## Supporting Information

## Self-powered behavior based on light-induced self-poling effect in perovskite-based

## transport layer-free photodetectors

Tiqiang Pang<sup>a</sup>, Renxu Jia<sup>\*, a</sup>, Yucheng Wang<sup>a</sup>, Kai Sun<sup>b</sup>, Ziyang Hu<sup>\*, b</sup>, Yuejin Zhu<sup>b</sup>, Suzhen

Luan<sup>a</sup>, and Yuming Zhang<sup>a</sup>

<sup>a</sup> School of Microelectronics, Xidian University, Key Laboratory of Wide Band-Gap

Semiconductor Materials and Devices, Xi'an 710071, China.

<sup>b</sup> Department of Microelectronic Science and Engineering, Ningbo University, Ningbo, 315211,

China

**Corresponding Authors** 

\* E-mail address: rxjia@mail.xidian.edu.cn.

\* E-mail address: huziyang@nbu.edu.cn.



Figure S1. Structure schematic of the perovskite based MOS photodetector.

Scanning Electron Microscope (SEM) and X-ray diffraction (XRD) measurements were carried out to investigate the surface topography and crystallinity of the perovskite films. Figure S2(a) shows the cross-sectional image of the as-prepared perovskite film on a SiO<sub>2</sub>/Si substrate. The sandwich structure consisting of perovskite, silicon dioxide and silicon from top to bottom is clearly visible, and the thickness of perovskite and SiO<sub>2</sub> are ~400 nm and ~300 nm, respectively. The inset shows that the perovskite surface is very dense and smooth, which is suitable for manufacturing photodetectors. In Figure S2(b), XRD patterns confirm the high purity of perovskite crystal in tetragonal phase. Three strong diffraction peaks located at  $14.18^{\circ}$ ,  $28.5^{\circ}$ , and  $31.94^{\circ}$  are assigned as (110), (220), and (310) planes of perovskite, respectively. The ultraviolet visible (UV-vis) absorption spectra of perovskite grown on FTO substrate is shown in Figure S2(c). A sharp change at band edge indicates a direct band gap. The band edge absorption of perovskite shows onset at ~785 nm, corresponding to 1.58 eV of optical bandgap, which is calculated from equation:

$$(\alpha h v)^2 = A(hv - E_g)$$
(S1)

where A,  $E_g$  and  $\alpha$  represent absorbance, optical bandgap and absorption coefficient, respectively. The normalized emission spectra of perovskite film grown on FTO substrate is given in Figure S2(d) with a 465 nm excitation. The film exhibits a strong and relatively narrow emission peak centered at 774 nm.



Figure S2. (a) Cross-sectional SEM image of Al/Si/SiO<sub>2</sub>/perovskite MOS structure, the inset is top view SEM image of the perovskite film, (b) X-ray diffraction patterns of the perovskite film, (c) UV-visible absorption spectra of the perovskite film, (d) photoluminescence spectra of the perovskite film with the excitation wavelength of 465 nm.



Figure S3. C-V data under dark and 5 mW/cm<sup>2</sup> light illumination at 1 kHz.



Figure S4. Partial curves (dark current) extracted from Figure 1(c).



Figure S5. The noise current shows the frequency-independent behavior in the dark at low

frequency.



Figure S6. *I-t* characteristic curves of the Pt/CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub>/Pt photodiode structure. (a) Illuminated under a light intensity of 5 mW/cm<sup>2</sup> by on/off switching at 0 V, (b) illuminated under a light intensity of 5 mW/cm<sup>2</sup> by on/off switching at various voltage.

Bi-exponential decay equation:

$$I = I_0 + A_1 \exp\left(-\frac{t}{t_1}\right) + A_2 \exp\left(-\frac{t}{t_2}\right)$$
(S2)

where  $A_1$  and  $A_2$  are constants,  $I_0$  is the attenuation constant,  $t_1$  and  $t_2$  are the slow time decay constants and fast time decay constants, respectively. The rise time  $\tau_r$  and the fall time  $\tau_f$  can be definite by the equation  $\tau = t_2 - t_1$ . Both the rise and fall edges comprise a fast-response and a slow-response process when the bias was applied.



Figure S7. *I-t* characteristic curves of the MOS photodetector at 0 V after polarization at -5 V under illuminated and dark.



Figure S8. (a) XPS survey spectra of perovskite and SiO<sub>2</sub> interface, (b) core level of O 1s in the 522–545 eV region, the inset is partial of O 1s, (c, d) valence band spectra of SiO<sub>2</sub> and MAPbI<sub>3</sub>,  $E_{V}^{SiO_2}$  is the energy difference between valence band maximum and Si 2p of SiO<sub>2</sub>,  $E_{V}^{MAPbI_3}$  is the energy difference between valence band maximum and I 3d by fitting the survey spectrum, their value are 0.5 eV and 5.05 eV, respectively.

X-ray photoelectron spectroscopy (XPS) was employed to qualitatively analyze the chemical state and structural properties at the perovskite/silicon dioxide interface. The data is calibrated using the electronic binding energy of 284.6 eV of C 1s, and the binding energy profile is smoothed using the mode of Wiener Filter. Figure S8(a) presents the XPS survey spectra of the perovskite/silicon dioxide interface with the binding energy in range from -10 to 1350 eV. The calibration error is 1.48 eV based on the 286.08 eV of C 1s peak in survey spectrum. The valence band offset between perovksite and silicon dioxide can be defined as:

$$\Delta E_V = E \frac{MAPbI_3}{V} - E \frac{SiO_2}{V}$$
(S3)

where  $E_{V}^{SIV_{2}}$  is the energy difference between valence band maximum and Si 2p of SiO<sub>2</sub>, and  $E_{V}^{MAPbI_{3}}$  is the energy difference between valence band maximum and I 3d. By fitting the survey spectrum, the calculated values of  $E_{V}^{SiO_{2}}$  and  $E_{V}^{MAPbI_{3}}$  are 0.5 eV and 5.05 eV, respectively. The

bandgap of SiO<sub>2</sub> is extracted by fitting the O 1s spectrum as shown in Figure S8(b). The peak of O 1s locates at 535.28 eV. The energy in inset of Figure S8(b) is 543.38 eV. The difference (8.1 eV) between 535.28 eV and 543.38 eV represents the bandgap of SiO<sub>2</sub>. The conduction band offset  $\Delta E_c$  can be calculated using the equation:

$$\Delta E_C = \Delta E_g - \Delta E_V = E_g^{SiO_2} - E_g^{MAPbI_3} - \Delta E_V$$
(S4)
$$SiO_2 = E_g^{MAPbI_3} - \Delta E_V$$

where  $E_{g}^{OO2}$  and  $E_{g}^{OO1}$  are the bandgap of SiO<sub>2</sub> and perovskite, as shown in Figure S8(c, d).

Under a small voltage (<5 V), the photocurrent can reach 10<sup>-9</sup> A in the Figure 1 of the main text. The leak mechanism was further analyzed. In Figure S9, we found that iodide ions appeared in SiO<sub>2</sub> or even in silicon through the elemental distribution X-ray (EDX) spectroscopy measurement (Table S1). Our XPS results also show that the perovskite is severely deficient in iodine, and the missing part of the iodide ion may enter into SiO<sub>2</sub> and silicon, as shown in Ref [44] of the main text. Since the larger atomic radius of the iodide ion is not likely to be free in the SiO<sub>2</sub> network. Therefore, it can be considered that the iodide ion is the fixed charge of the silicon dioxide, which would change the structure and the conductivity behavior of the silicon dioxide. For example, it will induce the traps. Based on the analysis above, the ion (trap) assisted transport mechanism (Frenkel-Poole) was used to explain the leakage current. The current-voltage curve under illumination was fitted by the FP mechanism. The leakage current density of the FP emission mechanism can be expressed as:

$$J = CE_{ox} exp\left[\frac{-q(\phi_t - \sqrt{qE_{ox}/\pi\varepsilon_i})}{\alpha KT}\right]$$

(S5)

that is  $\ln \left( \frac{I}{E_{ox}} \right) \propto \sqrt{E_{ox}} \operatorname{or} \ln \left( \frac{I}{V} \right) \propto \sqrt{V}$ . The fitted results are shown in Figure S10.



Figure S9. EDX spectroscopy acquired from different location marked in the spectrogram.

Table S1.	Element of	distribution	and conten	t in Pt-CH	<sub>3</sub> NH <sub>3</sub> PbI <sub>3</sub> -	SiO <sub>2</sub> -Si MO	S structure	corresponds
to the ener	rgy-disper	sive X-ray	(EDX) spe	ctroscopy f	form Figur	e S9.		

Spectrogram	State	C(wt%)	O(wt%)	Si(wt%)	I(wt%)	Pt(wt%)	Pb(wt%)	Total(wt%)
1	Yes			32.27		67.73		100.00
2	Yes	17.53		36.05	17.13	20.60	8.69	100.00
3	Yes		8.40	84.99	6.61			100.00
4	Yes		8.43	89.12	2.45			100.00
Maximum		17.53	8.43	89.12	17.13	67.73	8.69	
Minimal		17.53	8.40	32.27	2.45	20.60	8.69	



Figure S10. The fitted results of the photocurrent-voltage curves by the Frenkel-Poole emission

leakage mechanism.