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Sub-millimeter Light Detection and Ranging Using Perovskites

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Resolving the distance and velocity of objects with high accuracy is needed in 3D vision, and light detection and ranging (LiDAR) provides this via the temporally-resolved detection of backscattered short-pulsed light from imaged objects^{1,2}. Simultaneous improvements in the speed and signal-to-noise ratio of photodetectors are needed to enable demanding ranging applications. Silicon, in view of its low cost and ease of monolithic integration, has been a primary option for LiDAR photodetectors in the range of 850 to 950 nm; however its indirect bandgap leads to low absorption coefficient in the NIR^{3,4} and a trade-off between speed and efficiency. Here we report solution-processed PbSn binary perovskite photodetectors that unite external quantum efficiency of 85% at 850 nm with a dark current below 10^{-8} A/cm² and response faster than 100 picoseconds. The combined efficiency×speed is >2x higher than in fast silicon photodetectors and >100x higher than in the best previously-reported solution-processed photodetectors. We develop self-limiting self-reduced Sn precursors that enable perovskite crystallization at the desired stoichiometry and prevent the formation of interfacial defects with the hole transport layer. The approach removes oxygen from the solution, converts Sn⁴⁺ to Sn²⁺ through comproportionation, and leaves neither Sn nor SnO_x. We resolve sub-mm distances, highlighting the potential of solution-processed perovskite photodetectors in LiDAR.

1 Three-dimensional mapping of surroundings requires photodetectors that accurately estimate
2 distance using time of flight. Light detection and ranging (LiDAR) technology is an active
3 remote sensing system used in autonomous vehicles, machine vision, and augmented reality for
4 consumer devices. LiDAR measures the time for the short-pulsed light to scatter back from a
5 target object and return to a detector². The measured time is converted to distance using the
6 speed of light. By scanning illumination over a target scene, one reconstructs a 3D image¹.

7 Photodetector characteristics play a central role in the resolution, accuracy, and detection
8 limits of the system. The ideal LiDAR photodetector should be fast and efficient with a low dark
9 current at the operating bias. These metrics must be satisfied at industry-relevant LiDAR
10 wavelengths (>850 nm). In the window of 850 to 950 nm, silicon photodetectors have been a
11 primary option for industry due to their low cost and ease of system integration. However, as
12 modeled in Fig. 1a, there exists a trade-off between efficiency and speed in silicon
13 photodetectors. Silicon has a weak absorption coefficient at LiDAR-relevant wavelengths
14 ($\sim 2.7 \times 10^3 \text{ cm}^{-1}$ at 905 nm), which demands thick devices ($\sim 10 \text{ }\mu\text{m}$) to absorb 90% of incident
15 light in a single pass (Extended Data Fig. 1). However, to reach the 2 GHz bandwidth, the silicon
16 device thickness needs to be less than 3 μm . Silicon's indirect bandgap thus limits its combined
17 detection efficiency $\times$ speed (Fig. 1b).

18 Solution-processed perovskites have a high optical absorption coefficient ($> 10^4 \text{ cm}^{-1}$),
19 high carrier mobility (tens of $\text{cm}^2/\text{V.s}$), and long carrier diffusion length ($> 1 \text{ }\mu\text{m}$), making them
20 promising candidates for fast photodetection⁵⁻¹³. Alloying lead-halide perovskites with Sn
21 extends the detection range into LiDAR-relevant wavelengths (>850 nm)¹⁴⁻¹⁶. The ratio of Pb to
22 Sn also affects the crystallization process and film quality of the perovskite¹⁷. Calculations
23 shown in Fig. 1c indicate that PbSn at specific conditions could offer a route to unite speed and

1 efficiency (details in Extended Data Fig. 2). The modeling demonstrates that the thickness of
2 photoactive layer determines the trade-off between the response time and the external quantum
3 efficiency of the device. Accordingly, it is of interest to maximize the absorption coefficient
4 using a high-quality crystalline dense film and to minimize the defect density in the film to
5 permit the fast extraction of charges.

6 A challenge in fabricating PbSn perovskite devices is the high susceptibility of Sn^{2+} to
7 become oxidized in the precursor solution. The resulting Sn^{4+} species form trap states whose
8 nonradiative recombination decreases the diffusion length in perovskite films, and deteriorates
9 device performance^{14,15}. Several strategies have been reported to address Sn oxidation, including
10 the use of antioxidant additives such as SnF_2 , SnF_2 -pyrazine complex, and hydroxybenzene
11 sulfonic acid¹⁸⁻²². In particular, the tin powder-reduced precursor (TPRP) strategy has shown
12 significantly improved charge carrier diffusion length up to 3 μm in PbSn perovskite films¹⁵. We
13 sought to leverage these advances for NIR photon detection by perovskites.

14 The speed of a photodetector is dominated by the lowest carrier mobility inside the
15 layered device structure. Accordingly, it is essential to utilize high-mobility hole transport layers
16 (HTL) and electron transport layers (ETL) that do not limit the speed of the photodetector. The
17 high crystallinity of sol-gel NiO_x results in higher mobility $\sim 10^{-3}$ to $10^{-1} \text{ cm}^2/\text{Vs}$, compared to
18 typical organic alternatives such as PEDOT:PSS at $\sim 10^{-5}$ to $10^{-4} \text{ cm}^2/\text{Vs}$ ²³⁻²⁶. It has been shown
19 that the use of NiO_x as the HTL in pure-Pb perovskite devices leads to better film quality, i.e.
20 larger grain size, fewer pinholes, and higher stability compared to other HTLs such as
21 PEDOT:PSS^{25,27-29}. Despite these advantages of NiO_x , its use with PbSn binary perovskites has
22 been limited so far. Recent works with NiO_x HTL in PbSn perovskite solar cells have reported
23 conversion efficiencies up to $\sim 17\%$ ^{27,30}, lower than the 21% power conversion efficiency

1 obtained using PEDOT:PSS^{14,15}. Oxygen vacancies in the metal oxide may contribute to Sn
2 oxidation in the PbSn perovskite^{31,32}. We sought to develop a strategy to solve the
3 incompatibility of NiO_x and PbSn perovskites to realize fast and efficient solution-processed
4 photodetectors.

5 We began by fabricating photodetectors with an inverted planar architecture of ITO/
6 HTL/ PbSn / C60/ BCP/ Ag, where PbSn is MA_{0.3}FA_{0.7}Pb_{0.5}Sn_{0.5}I₃, and the HTL is NiO_x or
7 PEDOT:PSS as control (Fig. 1d). To limit the formation of Sn⁴⁺ vacancies in the perovskite film,
8 we adopted a metallic tin precursor strategy¹⁵. We added 0.5 mg/mL Sn metallic microparticles
9 with a diameter of <150 μm to the precursor solution, which we stirred vigorously for ten
10 minutes. We observed that the addition of metallic tin powder to the precursor solution decreased
11 the EQE of devices fabricated with NiO_x as the HTL (Fig. 1d). This finding is in contrast to the
12 improvement we saw in the control PEDOT:PSS devices with the addition of the Sn powder (see
13 Extended Data Fig. 3)¹⁵.

14 To explore the origins of the drop in EQE observed in the NiO_x devices upon the
15 incorporation of metallic Sn into the precursor solution (<65% at 900 nm), we considered the
16 possibility of residual metallic Sn and Sn oxides in the precursor solution. Microparticles of
17 small diameters or the product of Sn⁴⁺ reacting with Sn⁰ (*e.g.* SnO) may pass the final filtering
18 step (Fig. 2a) and become incorporated into the film. The quantity of these residual species is
19 low enough that it does not negatively impact the properties of the bulk of the film since the
20 performance of the devices with PEDOT:PSS did not decrease with the addition of the Sn
21 powder (see Extended Data Fig. 3)¹⁵. However, oxygen-exposed facets of the NiO_x surface can
22 be sensitive to the residue of Sn metal. Indeed, a Foster diagram shows that different forms of
23 Sn oxide have lower formation energies compared to Ni oxide (Extended Data Fig. 4). Exposed

oxygen on the surface of NiO_x may react with Sn species to form a layer of Sn oxide. Crystalline NiO_x can also act as a preferential surface for the growth of the interfacial SnO_x layer.

SnO_x has been used as an electron transport layer in solar cell fabrication and has been to act as a hole blocking layer with valence and conduction band at ~ -8.0 and -4.5 eV, respectively³³. DFT simulations (based on PBE within spin-polarized treatments) in Fig. 2b show the possibility of SnO formation on top of NiO. DFT calculations indicate that the formation of a layer of SnO ($\Delta E_{\text{vbm}}[\text{NiO}/\text{SnO}] = -1.10$ eV) or SnO_2 ($\Delta E_{\text{vbm}}[\text{NiO}/\text{SnO}] = -1.58$ eV) thin film on top of NiO disrupts band alignment: SnO_x acts as a hole blocking layer and prevents the extraction of holes to the ITO electrode (Fig. 2c). Moreover, the conduction band of SnO_x resides in the bandgap of NiO_x , and facilitates back injection and interfacial charge recombination, which deteriorates diode behavior and device performance. Details of the DFT calculations are given in Methods section and Extended Data Fig. 4.

We posited that using a macroscopic Sn surface, which is reactive to oxygen, can draw the oxygen from the precursor solution when the solution flow over a Sn metallic surface. The surface should be in a form that exposes the high surface area to the solution and does not disintegrate into smaller pieces during long-time or aggressive reactions with oxygen. When we satisfy these requirements, the Sn surface also acts as a self-limiting reducing agent for Sn^{4+} , so that the time of the reaction is not critical for optimization. We found that a few cm of helically folded tin wire with a diameter of 0.5 mm could satisfy these requirements. The reactive macroscopic surface of the Sn wire acts as a self-limiting reducing agent to convert unwanted Sn^{4+} to Sn^{2+} , allowing Sn wire to react with oxygen in the precursor without leaving metallic Sn or SnO_x residue after filtration. Fig. 2e shows that the NiO_x HTL with the tin wire-reduced precursor (TWRP) results in an EQE of $\sim 85\%$, which is higher than all the control PEDOT:PSS

1 devices. Moreover, the NiO_x device shows a lower dark current compared to PEDOT:PSS,
2 reaching values below 10^{-8} A/cm^2 (Fig. 2f). Representative dark current curves for PEDOT:PSS
3 and NiO_x are shown in Extended Data Fig. 3.

4 We compare these results with those of state-of-art photodetector technologies, which
5 include solution-processed photodetectors based on organics, quantum dots, and perovskites.
6 Fig.3a shows the EQE vs. dark current of the best-reported detectors we found from each
7 category that are characterized as photodetector with detection range $>850 \text{ nm}$. We have
8 included the data from the papers that they have reported the speed of their photodetectors
9 (Extended Data Table 2).

10 Integrating the TWRP strategy for PbSn perovskites with the NiO_x HTL offers 20
11 absolute percentage points higher EQE than in the highest-performing previously-reported
12 solution-processed photodetectors at LiDAR-relevant wavelengths ($>850 \text{ nm}$). We also include
13 metrics of state-of-art fast silicon detectors (BW of 1-2 GHz) from three suppliers in Fig. 3a. For
14 silicon, high speed can only be attained with thin active layers, which results in high dark
15 currents and low EQE values. Fig. 3b shows the overlay of the PbSn PD responsivity spectra
16 with high- and low-speed Si PDs. The quantum efficiency of slow commercial Si PDs
17 approaches $\sim 93\%$ at 905 nm , but these values are significantly reduced in fast silicon
18 photodetectors (EQE $<50\%$).

19 The ideal photodetector defined in Fig. 1b combines detection efficiency at LiDAR
20 wavelengths with fast response times. We used a transient photocurrent (TPC) setup shown in
21 Fig. 4a to measure the response time of our PbSn perovskite photodetectors. A two-point contact
22 (Signal-Ground) RF probe with a pitch of $1000 \mu\text{m}$ was used to contact the bottom ITO electrode
23 and the top Ag electrode, whose size defines the detection area. Fig. 4b shows the TPC results

for different pixel sizes. Analysis of response time vs. pixel area (Extended Data Fig. 6) shows that the response time decreases with pixel area and does not plateau even at the smallest pixel area of $\sim 0.005 \text{ mm}^2$. Considering a dielectric constant of $\epsilon \sim 51$, estimated with impedance spectroscopy (Extended Data Fig. 7), the geometrical capacitance of the PbSn perovskite plays a significant role in speed determination (Extended Data Fig. 6). This analysis suggests that even at the smallest pixel area, we had not reached transport-limited performance, and thus we were motivated to develop a strategy to circumvent the geometrical capacitance limitation.

Direct contact of the signal side of the RF probe with the ETL surface of the device resulted in a contact area less than $10 \times 10 \text{ }\mu\text{m}^2$. This strategy enabled us to reach a $<100 \text{ ps}$ full-width-half-maximum (FWHM) response time. Fig. 4c shows the comparison between the response time of the PbSn photodetector with the direct probe contact and a commercial fast Si and GaAs photodiode (see Extended Data Table 1 for the details of the commercial PD). We note that the data shown in Fig. 4c are not for the same detector area; however, a Si PD operates in a transport-limited regime and is therefore not limited by the geometrical capacitance. Consequently, a decrease in Si detector size does not lead to faster response time (see Extended Data Fig. 6). As it is clear from Fig. 4c, PbSn PD offer narrower FWHM and comparable fall time (90 to 10%) to 5.0 GHz GaAs photodetector.

We characterized the PDs for LiDAR applications to estimate the distance of objects. We used a Michelson interferometer configuration in a time-of-flight (ToF) setup (Fig. 5a). Using a beam splitter, we referenced the pulsed light to a commercial InGaAs at a fixed position. Fig. 5b shows the response of PbSn photodetector at different positions of the moving mirror of the interferometer. The contour graph in Fig. 5c shows the light travel distance vs. time, and the slope of the line gives a speed of light at 299 mm/ns . Fig. 5d shows the overlay of the PD

responses when the mirror had moved by 0.79 mm (reliable minimum travel distance of our digital linear stage). We plot the first derivative of the response in Fig. 5e to better visualize the data in Fig. 5d (see Extended Data Fig. 8). As shown in Fig. 5e, the system resolves a sub-mm distance from the peak position (where the derivative becomes zero). Together with the high EQE, the fast response makes the PbSn photodetectors ideal candidates for short-range high-accuracy LiDAR applications.

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Fig. 1. Silicon and PbSn photodetectors. **a**, Performance modeling of silicon p-i-n photodetector. Details and parameters of the modeling are given in Methods and Extended Data Fig. 1. **b**, Comparison of fast and slow silicon PD characteristics (see Extended Data Table 1). Desirable characteristics for LiDAR photodetection are also shown. **c**, Modeling of combined speed-efficiency characteristics for PbSn perovskites compared to silicon. BW stands for the bandwidth. Details and parameters for the modeling are given in Extended Data Fig. 2. **d**, Effect of tin powder-reduced precursors (TPRP) on the external quantum efficiency of the photodetectors with NiO_x as HTL. Inverted architecture of the fabricated devices is shown at the inset.

Fig. 2. Strategy to eliminate SnO_x formation. **a**, Schematic of the Sn metallic powder reducing precursor process. **b**, DFT simulated structure of formed SnO layer on top of NiO HTL. **c**, Energy level diagram for different layers of fabricated devices, including SnO_x . **d**, Schematic showing the Sn metallic wire reducing precursor process. **e**, EQE of the devices using TWRP strategy. **f**, Comparison of dark current density at 50 mV for devices fabricated with PEDOT:PSS, NiO_x , and without HTL with different Sn reducing strategy.

Fig. 3. Performance of PbSn photodetectors. **a**, Plot of maximum EQE for wavelengths > 850 nm vs. minimum dark current at the operating bias. For devices operating without external bias, dark current at 50 mV is plotted. Citations are given in Extended Data Fig. 5a and Table 2. **b**, The responsivity of our PbSn PD compared with commercial silicon fast and slow PDs. Details of the commercial fast and slow PDs from different companies are given in Extended Data Fig. 5b and Table 1.

Fig. 4. Speed measurements for PbSn devices. **a**, Schematics illustrating transient photocurrent measurements. Radio-frequency (RF) probe with two-point contact (signal-ground) is used to make a connection with the bottom ITO electrode and top Ag electrode with different pixel areas. Direct contact of RF probe with the surface of ETL (without Ag electrode) leads to a working device with a small area ($<10 \times 10 \mu\text{m}$). **b**, 3D plot showing the normalized response versus time for different pixel sizes. Y-axis is the diameter of the pixel in μm . **c**, comparison of PbSn response time (with direct probe contact) with commercialized 2.0 GHz silicon and 5.0 GHz GaAs photodetector. See Extended Data Fig. 5c and Table 1 for detailed characteristics of the shown commercial PD.

Fig. 5 | Time-of-flight measurements. **a**, Schematic of ToF measurement. Michelson interferometer configuration is used to trigger the oscilloscope and remove jitter of the fs laser. **b**, The response of PbSn PD at the indicated position of the moving mirror. The response of the InGaAs detector is shown as a reference (fixed position). **c**, Contour plot of data shown in panel A vs. the travel distance of light with respect to the reference. The slope of the line determines the measured speed of light. **d**, Graph showing the response when the mirror has moved by 0.79 mm. The inset shows a magnification near the peak of the response. **e**, The transformation function of the response shown in panel D. Indicated points at zero represents the peak of the response. See Extended Data Fig. 8 for the details of the used transformed function.

METHODS

Materials and Preparation. Unless indicated otherwise, all the materials were purchased from Sigma Aldrich and used as received. FAI, MAI, PbI_2 , and SnI_2 were acquired from Great Cell and Alfa Aesar. A perovskite precursor solution of 1.7 M was prepared by mixing of precursors based on the molar ratio of $\text{FA}_{0.7}\text{MA}_{0.30}\text{Pb}_{0.5}\text{Sn}_{0.5}\text{I}_3$ in the mixture of DMF:DMSO (3:1 v/v). The SnF_2 precursor was added by 10 mol% relative to the SnI_2 amount. We noticed that it is important to pre-heat the precursor glass vial at 100 °C for 15 min. The obtained mixture was prepared inside the nitrogen glovebox. After stirring at room temperature for 2 h, the solution was filtered through a 0.45 μm PTFE syringe filter. For the TPRP samples, tin powders (5 mg/ml) were added, stirred at room temperature for 10 min, and filtered using 0.45 μm PTFE syringe filter prior to use. For the TWRP samples, a few cm long Sn wire (99.999%, Millipore Sigma, 0.5 mm diameter) was dropped inside the solution which was stirred for an additional hour stirring before filtration. We noticed expanding the time of this reaction to more than one hour does not affect the performance. A 1.0 M of NiOx solution was prepared by the initial mixing of $\text{NiNO}_3 \cdot 6\text{H}_2\text{O}$ with ethylene glycol (anhydrous, 99.8%) followed by the addition of ethylenediamine (>99%) with a molar ratio of 1.1:1 in respect to the nickel precursor. The solution was stirred overnight, followed by its dilution to the favorable concentration of 0.23 M. The solution was filtered using a 0.45 μm PVDF syringe filter before deposition.

Device Fabrication. For NiOx films, the as-prepared NiOx solution was spin-coated on pre-cleaned ITO substrates at 4000 rpm for 90 s and annealed at 300 °C on a hotplate for 1 hour in ambient air. We tested the UV illumination post-treatment, but it had a negative impact on the device performance. For PEDOT:PSS films, the solution (Xi'an PLT) was spin-coated on the substrates at 4000 rpm for 30 s followed by annealing at 150 °C on a hotplate for 30 min in ambient air. The substrates were transferred to a nitrogen glovebox after annealing. We also diluted the PEDOT:PSS with methanol in a different ratio, but we did not observe the statistical and reproducible difference on EQE of devices. For the deposition of perovskite films, the as-prepared precursor solution was spin-coated in a two-step procedure: (1) 1000 rpm for 10 s with a ramping speed of 200 rpm/s, and (2) 4000 rpm for 50 s with an acceleration of 1000 rpm/s. During the second spin coating step, a 250 μL of chlorobenzene (anhydrous, 99.8%) was dispensed dynamically on the substrate at 25 s before the end of the procedure. Immediately after deposition, the substrates with PEDOT:PSS were annealed on a hotplate at 100°C for 10 min. The perovskite films deposited on NiO_x as HTL were annealed on a hotplate in two steps: first at 50°C for 5 min and then at 85 °C for another 5 min. C_{60} (Xi'an PLT), BCP (TCI Chemicals), and Ag electrode were deposited respectively in an Angstrom thermal evaporation system to form 20 nm C_{60} , 7 nm BCP and 250 nm Ag on top of the perovskite layer, respectively.

Device Characterization. Dark current-voltage (*JV*) characteristics were measured using a Keithley 2400 source-meter by scanning the bias between -0.3 V and 0.3 V for pixels with an active area of 0.1 mm². The EQE spectra were measured using a Newport Quant-X 300 system without applying any external bias. Both *JV* and EQE measurements were carried out under a constant flow of nitrogen. Transient photocurrent (TPC) measurement was done with a 26 GHz SG radiofrequency probe (T26A - MPI corporation) with 1000 pitch. The probe was connected with a fast SMA cable directly to the 50-ohm input of an oscilloscope (16 GHz Agilent DSAX91604A Infiniium). 150 femtosecond laser pulses at a 10 kHz repetition rate were produced using a regeneratively amplified Yb:KGW laser (PHAROS, Light Conversion). All reported experiments were done at 850 nm; however, we did not observe a change in response time at the illumination range of 600 to 950 nm. A 12 GHz bias tee connected to a Keithley 2602 in the circuit. The electrical output signal from the fs laser system was used to trigger the oscilloscope.

Impedance spectroscopy. Impedance spectroscopy is employed to estimate the dielectric constant of the PbSn perovskite film. For this purpose, the fabricated device with PEDOT: PSS as HTL is connected to Autolab Potentiostat/Galvanostat module. An AC voltage perturbation of 20 mV is applied while the device is kept at dark and short-circuit conditions. The impedance spectra are collected as the frequency scans from 1 Hz To 1 MHz (Extended Data Fig. 7a). The capacitance component *C* is calculated based on the relationship with impedance *Z* and angular frequency ω ³⁴:

$$C = \frac{1}{(i\omega Z)}$$

Plotting capacitance versus frequency (Extended Data Fig. 7b) exhibits a typical behavior consisting of two plateaus when decreasing frequency from 1 MHz to 1 Hz³⁵. The plateau located at low-frequency range (~ 1 Hz) is associated with the accumulated charges at interfaces, the high-frequency part of the spectra (> 1 KHz), on the other hand, represents the geometrical capacitance C_g corresponding to the dielectric response of the perovskite layer. Accordingly, the dielectric response (ϵ) of the perovskite layer can be calculated by:

$$C_g = \frac{A\epsilon\epsilon_0}{d}$$

where ϵ_0 is the permittivity of the free space, ϵ is the dielectric constant of the material, *d* is the thickness of the light-absorbing perovskite layer, and *A* is the overlapping area between two electrodes, which are 500 nm and 0.1 cm², respectively³⁶. To calculate the accurate value of C_g , a proper equivalent circuit representative of the resistive and capacitive responses of the system should be fitted (the solid lines in Extended Data Fig. 7a,b). Based on the previous studies on perovskite solar cells³⁶, the equivalent circuit

of choice is a modified version of the standard Randles circuit (Extended Data Fig. 7c), which delivers the best fit to the measured data. Fitting results, as well as the calculated dielectric constant, is tabulated in Extended Data Fig. 7d. The obtained value for dielectric constant is in good agreement with the values reported for metal halide perovskites^{9,37}.

LiDAR demo. For distance estimation, we used the same equipment and arrangement as the TPC setup to measure the time response, but we split the fs laser using a 50:50 beam-splitter before sample. One part of the light was directed to a 30 GHz InGaAs photodetector (Thorlabs, DXM30BF). The oscilloscope was triggered by the photodetector signal connected to channel 2, and also it was used as a reference with a fixed position. The second part of the light was directed to the mirror installed on the linear stage (Newport) with a maximum travel distance of ~ 250 mm. The reflected light from the mirror was directed to the PbSn photodetector and focused on the corresponding pixel with a series of eyeball lenses.

DFT calculation. The DFT calculations were performed using the FHI-aims all-electron code³⁸⁻⁴⁰. The default numerical settings, referred to as “tight” in FHI-aims were used. Spin-polarized treatment for Ni atom was incorporated into all calculated electronic properties and geometry relaxation. More specifically, the NiO in all structures (i.e., bulk calculations, superlattice calculations) are adopted a type-II anti-ferromagnetic phase (i.e., the spin ordering vector are along [111] direction). Local minimum-energy geometries of the Born-Oppenheimer surface were obtained with residual total energy gradients below 1×10^{-2} eV/Å for atomic positions by PBE-GGA functional. In order to analyze the band alignment of NiO/SnO and NiO/SnO₂, we adopted the method according to the reference⁴¹, in which the valence-band offset, ΔE_{VBM} , is defined as

$$\Delta E_{VBM}[NiO/SnO, SnO_2] = (E_{VBM}^{SnO/SnO_2} - E_{VBM}^{NiO}) + \Delta V$$

Where E_{VBM}^{SnO/SnO_2} (E_{VBM}^{NiO}) represents the position of the valence band maximum (VBM) with respect to average electrostatic potential in materials SnO/SnO₂ (NiO), and ΔV represents the potential alignment term obtained from the superlattice calculations (Extended Data Fig. 4). According to this reference (4), the E_{VBM}^{SnO/SnO_2} (E_{VBM}^{NiO}) is obtained by using a hybrid functional (HSE06), and the potential alignment term ΔV is calculated based on a fully relaxed superlattice by the PBE-GGA functional (which is proved to give similar accuracy as HSE06, but within significantly less computational cost). More specifically, instead of using the plane-average electrostatic potential to calculate this potential alignment term ΔV , the electronic potential at the cores of oxygen atoms are used in order to eliminate the oscillations caused by the ionic cores (as shown in Extended Data Fig. 4b,c). The final band-alignment schematic plots are shown in Extended Data Fig. 4d,e.

Photodetector performance modeling. The temporal response (τ_R) of a photodetector is modeled based on its dependence on the carrier transient time (τ_{tr}), RC-limited time response (τ_{RC}) and diffusion time (τ_{diff}) as follows:

$$\tau_R = \sqrt{(\tau_{tr})^2 + (\tau_{RC})^2 + (\tau_{diff})^2}$$

The transient time is predicted based on the bias across the sample (V), the mobility (μ) and the film thickness (d):

$$\tau_{tr} = \frac{d^2}{\mu V}$$

The RC constant is another limitation to the photodetector speed as it defines the time it takes to charge/discharge of the capacitors in the electrical circuit. Assuming a simple parallel plate capacitance model, the equation is derived as below:

$$\tau_{RC} = 2.2RC = \frac{2.2RA\epsilon\epsilon_0}{d}$$

In the calculations, we have assumed that the diffusion time is negligible compared to drift and RC time constant, and field is linear across the sample thickness.

Finally, the -3dB bandwidth of a photodetector relates to the temporal response according to the following equation:

$$BW = 0.35 / \sqrt{\left(\frac{2.2AR\epsilon\epsilon_0}{d}\right)^2 + \left(\frac{d^2}{\mu V}\right)^2}$$

Using the Beer-Lambert law and assuming that the reflectance is negligible, the absorbance of a material relates to its transmittance (T), absorption coefficient (α), and thickness (d) as below:

$$A = 1 - T = 1 - e^{-\alpha d}$$

The external quantum efficiency (EQE) is defined as the number of photogenerated carriers divided by the number of incident photons. The internal quantum efficiency (IQE) is defined as the ratio of photogenerated carriers to the number of absorbed photons. Therefore, the division of these two quantities gives the percentage of the absorbed photons (A). As a result, the following equation describes the relationship between the EQE and thickness of the photoactive layer:

$$EQE = IQE \times (1 - e^{-\alpha d})$$

In this paper, for comparison between silicon and PbSn, it is assumed that IQE at 905 nm is equal to unity for both of architectures ($IQE = 1.0$)

Data availability. The datasets generated during and/or analysed during the current study are available from the corresponding author on reasonable request.

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Extended Data Fig. 1 | Performance modeling of the photodetector. Equations are provided in Methods section. **a**, Percentage of absorbed light vs. thickness at indicated absorption coefficients. EQE and bandwidth of **b**, Silicon and **c**, PbSn perovskite vs. film thickness. **d**, Comparison of silicon and PbSn perovskite from the last two panels. Parameters used for the modeling are given in Extended Data Fig. 2a.

a

Parameters	Silicon	PbSn PVK	Units
Dielectric constant	11	51	-
ϵ_0 (Vacuum permittivity)	8.85×10^{-14}	8.85×10^{-14}	F/cm
Device Area	7.0×10^{-5}	4.0×10^{-6}	cm ²
Resistance	50	50	Ohm
Mobility	450	80	cm ² /V.s
Voltage	1	0.82	V
Abs. coefficient at 905 nm	2.70×10^3	2.40×10^4	1/cm
IQE	1	1	-

c

	Simulated results	Experimental results	Thickness (d, nm)	Reference
1	EQE 81% BW 4.4 GHz ^b	EQE > 80% BW > 4.0 GHz	750 nm ^a	This work
2	EQE 55% BW 2.0 GHz	EQE 55% BW 2.0 GHz	3 μm	Thorlabs DET025A Table S1
3	EQE 92% BW 150 MHz	EQE 94% BW 10 MHz ^c	10 μm	Thorlabs PDA100A2Ta ble S1

^a d in the table is the same as active layer thickness in graph
^b BW stands for bandwidth of the photodetector
^c RC limited due to the high area $\sim 0.75 \text{ cm}^2$

Extended Data Fig. 2 | Combined speed × efficiency characteristic of the photodetector. **a**, Parameters used in the modeling of PbSn and Silicon photodetectors. **b**, Combined speed × efficiency modeling of silicon and PbSn PVK. **c**, Comparison between estimated performance and actual devices.

Extended Data Fig. 3 | Performance of NiO_x vs PEDOT:PSS HTL. **a**, EQE comparison between PEDOT:PSS and NiO_x using tin-powder reduced precursor (TPRP) strategy. **b**, Representative current density vs. voltage (*JV* curves) under the dark condition for the mentioned HTL. Tin wire-reduced precursor strategy is used for all three shown cases.

Extended Data Fig. 4 | Possibility of interfacial SnO_x formation. **a**, Diagram comparing the formation energy of different form of oxide for Ni and Sn. Electrostatic potential (in eV) at the cores of oxygen atoms along the longitudinal direction of the **b**, NiO/SnO (001) and **c**, NiO/SnO₂ (001) longitudinally lattice-matched supercell calculated by DFT-PBE within spin-polarized treatment for Ni. In each subplot, the top are the atomic structures of a (001)-oriented NiO/(SnO/SnO₂) superlattice; Ni atoms are shown in grey, Sn atoms are purple, and O atoms are red. Schematic plots of the band alignment for **d**, NiO/SnO and **e**, NiO/SnO₂ interface. The bandgap values are obtained according to a bulk calculation with HSE06 functional.

Extended Data Fig. 5 | Citation for the data used in the manuscript: a, Figure 3a; b, Figure 3b; c, Figure 4c. The numbers shown in the Figure, refer to the raw number in Extended Data Table 1 and 2.

Extended Data Fig. 6 | Geometrical capacitance effect in photodetectors time response. Measured fall time of the pixels is plotted vs. pixel area (mm²). The area for direct probe connection is estimated with the extension of the capacitance-limited regime. The area could be smaller than the estimated one. Area effect on response time of silicon photodetector is also compared with PbSn. Silicon below 0.1 mm² reaches the plateau, and further decrease in the area does not decrease the response time. This behavior indicates that the relatively poor carrier mobility limits the speed of Si PIN PDs.

Extended Data Fig. 7 | Impedance measurement of the PbSn device. **a**, Impedance plot measured in the dark under short-circuit conditions. **b**, Capacitance spectra obtained under the same condition as panel a. Black lines correspond to fits. **c**, Modified Randles equivalent circuit used for the fitting with R_s , C_g , and C_s related to series resistance, geometrical capacitance, and interface accumulation capacitance and R_2 and R_1 as surface recombination resistance. **d**, Parameters obtained by fitting the impedance data with Randles equivalent circuit

Extended Data Fig. 8 | Sub-mm resolved distance in LiDAR Demo. **a**, Overlay of the responses when the mirror has moved from the position of 123.35 to 124.17 mm. **b**, In order to make the separation clear, the response in the panel a has multiplied by a power of 400. **c**, To further clear the peak position, we can use a derivative function on panel B. At peak position, the derivative becomes zero and changes the sign from positive to negative. Note that the mathematical approach in panel b and c does not change the position of the peaks or enhance the resolution. We have used these functions to make the separation recognizable.

1

Extended Data Table 1 | Comparison of commercial silicon photodetector

code No.	Company	Model	R (A/W) @ 850 nm	EQE @ 850 nm	Speed (GHz)	Rise time (ps)	Dark (A)	Diameter (mm)	Area (cm ²)	Current Density
a1	Thorlabs	DET025A	0.38	0.55	2.0	230	3.5×10^{-11}	2.5×10^{-4}	4.9×10^{-4}	1.4×10^{-7}
a2	Hamamatsu	S9055-01	0.25	0.36	2.0	250	2.0×10^{-12}	1.0×10^{-4}	7.8×10^{-5}	2.5×10^{-8}
a3	Newport	818-BB-20	0.14	0.20	1.0	350	1.1×10^{-10}	8.8×10^{-5}	6.1×10^{-5}	1.8×10^{-6}
a4	Newport	818-BB-21	0.47	0.69	1.2	300	1.0×10^{-10}	4.0×10^{-4}	1.3×10^{-3}	7.9×10^{-8}
a5	Thorlabs	PDA100A2	0.64	0.94	<0.01	30000>	$<1\times10^{-9}$	9.8	0.75	$<1.3\times10^{-9}$

2

1 **Extended Data Table 2 | Comparison of solution-processed photodetector**

# code	HTL/Absorber /ETL	Max EQE% @ $\lambda > 850$ nm	Min Dark Current (A/cm ²) @ 50 mV	Response time			Ref.
				Fall time (ns)	Area (mm ²)	Bias (V)	
1	PTAA/ MAPbI ₃ / F8IC:PTB7-Th/ C ₆₀	54	1×10^{-8}	5.6	0.1	0	42
2	MoO ₃ / PBTTT:PCBM/PEIE	23	8×10^{-10}	230	0.5	0	43
3	PEDOT:PSS/ PTT:PCBM	17	1×10^{-9}	62	1	0	44
4	MoO _x / PbS-QD/ TiO ₂	30 @ 0.5 V	1×10^{-8}	292	-	0	45
5	PEDOT:PSS/ (FASnI ₃) _{0.6} (MAPbI ₃) _{0.4} / C ₆₀	64 @ 0.2 V	8×10^{-8}	9100	3.8	0.2	46
6	PTAA/ MAPbI ₃ / PDPPTDTP:PCBM	20 @ 0.2 V	4×10^{-9}	5	0.1	0.2	47
7	PbS-QD	33	1×10^{-7}	70	1.96	5	48
8	NiO _x / PbSn/ C60/ BCP/ Ag	85	5×10^{-9}	<0.2	<0.001	0	This work

Figures

Figure 1

Silicon and PbSn photodetectors. a, Performance modeling of silicon p-i-n photodetector. Details and parameters of the modeling are given in Methods and Extended Data Fig. 1. b, Comparison of fast and slow silicon PD characteristics (see Extended Data Table 1). Desirable characteristics for LiDAR photodetection are also shown. c, Modeling of combined speed-efficiency characteristics for PbSn perovskites compared to silicon. BW stands for the bandwidth. Details and parameters for the modeling are given in Extended Data Fig. 2. d, Effect of tin powder-reduced precursors (TPRP) on the external quantum efficiency of the photodetectors with NiOx as HTL. Inverted architecture of the fabricated devices is shown at the inset.

Figure 2

Strategy to eliminate SnO_x formation. a, Schematic of the Sn metallic powder reducing precursor process. b, DFT simulated structure of formed SnO layer on top of NiO HTL. c, Energy level diagram for different layers of fabricated devices, including SnO_x. d, Schematic showing the Sn metallic wire reducing precursor process. e, EQE of the devices using TWRP strategy. f, Comparison of dark current density at 50 mV for devices fabricated with PEDOT:PSS, NiO_x, and without HTL with different Sn reducing strategy.

Figure 3

Performance of PbSn photodetectors. a, Plot of maximum EQE for wavelengths > 850 nm vs. minimum dark current at the operating bias. For devices operating without external bias, dark current at 50 mV is plotted. Citations are given in Extended Data Fig. 5a and Table 2. b, The responsivity of our PbSn PD compared with commercial silicon fast and slow PDs. Details of the commercial fast and slow PDs from different companies are given in Extended Data Fig. 5b and Table 1.

Figure 4

Speed measurements for PbSn devices. a, Schematics illustrating transient photocurrent measurements. Radio-frequency (RF) probe with two-point contact (signal-ground) is used to make a connection with the bottom ITO electrode and top Ag electrode with different pixel areas. Direct contact of RF probe with the surface of ETL (without Ag electrode) leads to a working device with a small area (<10×10 μm). b, 3D plot showing the normalized response versus time for different pixel sizes. Y-axis is the diameter of the pixel in μm. c, comparison of PbSn response time (with direct probe contact) with commercialized 2.0 GHz silicon and 5.0 GHz GaAs photodetector. See Extended Data Fig. 5c and Table 1 for detailed characteristics of the shown commercial PD.

Figure 5

Time-of-flight measurements. a, Schematic of ToF measurement. Michelson interferometer configuration is used to trigger the oscilloscope and remove jitter of the fs laser. b, The response of PbSn PD at the indicated position of the moving mirror. The response of the InGaAs detector is shown as a reference (fixed position). c, Contour plot of data shown in panel A vs. the travel distance of light with respect to the reference. The slope of the line determines the measured speed of light. d, Graph showing the response when the mirror has moved by 0.79 mm. The inset shows a magnification near the peak of the response. e, The transformation function of the response shown in panel D. Indicated points at zero represent the peak of the response. See Extended Data Fig. 8 for the details of the used transformed function.