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Low-noise X-ray PIN photodiodes made of perovskite single crystals by Solution-processed doped epitaxial growth

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X-ray photodiodes made of metal halide perovskites (MHPs) which directly convert X-ray photons into electron-hole pairs have shown advantages in low-cost and high X-ray detection sensitivity. However, devices fabricated by spin-coating and evaporation methods suffer from high traps density near poor interfacial layers (n-type/intrinsic and p-type/intrinsic) which lead to high dark current and noise current under large reverse bias. In this work, solution-processed doped epitaxial growth is employed to limit these traps through epitaxially growing n-type MHPs (bismuth-doped) and p-type MHPs (silver-doped) on opposite faces of intrinsic $\text{CH}_3\text{NH}_3\text{PbBr}_{2.5}\text{Cl}_{0.5}$ MHP single crystals. Through energy structure design, effective electron/hole blocking layers could decrease the noise and dark current, these X-ray PIN photodiodes work under a large external electrical field, which enables a state-of-art response speed (fall) of 750 ns and a lowest detectable dose rate of $17.7 \text{ nGys}^{-1}(40 \text{ kVp})$. This work will motivate new strategies to fabricate high-performance devices based on perovskites using solution-processed methods. These founding also explore a new generation of low dose and high dynamic X-ray detectors based on MHPs.

X-ray photodiodes, which directly convert X-ray photons into electron-hole pairs, play an increasingly important role in low-dose and high-resolution X-ray radiography. Besides CdZnTe single crystals¹, CdTe single crystals², and amorphous selenium³, metal halide perovskite single crystals (MHPSCs) $\text{CH}_3\text{NH}_3\text{PbX}_3$ (X=Cl, Br, Pb) are considered to be the next generation of room-temperature semiconductors for X-ray detection due to their high absorption of X-ray photons, balanced and high charge mobility-lifetime products, and the fact that they can be synthesized, deposited, and epitaxially grown by solution-processing methods inexpensively⁴⁻¹⁰.

However, to capture hard X-ray photons (>100 keV), the thickness of the MHPSCs must be at least 1 mm. Consequently, a long penetration path requires a large electrical field to drift the photoinduced charges for high-efficiency charge collection. However, the dark current increases with the applied bias in MHPSC-based photodiodes. Meanwhile, the noise current increases and floods the weak signal current induced by X-ray photons. Therefore, the X-ray sensitivity, response speed, and detection limit must be balanced against the noise current and dark current when setting the value of the external bias.

In addition to the crystallization quality improvements¹¹⁻¹³, several photodiode structures have been investigated to decrease the dark current of MHPSC-based photodiodes, such as sandwiched MHPSC-based PIN photodiodes fabricated using two deposited charge-blocking layers¹⁴⁻¹⁶, MHPSC-based PN junctions formed by doping^{17,18}, and MHPSC-based Schottky diodes realized using asymmetric metal electrodes^{10,19,20}. However, most MHPSC-based PIN photodiodes use organic semiconductors²¹, nano-oxides²² and carbon derivatives²³ as blocking layers that are not lattice-matched with MHPSCs, and the traps near interfacial layers (n-type/intrinsic and p-type/intrinsic) lead to the leakage of dark current. MHPSC-based PN junctions realized by growing n-type doped MHPSCs (Bi^{3+} , Se^{2+}) on undoped p-type MHPSCs suffer from narrow depletion layers, rendering X-ray detection inferior compared to that with MHPSC-based PIN photodiodes^{17,18}. MHPSC-based Schottky diodes can effectively decrease the dark current, but metals such as Al, Ga, Ag, and Cr could react with halide ions in days due to their low work function, leading to performance degradation^{10,19,20}. As a result, PIN photodiode structure is suitable for X-ray detectors and low traps interfaces could further decrease the noise. Thus, MHPSC-based PIN photodiodes fabricated by lattice-matched blocking layers epitaxially grown²⁴⁻³⁰ on intrinsic MHPSCs may further decrease the traps near the interfaces and lead to low dark current and noise.

In this work, we developed an MHPSC-based X-ray PIN photodiode with the structure of (n-type, bismuth-doped MAPbBr_3)/(intrinsic, $\text{MAPbBr}_{2.5}\text{Cl}_{0.5}$)/(p-type, silver-doped MAPbBr_3). The traps near the interfaces can be suppressed by solution-processed doped epitaxial growth (SPDE) grown n-type and p-type lattice-matched MHPSCs on the opposite face of the intrinsic layer. Differing from the spin-coating and evaporation fabrication strategy of nanometer-scale thickness films⁸, p-type and n-type layers, tens of micrometers thick, can effectively block the injected charges from the large voltage source without leakage current from pinholes. This work not only demonstrates that SPDE methods are able to fabricate high-quality PIN photodiodes for X-ray detection, but also provides an important guide to improve solution-processed and perovskite-based devices.

Results:

Figure 1 | Energy structure design of the X-ray PIN photodiodes. a, Thermal-probe-induced current of MAPbBr₃ MHPSC with different dopants. **b,** Diagram of the PIN photodiodes and its work mode. **c,** X-ray diffraction data for each layer from 30° to 31.2°. **d,** Photoluminescence versus wavelength of intrinsic layer and doped layers. **e,** Minority carrier bulk lifetime of intrinsic layer and doped layers. **f,** VBM of each layer from -4 eV to 6 eV by XPS. **g,** UPS of each layer (using the He-I line with a photon energy of 21.22 eV).

To find suitable dopants, pristine MAPbBr₃ MHPSCs were used as the substrates and metal bromide (0.1 M) was dissolved in the precursor solution of MAPbBr₃. Pristine MAPbBr₃ MHPSCs were then dipped into the doped precursor for approximately 30 min at 70 °C. Approximately 0.2 mm-thick doped MAPbBr₃ single crystals were grown on the substrates, as shown in Supplementary Fig. 1. To determine the conduction type of the doped MAPbBr₃ MHPSCs, a thermal probe method was used, as shown in the inset of Fig. 1a. Due to the temperature difference between the two probes, the majority charge carriers underwent diffusion from the hot electrode to the cold electrode, generating a diffusion current. The value of the detected current could qualitatively determine the type and magnitude of the majority charge carriers of the epitaxial doped MAPbBr₃ MHPSCs. Among the 16 types of metal bromide investigated, bismuth bromide³¹⁻³⁶ (BiBr₃) and

silver bromide³⁷ (AgBr) are considered the most effective donors and acceptors, respectively, due to the high thermally induced diffusion current.

Based on the chosen dopants, the structure of the X-ray PIN photodiode is shown in Fig. 1b. Bi-doped MAPbBr₃ MHPSC and Ag-doped MAPbBr₃ MHPSC are n-type and p-type layers, respectively. The intrinsic layer is made of MAPbBr_{2.5}Cl_{0.5} MHPSCs which shows lowest traps density in MHPSCs in our previous reports³⁸. When the X-ray PIN photodiode is employed under a large reverse bias, the Bi-doped MAPbBr₃ layer is expected to prevent hole injection from the cathode and improve the collection of photoinduced electrons. By contrast, the Ag-doped MAPbBr₃ layer should stop the injection of electrons from the anode and improve the collection photoinduced holes. Compared with Schottky structures such as Au/CsPbBr₃/Ga¹⁰, Au/MAPbBr₃/Ga³⁹ and ITO/CsPbBr₃/Ag¹⁹, micrometer-thick n-type and p-type layers more effectively block the injected charges. This issue is to control the quality of SPDE growth and determine a suitable doping concentration.

To ensure the quality of SPDE growth of doped MAPbBr₃ MHPSCs on a MAPbBr_{2.5}Cl_{0.5} MHPSC (lattice constant 5.871 Å) substrate, the lattice constant is first calculated by the Bragg equation, $2d\sin\theta = n\lambda$, where the λ is 0.15416 nm, from the X-ray diffraction (XRD) pattern shown in Fig. 1c. The lattice constant of the Bi-doped MAPbBr₃ MHPSC decreases from 5.925 to 5.906 Å (Bi-doped), while that of the Ag-doped MAPbBr₃ MHPSC remains the same. The XRD data of other doping concentrations are shown in Supplementary Fig. 2. Thus, the highest mismatch rates ($f = \frac{a_1 - a_2}{a_1 + a_2}$, where a_1 and a_2 are the lattice constants of the substrate and epitaxial layer, respectively)

are approximately 0.41% and 0.25% for p-type/intrinsic and n-type/intrinsic, respectively, which are good enough for epitaxial growth⁴⁰

To design the energy structure of the X-ray PIN photodiode, the band gap of each layer was investigated by absorption spectroscopy, the results of which are shown in Supplementary Fig. 3. The Urbach energy^{41,42} is lower in pristine MAPbBr_{2.5}Cl_{0.5} and MAPbBr₃ MHPSCs than in the Bi-doped and Ag-doped layers, which indicates that more traps exist inside the doped layers. The band gap remains at 2.19 eV for the doped MAPbBr₃ MHPSC as reported previously^{33,43}. Further, the photoluminescence (PL) data for the pristine MAPbBr₃ MHPSC, Ag-doped MAPbBr₃ MHPSC, and Bi-doped MAPbBr₃ MHPSC are shown in Fig. 1d. The peak of the PL for all remains at 592 nm, while the full width at half maximum (FWHM) increases from 40 nm in W/O MAPbBr₃ MHPSC to 73 nm and 95 nm in Ag-doped MAPbBr₃ MHPSC and Bi-doped MAPbBr₃ MHPSC, respectively. The widened PL peaks indicate more traps exist inside the doped MAPbBr₃ MHPSCs. In addition, the time-resolved PL of these layers was investigated, as shown in Fig. 1e. The fast component (surface carrier lifetime) increases from 345 to 937 ns after doping. By contrast, the slow component (bulk carrier lifetime) decreases from 11.02 to 3.85 μs after doping, which indicates that doping-induced traps inside the doped layers can accelerate the charges recombination. The traps induced by Bi play the role of dopants, as calculated in a previous report³³. The Ag-doped p-type layer may be formed due to the Ag dopants, leading to a higher excess of Br in the MAPbBr₃ MHPSC and making the MHPSC more p-type³⁷.

To further investigate the band structure of n-type layers with different Bi-doping concentrations and p-type layers with different Ag-doping concentrations, the energy differences between the valence band maxima (VBM) and the Fermi level were measured by X-ray photoelectron spectroscopy (XPS). As shown in Fig. 1f, the energy differences were measured as 0.65 eV, 1.15 eV, and 1.91 eV for the 0.1 M Ag-doped MAPbBr₃ MHPSC, the intrinsic layer, and 0.2 M Bi-doped MAPbBr₃ MHPSC, respectively, which correspond to the p-type, intrinsic, and n-type layers. In addition, the work function was investigated by ultraviolet photoelectron spectroscopy (UPS) as shown in Fig. 1g, and Bi³⁺-doped MAPbBr₃ MHPSC exhibited a lower work function of -7.36 eV, which indicates a better moisture stability. The higher binding energies of Br and Pb in the Bi-doped MAPbBr₃ MHPSC were observed by XPS, and the profiles are shown in Supplementary Fig. 4.

Figure 2 | Fabrication and electronic properties of the X-ray PIN photodiodes. **a**, Designed energy structure of the PIN photodiode. **b**, Fabrication process and optical images (left: cross-section view, right: top view) of the PIN photodiode ($6.11 \times 5.12 \times 3.91 \text{ mm}^3$), scale bar 2 mm. **c**, Characterization of current density-voltage from -500 to 150 V. **d**, Average charge mobility of electrons (left) and holes (right) measured by TOF curves. **e**, Long-term

stability of dark current under -200 V. **f**, Voltage bias scan from -150 V to -50 V. **g**, Noise current at different X-ray photodiode frequencies with varying voltage bias.

Based on the key information (Fig. 1f and Fig. 1g) of the band structure, the energy structure of these layers is shown in Fig. 2a. Owing to the low VBM (-7.36 eV) and high conduction band minimum (CBM) (-2.67 eV) of MAPbBr₃ MHPSCs with 0.2 M Bi and 0.1 M Ag doping concentrations, the 0.2 M Bi-doped and 0.1 M Ag-doped MAPbBr₃ MHPSCs were chosen as n-type and p-type layers, respectively. Meanwhile, the majority-carrier densities of the p-type and n-type are calculated as $\sim 10^{14} \text{ cm}^{-3}$ (holes) and $\sim 10^{19} \text{ cm}^{-3}$ (electrons) by $n_0 = n_i e^{\frac{(E_F - E_i)}{kT}}$, $p_0 = n_i e^{\frac{(E_i - E_F)}{kT}}$ (where n_i is the intrinsic carrier concentration $\sim 10^7 \text{ cm}^{-3}$, k is the Boltzmann constant and T is the temperature)¹⁶. When these MHPSCs contact and the Fermi levels have the same value, the VBM difference between n-type and intrinsic layers is obtained as 0.76 eV, while the CBM difference between p-type and intrinsic layers is 0.41 eV. Additionally, the large energy barriers of 1.91 eV and 1.56 eV prevent hole and electron injection.

As shown in Fig. 2b, the MAPbBr_{2.5}Cl_{0.5} MHP single crystals were first grown by inverse temperature crystallization (ITC)⁶ for use as substrates. The bottom face of the substrate was then dipped into a 0.1 M AgBr-doped MAPbBr₃ solution for p-type layer SPDE growth, and the top face of the substrate was dipped into a 0.2 M BiBr₃-doped precursor to grow the n-type layer. Finally, two gold electrodes were deposited on the opposite faces of the device. The optical photographs (Fig. 2b) of the X-ray photodiode (6.11 mm × 5.12 mm × 3.91 mm).

Fig. 2c shows the current density-voltage characteristics of the X-ray PIN photodiode from -500 to 150 V with a step of 2 V s⁻¹ at 20 °C. The current density approached 61 $\mu\text{A cm}^{-2}$ at 150 V, while it was approximately 11.04 nA cm⁻² at -150 V, which is typical diode behavior. The low reverse current density is attributed to the energy barriers successfully blocking the injected charges.

To investigate the charge drift process, the average mobility of electrons and holes in this X-ray PIN photodiode was measured by time-of-flight (TOF) spectroscopy, as shown in Fig. 2d because the X-ray PIN photodiode made of different MHPSCs. The average electron and hole mobilities were measured as 830 cm²V⁻¹s⁻¹ and 1265 cm²V⁻¹s⁻¹, respectively, using $\tau = \frac{L^2}{\mu} V^{-1}$. The higher mobility measured here is approximately 4 times that of a single MAPbBr₃ MHPSC (measured by Au/MAPbBr₃ MHPSC/Au for holes and Ag/n-type/MAPbBr₃/n-type/Au for electrons), which indicates that the band structure improves the charge drift movements. Considering that the bulk lifetime of minority carriers is $\sim 11 \mu\text{s}$ for pristine MAPbBr₃ MHPSCs, the product $\mu\tau$ is $1.39 \times 10^{-2} \text{ cm}^2 \text{ V}^{-1}$.

The long-term stability of the dark current under a -200 V bias on the X-ray PIN photodiode was

measured (Fig. 2e). It was found that ion migration inside bulk MAPbBr_{2.5}Cl_{0.5} under bias requires approximately 1.5 h to achieve stability, and the dark current density drifts approximately ~3 pAcm⁻², which indicates a very low noise. The stability may be attributed to the ultralow rate of charge injection. Fig. 2f shows the magnified forward and reverse current density-voltage from -150 V to -50 V with step 1Vs⁻¹. The current density varies by 0.072 nAcm⁻² and 0.041 nAcm⁻² in the forward and reverse scans, respectively. Thus, the current-density-voltage hysteresis⁴⁴ is only 0.031nAcm⁻² under -150V bias which is much smaller than spin-coating based PIN photodiodes and Schottky diode (Supplementary Fig. 5). Consider the same intrinsic layer, the tiny low traps density of lattice-matched interfacial layers leads to this tiny current-density-voltage hysteresis.

The noise current of this photodiode under different voltage bias was investigated and the results are shown in Fig. 2g. The noise currents are 0.11 pAHz^{-0.5} (-10 V), 0.36 pAHz^{-0.5} (-200 V), and 1.47 pAHz^{-0.5} (-500 V) at 30 Hz. The shot noise current limit is calculated as 18–23 fA Hz^{-0.5} from the dark current. Considering that the area of this device is 31.28 mm², the noise current is only 0.47 fA Hz^{-0.5} for each 100 μm × 100 μm pixel at -200 V, which is comparable to those for Au/Cs₂AgBiBr₆/Au⁴⁵ and Ag/(NH₄)₃Bi₂I₉/Ag⁴⁶-based low noise X-ray detectors. Such low noise current arises from the two SPDE-grown charge-blocking layers, which limit charge injection. To investigate the response speed of the X-ray PIN photodiode, the terminal capacitances are approximately 0.104 pF and 0.074 pF for steady and 10 kHz (Supplementary Fig. 6), and result in a small RC product of ~5 ps (typical load resistor 50 Ω), which indicates that the response speed is mainly limited by the collection of photo generated charges.

Figure 3 | Characterization of the SCR under bias. **a**, Illustration of the KPFM experiments. **b**, Contact potential difference of intrinsic/n-type(up) and p-type/intrinsic(down) interfaces. **c**, Line profile of the CPD. **d**, Illustration of the secondary electron variance with electron density in the SEM cavity. **e**, SEM images of the sample under 0 bias. **f**, Magnified cross-section of the two interfaces, HR-TEM photons of the n-type and p-type layers. **g**, SEM screenshots of the PIN photodiode under different voltage bias and line profile of the normalized gray value as a function of width. inset: width of the SCR verses reverses voltage.

In addition to the electrical properties, the space charge region (SCR) plays an important role in PIN junctions. Here, Kelvin probe force microscopy⁴⁷ (KPFM) was used to measure the contact potential difference (CPD) between the n-type/intrinsic and p-type/intrinsic layers. As shown in Fig. 3a, the distance between the KPFM probe and the polished surface is set at 150 nm, which is greater than the roughness of the samples of 96 nm and 51 nm, respectively, as shown in Supplementary Fig. 7. Fig. 3b shows the potential distribution of the scan areas, the CPDs are 0.86 mV and -0.55 mV, respectively, which correlate with the energy band differences of 0.83 eV and 0.52 eV calculated from the XPS (Fig. 1f) and UPS profiles (Fig. 1g). Fig. 3c shows the line profile of the CPD, the SCR is located near the interfaces of n-type/intrinsic and p-type intrinsic layers. Due

to the intrinsic layer being over 4-mm-thick, it is impossible for electrons in the n-type layer to diffuse into the p-type layer without a bias voltage. The width of the SCR in both cases is below 100 nm under illumination (650 nm).

In addition to the zero-bias situation, the SCR is more important when the PIN junction operates at hundreds of volts; however, it is not feasible to apply such a large bias to the KPFM system and to scan at the millimeter scale using electron beam-induced conductivity methods. There is a high charge density difference across the SCR under reverse bias, while the excited secondary electrons in scanning electron microscopy (SEM) are sensitive to the electron density of the surface. Here, a probe station is installed inside the SEM cavity (Supplementary Fig. 8) to apply voltage to the photodiode, and the SEM images can reveal the counts of secondary electrons of the photodiode surface, as shown in Fig. 3d⁴⁸⁻⁵⁰.

Fig. 3e shows the SEM image of the X-ray PIN junction under 0 V bias, and when the thicknesses of the p-type, intrinsic, and n-type layers approached 80, 4200, and 200 μm , respectively. The p-type layer is slightly darker than the n-type layer owing to the lower electron density, and the high-resolution transmission electron microscope (HR-TEM) shows the lattice structure of the n-type and p-type layers which remains single crystalline as shown in Fig. 3f. Typical HR-TEM photos and electron diffraction image are shown in Supplementary Fig. 9. The elemental distribution was investigated by energy-dispersive X-ray spectrometry (Supplementary Fig. 10). The screenshots of the PIN junction under 50 V, -50 V, -100 V, -200 V, and -400 V are shown in Fig. 3g. The video of the device under sweep bias from -200 to 0 V is shown in the Supplementary video. When 50 V is applied to the PIN junction, the dark photo represents a high density of holes and electrons transported throughout the device. When under reverse bias, the dark area represents a high hole density and the bright area represents a high electron density. Owing to the external bias voltage, the SCR is located inside the intrinsic layer. As shown in the line profile in Fig. 3g, the width of the space charge region increases from 0.51 to 0.82 mm when the voltage bias increases from -50 V to -400 V. After fitting to the equation, $W = \left[\frac{12\varepsilon_r(-V)}{q\Delta n} \right]^{1/3}$ ⁵¹, where ε_r is the relative permittivity ($23.5\varepsilon_0$), q is the elementary charge ($1.6 \times 10^{-19}\text{C}$), Δn is the hole density (10^{19}cm^{-3}), and V is the applied voltage. A is calculated as 0.317 ± 0.05 , which approaches 0.33 in a linear graded junction⁵¹ which demonstrates the excited secondary electrons image can roughly measure the SCR in large thickness devices.

Figure 4 | X-ray detection performance and X-ray imaging. **a**, Photo/dark current density with different voltage bias **b**, Charge collection efficiency by fitting to the Hecht equation. **c**, Photo/dark current density with different dose rate (40 kVp) under -200 V bias. **d**, 40 kVp X-ray sensitivity of the X-ray photodiode. **e**, X-ray sensitivity of the X-ray photodiode for X-ray photons with different photon energy. **f**, Response speed of the X-ray photodiode under -200 V bias. **g**, X-ray image captured by the X-ray photodiode.

The photodetection performance of the X-ray PIN photodiode for 70 kVp X-ray photons and a 530 nm laser was first investigated. The X-ray photodiodes ($0.91 \times 1.12 \times 4.12 \text{ mm}^3$) show a responsivity of 0.65 A W^{-1} for 532 nm photons and X-ray detection sensitivity of $7.72 \mu\text{C mGy}^{-1}\text{cm}^{-2}$ for X-ray photons (70 kVp) when the applied bias swept from -5 V to -350 V as shown in Fig. 4a. Two different $\mu\tau$ products of $1.6 \times 10^{-2} \text{ cm}^2\text{V}^{-1}$ and $0.64 \times 10^{-2} \text{ cm}^2\text{V}^{-1}$ are derived from the 530 nm and X-ray photoconductivity curves by the Hecht equation^{52,53} $\frac{J}{J_0} = \frac{\mu\tau V}{d^2} \left(1 - e^{-\frac{d^2}{\mu\tau V}}\right)$, where J/J_0 is the charge collection efficiency, J_0 is the asymptotic current density, V is the applied voltage, and d is the thickness of the X-ray PIN photodiode, as shown in Fig. 4b. The

large penetration depth of X-ray photons requires a strong electrical field to drift to the electrodes. Consequently, to realize high charge collection efficiency X-ray detection, large reverse is necessary and -200V is chosen as operating bias. The $\mu\tau$ product measured here is in agreement with the $\mu\tau$ product calculated from independent TOF and TRPL measurements ($1.39 \times 10^{-2} \text{cm}^2 \text{V}^{-1}$, Fig. 1e and Fig. 2d).

Fig. 4c shows the photocurrent response to low-dose-rate X-ray photons; the anode voltage is set at 40 kVp, while varying the anode current controls the dose rate; aluminum of thickness 2 mm is used as a filter. The voltage bias is set at -200 V for efficient charge collection. The lowest measured dose rate from our X-ray tube is 41 nGys^{-1} limited by the minimum anode current of our X-ray tube (40 kVp, 0.1 mA), which leads to a photocurrent density of 0.28 nAcm^{-2} . The signal noise of the X-ray PIN photodiode for 40kVp X-ray under -200 V was measured as $\sim 0.005 \text{ nAcm}^{-2}$. By fitting the photocurrent density versus the dose rate, the detection sensitivity for 40 kVp X-ray is measured as $9.62 \mu\text{C mGy}^{-1} \text{cm}^{-2}$ and the lowest detectable 40kVp X-ray dose rate with signal-to-noise ratio of 3 was 17.7 nGys^{-1} as shown in Fig. 4d. The X-ray sensitivity of the X-ray PIN photodiode is related to the photon energy, mainly due to the different absorption coefficients. Therefore, the X-ray detection sensitivities with 50 kVp, 100 kVp, and 120 kVp were then measured, as shown in Fig. 4e. The X-ray detection sensitivity decreases from $8.0 \mu\text{C mGy}^{-1} \text{cm}^{-2}$ to $4.03 \mu\text{C mGy}^{-1} \text{cm}^{-2}$, and $3.15 \mu\text{C mGy}^{-1} \text{cm}^{-2}$, while the X-ray photons become harder.

In addition to the X-ray detection sensitivity, higher response speeds can shorten the exposure time, which is suitable for high frame counts and low-dose radiography. The response speed was investigated by an X-ray photodiode-external resistance ($0.1 \text{ M}\Omega$) series circuit corresponding to an RC lifetime of 10.4 ns, as shown in Fig. 4e. The rising time (from 0% to $(1-1/e)\%$) and fall time (from 100% to $(1/e)\%$) were measured as $2.55 \mu\text{s}$ and $0.75 \mu\text{s}$, respectively. The response time is comparable to the transmission time calculated from the drift movement equation, $T = \frac{L}{\mu E} = 0.67 \pm 0.3 \mu\text{s}$. This high response speed is attributed to the high and balanced charge mobility of the intrinsic layer and the high electrical field inside the PIN photodiode. This response speed and current noise are superior to those reported in previous work^{15,16,54}, and the X-ray sensitivity is comparable to that of spin-coating-based devices. The comparison is shown in Supplementary Table 1.

Subsequently, the X-ray PIN photodiode was used for X-ray imaging, as shown in Fig. 4f; two screws were used as the object and a two-direction slide table was used to move the X-ray PIN photodiode to realize space scanning. In the high-current-threshold image, the screw thread is clear from the background owing to the dose difference. In the low-current-threshold image, owing to the low noise current, the X-ray PIN photodiode could recognize the screw thread on the screws where the transmitted X-ray dose was extremely weak. This image suggests that this low-noise-current X-ray PIN photodiode could possibly realize better contrast in objects.

Figure 5 | Stability of the PIN photodiode. **a**, Thermal stability of the PIN photodiode **b**, Dark current density of the PIN photodiode after 9 months and irradiation with high-dose X-rays.

In addition, ion exchange and migration⁵⁵⁻⁵⁸ may degrade perovskite-based devices; here, the device is placed at temperatures from 15 (room temperature) to 90 °C in air to accelerate this phenomenon (Fig. 5a). The dark current density increased with the temperature (nearly 1 nAcm⁻²/°C), indicates this device could be applied in thermal detection⁵⁹. Then, the device was maintained 90 °C for 12 h as shown in Fig. 5b, the dark current density maintains ~104 nAcm⁻². After that, when the device was cooled back to 15 °C and the dark current density recovered without degradation (Fig. 5a). This proves that the ion exchange and migration speeds are extremely low in this X-ray photodiode and this X-ray PIN photodiode shows a better thermal stability than amorphous selenium. Further, as shown in Fig. 5c, the dark current density of this X-ray photodiode was investigated after 9 months in air without protection and after irradiation by high-dose X-rays in air without shielding; the drift of the dark current density is less than 0.1%, which demonstrates the high stability of the X-ray PIN photodiode.

Discussion

In conclusion, the SPDE method for growing X-ray PIN photodiodes is demonstrated in this work. Based on the doping concentration and device structure design, the X-ray PIN photodiodes exhibit remarkably low dark current and noise current under large bias. A record response time of 750 ns was achieved and a 40 keV X-ray sensitivity of 9.62 $\mu\text{C mGy}^{-1}\text{cm}^{-2}$ was observed in this work, which could provide high-contrast and high-speed X-ray images. This work not only demonstrates that the SPDE method is capable of fabricating high-quality PIN photodiodes for X-ray detection, but also provides important insights to guide the future development of solution-processed and perovskite-based devices.

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Methods:

Materials. Lead bromide (PbBr₂, 99%) and lead chloride (PbCl₂, 99%) were purchased from Sigma Aldrich, USA. Methylammonium bromide (MABr) and methylammonium chloride (MACl) were purchased from Sigma Aldrich, USA. Bismuth bromide (BiBr₃, 99.9%), silver bromide (AgBr, 99.9%), and other metal bromides were purchased from Sigma Aldrich, USA. Dimethyl sulfoxide (DMSO), dimethylformamide-d₇ (DMF), and γ -butyrolactone (GBL) were obtained from Aladdin. Metallic gold, silver, and gadolinium were purchased from Chinese reagent, China. All commercial products were used as received.

Fabrication of X-ray photodiodes. The substrate MAPbBr_{2.5}Cl_{0.5} was grown by the inverse temperature crystallization method⁶. Specifically, PbCl₂ (0.25 mol L⁻¹), PbBr₂ (0.75 mol L⁻¹), and MABr (1 mol L⁻¹) were dissolved in DMF (60 mL) and MSO (5 mL) mixed solution. The solutions were then filtered through a PTFE filter with a 30 μ m pore size. The filtrate was then transferred to a culture dish, which was placed on a programmable heating station (IKA-RET control-visc). The temperature was controlled from 40 °C to 65 °C. For SPDE layer growth, the temperature was controlled from 60 °C to 80 °C for the doped MAPbBr₃ precursor, whereas the temperature was controlled from 60 °C to 80 °C for MAPbBr₃. A vacuum pad was used to control the location of the substrate, and an electric-driven slide was used to control the depth of the substrate dipped in the SPDE solution. To polish and cut the additional thickness and parts of the sample, diamond powder with different sizes dissolved in diamond

oil was used as an abrasive paste and a polishing fluid. Gold (100 nm thickness) was then deposited on the doped faces of the photodiode as electrodes, and the shape of the electrode was controlled by metal masks.

Characterization of X-ray photodiodes. X-ray diffraction patterns were obtained using an X'TRA system with a Cu target (Switzerland). Optical absorption spectra were measured by UV-vis spectroscopy in the range of 300 to 2000 nm (Lab Tech Bluestar, USA). X-ray photoelectron spectra were obtained using a PHI 5000 VersaProbe (Japan). The PL and PL decay processes were measured using a SpectraMax instrument (UK). The MHPSCs were characterized in sequence since they grow from a solution without any other process. SEM images were obtained using a Quanta 200 FEI microscope. The HR-TEM is characterized with TEM (JEM-200CX, JAPAN) for Fig. 3f. with a high voltage 220kV. The TEM photo is analyzed by ImageJ software. To avoid the influence of the surface, we broke the MHPSCs to measure the element distribution via EDX measurements. For the SCR, an FEI Nano manipulator (China) was used to apply voltage bias inside the SEM cavity. In addition, to ensure that the detectors receive enough X-ray photons in EDX, the counts per second is controlled nearly 1200 in the experiments. The KPFM probe is station (Multimode-8-AM, USA) was used to measure the CPD. Dark current density-voltage (J - V) characteristics were measured using a Keithley 4200 semiconductor analyzer (USA) in the dark. The response time was measured using an Agilent oscilloscope (7.5G, USA) with a Keithley 2400 voltage source (USA) and a commercial X-ray tube operated in the pulse mode (15 mA, 120 kV, 10 Hz) as the illumination source. The noise current was measured using an Agilent oscilloscope (USA, 7.5G) to record the voltage variations with a 100 k Ω load. The X-ray photodetection was performed in a lead room. The X-ray imaging system was manufactured by PERLOVE MEDICAL (China). The two-direction scanning system was custom-made.

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Author contributions

W. L. and X. W. supervised the project during the whole process of all experiments. X. W., Y. B., Y. P. and Y. L. grew the substrates. X. W., and Y. B., investigated the SPDE method and found suitable dopants. X. W. and Y. P. did the polish and cut process. X. W. and Y. L. did the electrical experiments. X. W. and Q. L. did the SCR measurements. X. W., J. X., J. C., E. E., D. O., J. A. and X. Z. analyzed the results. X. W. and W. L. wrote the manuscript. All authors make comments on the manuscript.

Additional information

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Competing financial interests

The authors declare no competing financial interests.

Figures

Figure 1

Energy structure design of the X-ray PIN photodiodes. a, Thermal-probe-induced current of MAPbBr₃ MHPSC with different dopants. b, Diagram of the PIN photodiodes and its work mode. c, X-ray diffraction data for each layer from 30° to 31.2°. d, Photoluminescence versus wavelength of intrinsic layer and doped layers. e, Minority carrier bulk lifetime of intrinsic layer and doped layers. f, VBM of each layer from -4 eV to 6 eV by XPS g, UPS of each layer (using the He-I line with a photon energy of 21.22 eV).

Figure 2

Fabrication and electronic properties of the X-ray PIN photodiodes. a, Designed energy structure of the PIN photodiode. b, Fabrication process and optical images (left: cross-section view, right: top view) of the PIN photodiode (6.11×5.12×3.91 mm³), scale bar 2 mm. c, Characterization of current density-voltage from -500 to 150 V. d, Average charge mobility of electrons (left) and holes (right) measured by TOF curves. e, Long-term stability of dark current under -200 V. f, Voltage bias scan from -150 V to -50 V. g, Noise current at different X-ray photodiode frequencies with varying voltage bias.

Figure 3

Characterization of the SCR under bias. a, Illustration of the KPFM experiments. b, Contact potential difference of intrinsic/n-type(up) and p-type/intrinsic(down) interfaces. c, Line profile of the CPD. d, Illustration of the secondary electron variance with electron density in the SEM cavity. e, SEM images of the sample under 0 bias. f, Magnified cross-section of the two interfaces, HR-TEM photons of the n-type and p-type layers. g, SEM screenshots of the PIN photodiode under different voltage bias and line profile of the normalized gray value as a function of width. inset: width of the SCR verses reverses voltage.

Figure 4

X-ray detection performance and X-ray imaging. a, Photo/dark current density with different voltage bias b, Charge collection efficiency by fitting to the Hecht equation. c, Photo/dark current density with different dose rate (40 kVp) under -200 V bias. d, 40 kVp X-ray sensitivity of the X-ray photodiode. e, X-ray sensitivity of the X-ray photodiode for X-ray photons with different photon energy. f, Response speed of the X-ray photodiode under -200 V bias. g, X-ray image captured by the X-ray photodiode.

Figure 5

Stability of the PIN photodiode. a, Thermal stability of the PIN photodiode b, Dark current density of the PIN photodiode after 9 months and irradiation with high-dose X-rays.

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