dB bandwidth above 0.9 MHz (the highest among those with a reasonable active area >0.1 cm²) without exterior power supply. Remarkably, all these have been achieved with an excellent air-exposure stability for

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annealing at 150 °C, which can be assigned to the evaporation mass loss and the formation of pinholes in the perovskite thin films.

Since the density of the PbI_2 and $\text{CH}_3\text{NH}_3\text{PbI}_3$ are 5.85 g cm^{-3} , and 4.17 g cm^{-3} , respectively, a gradual expansion to roughly 40% in volume is expected during the grain formation reaction.²⁸ And this gradual expansion of the perovskite grains is indeed beneficial to fill in or eliminate the voids or vacancy among the perovskite crystals. Meanwhile, we present also atomic force microscopy (AFM) characterizations of the LFCVD perovskite film in Fig. 3c and d, over an area of $10 \mu\text{m} \times 10 \mu\text{m}$ after annealing at 120 °C for 30 min. We found that the surface roughness of the perovskite films is only 23 nm (or <18 nm within $2 \mu\text{m} \times 2 \mu\text{m}$, see in Fig. S1 (ESI†)). This excellent thin film uniformity, resulting from a gently controlled and slow LFCVD process, is even better than that of previous reports *via* solution processed films ($\sim 25 \text{ nm}$).³⁹ Note that thin film uniformity is particularly important for improving the junction quality and for preventing the formation of electric leakage path, a prerequisite for high speed and efficient photodetector applications.

Assembled in a complete photovoltaic device, with multi-layer structure as indicated in Fig. 2f, the current density and bias voltage (J - V) curves of the perovskite solar cells were measured under AM 1.5 irradiation and presented in Fig. S2 and S3.† The parameters of V_{oc} , J_{sc} , FF and PCE are extracted and summarized in Table S1.† It is shown that the original sample suffers from a poor contact and large leakage, while post-annealing helps to improve the overall performance substantially, with the highest PCE achieved after annealing at 120 °C, with a high V_{oc} , J_{sc} , FF and PCE of 1.03 V, 21.25 mA cm^{-2} , 0.69 and 15.1%, respectively. Meanwhile, the J_{sc} calculated from the solar-spectrum-weighted integral of the corresponding IPCE curve, as seen in Fig. S2,† is 20.2 mA cm^{-2} . However, annealing at higher temperatures leads to a high leakage current and decreased V_{oc} , most likely due to the formation of large pin holes as seen in Fig. 2d. In addition, a hysteresis behaviour is also observed for the LFCVD-processed perovskite thin film photovoltaic device, as witnessed in the forward and backward scan J - V curves presented ESI Fig. S3.†

Serving as a self-driven photodetector, the J - V characteristics of the perovskite photovoltaic device were measured in the dark and under 650 nm light irradiations (with a power density of 1 mW cm^{-2}) and presented in Fig. 4a. A high $J_{\text{light}}/J_{\text{dark}}$ ratio $\sim 10^4$ (under -0.1 V bias) has been achieved, under regulated illumination at zero bias (without the need of any external power supply). As an important figure-of-merit for photodetector, the responsivity (R) and the detectivity (D^*) of the perovskite devices are extracted according to the formula below,

$$R = \frac{\Delta I}{PA}, \quad (1)$$

$$D^* = R \sqrt{\frac{A}{2qI_d}}, \quad (2)$$

where ΔI is the photo-current, P is the incident power intensity, A is the active area, I_d is the dark current and q is the elementary

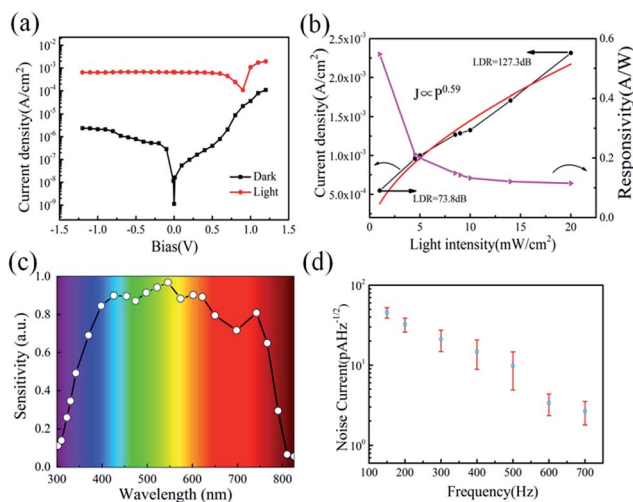


Fig. 4 (a) J - V curves of the perovskite photovoltaic device in the dark and under 650 nm irradiation. (b) Linear dynamic range of the perovskite device and the responsivity. (c) Spectral response of the perovskite photodetector. (d) The noise current of the perovskite device measured under dark condition by using a lock-in amplifier (SR830) from 150–700 Hz frequencies at zero bias.

charge. The extracted specific response and detectivity are 0.55 A W^{-1} and $\sim 10^{12}$ Jones (or $\text{cm Hz}^{1/2} \text{ W}^{-1}$), respectively. Fig. 4c presents the corresponding wavelength-dependent photocurrent response in the wavelength region of 300–800 nm, used to determine the relative sensitivity to different wavelengths. And the light response of the device at the 400–750 nm range is much higher than other wavelength, which is accordance with the IPCE curve in the Fig. S2.† Varying the laser illumination intensity from 1 mW cm^{-2} to 20.2 mW cm^{-2} at 650 nm, the photocurrent I_p increases monotonically, as shown in Fig. 4b, with a best fitting of

$$I_p = aP^b \sim P^{0.59} \quad (3)$$

Meanwhile, linear dynamic range (LDR) is another key parameter for photodetector, which is defined as

$$\text{LDR} = 20 \log \left(\frac{I_p}{I_d} \right) \quad (4)$$

At zero bias, the LDR is estimated to be above 120 dB, which is comparable to the commercial Si photodetector (LDR = 120 dB) and the highest LDR on perovskite photodetectors (LDR = 100 dB).^{10,40} Note that, this also outperforms most of the 2D nanosheets of transition metal dichalcogenides (TMDs) photodetectors (LDR = 40–80 dB).⁴⁰ Meanwhile, the noise equivalent power (NEP) of the perovskite photodetector, a measure of the minimum impinging optical power that a device can distinguish from the noise, is defined as

$$\text{NEP} = \frac{i_n}{R} = 4 \times 10^{-12} \text{ W Hz}^{-1/2} @ 700 \text{ Hz} \quad (5)$$



Table 1 A summary and comparison of the perovskite-based photodetector performance in literature to what achieved in this work

Device	Preparation process	Active area [cm ²]	Rise/fall time [μs]	Bandwidth (f _{3dB}) [MHz]	Ref.
FTO/TiO₂/perovskite/Spiro-OMeTAD/Ag	LFCVD	0.1	0.46/0.94	0.9	This work
ITO/perovskite/TPD-Si/MoO ₃ /Ag	Solution	0.06	5.7/41	—	12
FTO/TiO ₂ /Al ₂ O ₃ /PCBM/perovskite/Spiro-OMeTAD/Au/Ag	Solution	0.07	1/3	—	13
FTO/TiO ₂ /perovskite/Spiro-OMeTAD/Au	Solution	0.16	17/20	—	44
ITO/PEDOT:PSS/perovskite/PC ₆₀ BM/C ₆₀ /LiF/Ag	Solution	0.2	1.7/1	0.5	45
ITO/PEDOT:PSS/perovskite/PCBM/Al	Solution	0.1	0.97/1.1	0.8	10
		0.01		2.9	
ITO/PTAA/perovskite/C ₆₀ /BCP/Cu	Solution	0.07	0.115 ^a	—	51
ITO/OTPD/perovskite/PCBM/C ₆₀ /BCP/Al	Solution	0.07	0.28 ^a	2.9	11
Au/perovskite/Au	Solution	—	300/300	—	46
WS ₂ /perovskite heterojunction	Vapor	—	2.7/7.5	—	47
MoS ₂ /Si heterojunction	—	—	3/40	—	48
In/Ga/n-SiNW/CQDs/Au	—	—	20/40	—	49

^a Values deduced from time-resolved photoluminescence-lifetime measurements, instead of under direct light signal modulation.

just on the top surface but all through the thin film down to the root, which is critical to minimize the leakage path of photo-carriers in photovoltaics and photo-detection.

Furthermore, it is important to note that the strain distribution of in the LFCVD perovskite thin film is not uniform, and most of the strain is accumulated at the grain boundaries during the expansion formation of the perovskite grains. As a consequence, during the post-growth annealing, the disintegration and the evaporation of MAI will preferentially happen at the grain boundary regions. This is because, according to the Gibbs-entropy law, if the local pressure is p , the decomposition and evaporation of MAI will become easier and faster as $R \sim e^{\Delta E/kT}$ and $\Delta E = p\Omega$. Therefore, a thin layer of PbI₂ could be left selectively at the grain boundaries, as schematically depicted in Fig. 7. It has been known that, the PbI₂ layer has a wider bandgap than perovskite³⁵ and thus provides a good passivation to the boundary of perovskite grains,^{14,35} which can help to suppress the recombination centres at the boundary, as well the local current leakage along the boundary cracks or voids, as illustrate in Fig. 7b.

This passivation effect can also be inferred from the improved photo-carrier generation and detection in simple planar transport characterizations, where the perovskite thin film is deposited upon SiO₂ (300 nm)-coated Si substrates with paired Ti/Au (15 nm/20 nm) electrodes. The channel width and

length are 200 μm and 2 μm, respectively as depicted in the inset of Fig. 7c. The I - V curves (under 650 nm illumination, 1 mW cm⁻²) of the perovskite films treated by different annealing conditions are presented in Fig. 7c, where the linear and symmetric I - V curves imply an ohmic contact between the perovskite thin film and Ti/Au electrodes. Furthermore, Fig. 7d presents time-dependent photoresponse under 5 V bias of the corresponding perovskite thin films, under modulated 650 nm illumination. This observation indicates that the current signals arise indeed from the photo-carriers generated in the perovskite thin film under illumination. Obviously, the highest photo-current response has been achieved for the sample after

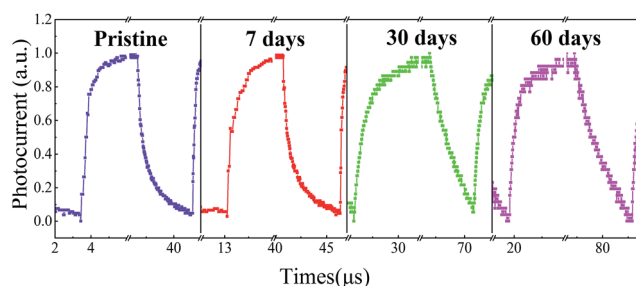


Fig. 6 Photo response behaviour of the perovskite device stored in air for 60 days.

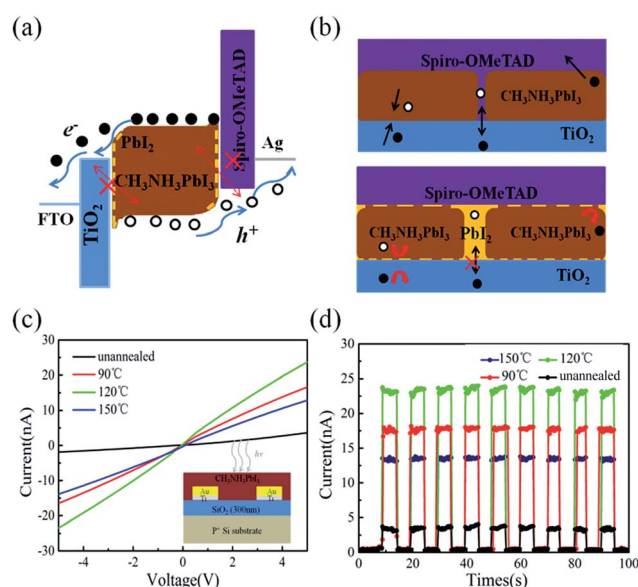


Fig. 7 Schematic diagram of (a) band gap of perovskite, PbI₂ and perovskite device after passivation, (b) electrons and holes transfer process in the pristine and passivated perovskite film. (c) The current–voltage (I - V) and (d) current–time (I - t) characteristic curves of the perovskite film annealed at different temperatures on the Si substrates under illumination (650 nm, 1 mW cm⁻²).



optimal annealing at 120 °C. This can be attributed to the fact that the residual PbI₂ passivation at the grain boundary help to passivate and reduce the recombination centres in the perovskite thin films, and thus a longer photo-carrier lifetime and higher population contribute to a higher photo-current response in the *I-V* measurement.

Most importantly, as mentioned above, the devices without annealing and annealing at 90 °C and 150 °C show a poor response time estimated to 3.7 μs/4.0 μs, 1.1 μs/1.4 μs and 0.8 μs/3.1 μs, respectively, which is much more slowly than that annealing at 120 °C (0.46 μs/0.94 μs). It indicates that the defect in the film and boundary, to some extent, block the transportation of the exciton and increase the recombination chance, leading to a long response time. These results support that the PbI₂ provides a good passivation to the boundary to reduce the recombination centre and effectively increases the photocurrent and improve the response time, leading to a high performance of perovskite photodetector.

Conclusions

In summary, we have demonstrated a well-controlled LFCVD fabrication of high quality perovskite thin film that enables high performance and stable self-sustained photodetector application. The photovoltaic devices under 120 °C annealing for 30 min achieve a PCE as high as 15.1%. Photodetector exhibits a responsivity of 0.55 A W⁻¹, detectivity up to ~10¹² Jones, a fast response (with rise and fall times of 460 ns/940 ns) and a wide 3 dB bandwidth up to 0.9 MHz, with outstanding stability to 60 days air exposure. We propose that the accumulated strain at the colliding grain interfaces leads to a selective formation of PbI₂ layer at the grain boundaries that help to passivate local recombination centers and block local current leakage. These benefits combined indicate a new and reliable manufacturing of high performance self-driven photovoltaic and photodetector applications.

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