

Double-Side Crystallization Tuning to Achieve over 1 μm Thick and Well-Aligned Block-Like Narrow-Bandgap Perovskites for High-Efficiency Near-Infrared Photodetectors

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Solution-processed narrow-bandgap Sn–Pb perovskites have shown their potential in near-infrared (NIR) photodetection as a promising alternative to traditional silicon and inorganic compounds. To achieve efficient NIR photodetection, high-quality Sn–Pb perovskite thick films with well-packed, smooth, and pinhole/void-free features are highly desirable for boosting the spectral absorption. Understanding the crystallization kinetics and tuning the crystallization are fundamentally important to reach such high-quality thick Sn–Pb perovskite films, and have been limitedly explored. Herein, an approach of double-side crystallization tuning through low-temperature space-restricted annealing in methylammonium-free Sn–Pb perovskite films with over 1 μm thickness is proposed. More specifically, through simultaneously retarding the crystallization in the top of precursor films and promoting the crystal growth of the bottom of precursor films, high-quality and block-like thick $\text{FA}_{0.85}\text{Cs}_{0.15}\text{Sn}_{0.5}\text{Pb}_{0.5}\text{I}_3$ perovskite films with improved crystallinity, preferred out-of-plane orientation, and reduced trap density are achieved. Finally, photovoltaic-mode Sn–Pb perovskite NIR photodetectors show a high external quantum efficiency of $\approx 80\%$ at 760–900 nm, a recorded responsivity of 0.53 A W^{-1} , and a high specific detectivity of 6×10^{12} Jones at 940 nm. This study offers the fundamental understanding of the crystallization kinetics of thick perovskite films and paves the way for perovskite-based emerging NIR photodetection and imaging applications.

1. Introduction

Photodetectors (PDs), converting optical signals to electrical signals, have gained widespread attention. Specifically, near-infrared (NIR) PDs sensing the 780–1000 nm region have extensive applications in a number of fields including autonomous vehicles, food safety, functional NIR spectroscopy, biometric identification, smart agriculture, machine vision, as well as biomedical imaging.^[1–3] For example, NIR imaging can be used to investigate drawings beneath ancient oil painting,^[4] to make biochemical and pharmacological sensing,^[5] and to inspect bruises in the agri-food industry.^[6] Currently, commercialized NIR PDs mainly employ inorganic photoactive semiconductors such as crystalline silicon, germanium, and III–V compound semiconductors.^[7,8] These traditional materials are mechanically inflexible and fragile. They also require costly, high carbon-footprint, and complicated processes including ultrahigh vacuum growth and fabrication procedures, high temperature annealing, and numerous skill-demanding processing steps.^[9] There-

fore, alternative narrow-bandgap semiconductors with facile fabrication processability are highly desirable.

In recent years, solution-processed thin films are much more welcome compared to traditional vapor-assisted deposition methods. The low-cost method greatly reduces the energy consumption and promotes their applications in flexible electronics. Many materials have been produced by various solution chemical methods, such as inorganic,^[10–13] organic,^[14,15] and hybrid materials.^[16,17] Among emerging materials, hybrid organic–inorganic halide perovskites (ABX_3 ; A = methylammonium [MA], formamidinium [FA], rubidium, and cesium [Cs]; B = Pb, Sn; X = Cl, Br, I) present great potentials as photoactive materials of PDs.^[18–21] They not only can be easily prepared by the simple low-temperature solution-based method, but also harbor remarkable optoelectronic properties, especially the outstanding absorption coefficient with over an order of magnitude higher than that of silicon.^[22,23] However, typical lead-based perovskite PDs are intrinsically limited by the band-edge

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wavelength of ≈ 800 nm and hinder their applications in NIR bandwidth. To extend the spectral coverage to longer wavelength region, there are some works combining lead-based perovskites with several narrow-bandgap materials such as polymers and quantum dots, but the weak optical absorption and inefficient charge extraction result in a relatively low NIR efficiency.^[24–27] Notably, partial incorporation of Sn into lead-based perovskites is a direct and effective way to achieve the NIR spectral response.^[28,29] From literatures, the bandgap of $\text{MASn}_x\text{Pb}_{1-x}\text{I}_3$ perovskites can be tuned from 1.5 eV to the lowest value of 1.17 eV, making them possible for the NIR photodetection.^[30,31] Typically, most reported Sn–Pb perovskite NIR PDs consist a certain amount of MA components which are thermally unstable and easy to chemically decompose.^[29,32] It greatly increases the probability of defect formations, further enlarges dark current and reduces photocurrent, and thus result in the severe device degradation during the long-term operation of PDs.

MA-free Sn–Pb perovskites with the mixed FA–Cs cations show the better light and thermal stability in photovoltaic applications compared with MA-based counterparts.^[33,34] Therefore, it can be expected that FA–Cs-based narrow-bandgap Sn–Pb perovskites are the promising candidate for achieving better-performance NIR photodetectors. Until now, Sn–Pb perovskite NIR PDs with FA–Cs mixed cations have not been reported yet. Moreover, to reach efficient NIR photodetection, thick Sn–Pb perovskite films (over 1 μm) are the key prerequisite for achieving sufficient absorption and thus high external quantum efficiency (EQE) in the NIR region. In general, solvent engineering and sequential annealing are employed to grow ≈ 500 nm thick FA–Cs-based perovskite films.^[34,35] However, growing over 1 μm thickness FA–Cs-based high-quality perovskite films is still a grand challenge. Consequently, understanding the underlying crystallization mechanism of thick Sn–Pb perovskites and producing dense, smooth, and void/pinhole-free thick films (over 1 μm) are critical and highly desirable to develop high-efficiency narrow-bandgap Sn–Pb perovskite NIR PDs.

In this study, we first propose and demonstrate an approach of double-side crystallization tuning (DSCT) through the low-temperature space-restricted annealing process to successfully grow high-quality FA–Cs-based Sn–Pb thick perovskite films. The process of space-restricted annealing can preserve the escaped residual solvents and formulate the solvent atmosphere for growing thick precursor films, which retard the crystallization of the top of precursor films. Simultaneously, low-temperature annealing promotes the crystal growth of the bottom of precursor films, which accompanies the release of residual solvents facilitated by the enriched solvent atmosphere. Finally, through the controllable crystallization manner, we achieve smooth, pinhole-free, and void-free FA–Cs Sn–Pb perovskite thick films with improved crystallinity, preferred out-of-plane stacking patterns, and low trap density. The high-quality thick perovskite films contribute to reducing the dark current and enhancing the photocurrent of PDs. Ultimately, we achieve photovoltaic-mode perovskite NIR PDs with a high and flat EQE of $\approx 80\%$ at 760–900 nm, a remarkable responsivity (R) of 0.53 A W^{-1} and a high specific detectivity (D^*) of 6×10^{12} Jones at 940 nm. Overall, this work offers the fundamental understanding of

the crystallization kinetics of thick perovskite films, high-quality MA-free Sn–Pb perovskite thick films as well as high performance NIR PDs. The work therefore advances new cost-effective alternatives from traditional inorganic semiconductors.

2. Results and Discussion

2.1. Over 1 μm Thick Films for Enhanced Near-Infrared Absorption

To demonstrate the film thickness of Sn–Pb perovskites in a control manner and its contribution to the absorption in NIR region, we first theoretically and experimentally study three film thickness (i.e., 0.5, 0.7, and 1.1 μm , respectively) on the device absorption evolution. The architecture of narrow-bandgap Sn–Pb perovskite NIR PDs is designed as indium tin oxide (ITO)/poly(3,4-ethylenedioxythiophene)–poly(styrenesulfonate) (PEDOT:PSS)/Sn–Pb narrow-bandgap perovskites/phenyl- C_{61} -butyric acid methyl ester (PC_{61}BM)/zirconium acetylacetonate (ZrAcac)/Ag. Clearly, as shown in Figure 1a, the simulated NIR device absorption shows the significant enhancement with the increase of perovskite thickness. On the basis of 500 nm thick films, the NIR absorption enhancement ratios (i.e., the absorption of the thick films over that of 500 nm thick films) achieve 1.2 and 1.6 for 700 and 1100 nm thick perovskite films at the wavelength of 940 nm, respectively (Figure S1, Supporting Information). The enhanced device absorption can be ascribed to the increased thickness of Sn–Pb perovskite films and weak device interference effects.^[36] Experimentally, the absorption of Sn–Pb perovskite PDs in the NIR region also presents the remarkable increment by about 1.1 and 1.5 times at the 940 nm wavelength when perovskite film thickness raises from 500 to 700 and to 1100 nm, respectively (Figure 1b and Figure S1, Supporting Information). Overall, the experimental absorption enhancement is consistent with the theoretical result. The less obvious peaks in the experimental results result from the weaker cavity effect compared with that in the simulation. It should be noted that the reflectance of ITO substrates contributes to $\approx 15\%$ device optical loss in the NIR region (Figure S2, Supporting Information). This implies that Sn–Pb perovskite films with 1100 nm thickness can harvest near 95% incident NIR light over 760 to 940 nm. Hence, we conclude that Sn–Pb perovskite films with 1100 nm thickness have the high and flat NIR device absorption covering 760–940 nm (shown in Figure 1a,b), which are prerequisite for achieving high-efficiency narrow-bandgap perovskite NIR PDs.

2.2. Crystallization Tuning toward High-Quality Sn–Pb Perovskite Thick Films

Sn–Pb perovskite thick films are prepared by the revised anti-solvent washing. In order to obtain high-quality thick films, three different annealing methods (depicted in Figure S3, Supporting Information) are introduced to treat the post-washed Sn–Pb perovskite precursor films to tune the film crystallization. The three different annealing methods contain direct

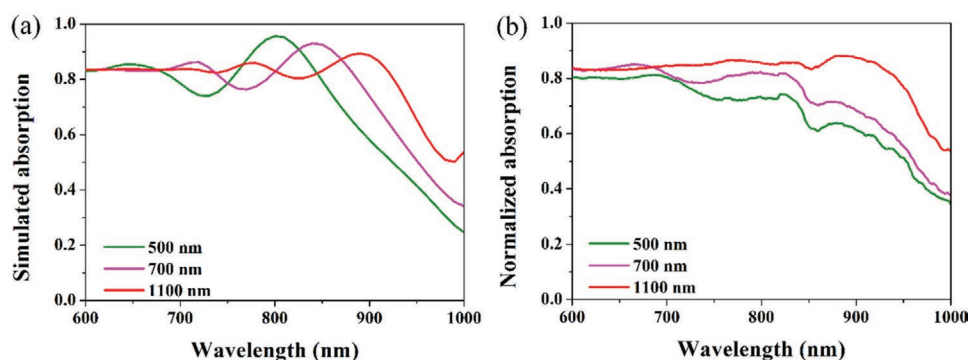


Figure 1. a) Theoretical and b) experimental absorption spectra of Sn–Pb perovskite PDs with different perovskite thicknesses of 500, 700, and 1100 nm, respectively.

high-temperature annealing (termed Method 1), low-temperature free-space annealing (termed Method 2), and low-temperature space-restricted annealing (called DSCT). The detailed information for perovskite film preparation is described in the Experimental Section.

We first employ a scanning electron microscope (SEM), a cross-sectional SEM, and an atomic force microscope (AFM) to investigate different crystallization methods on the film morphologies. It can be clearly seen from **Figure 2a,b** that Sn–Pb perovskite thick films prepared by Method 1 and Method 2 both manifestly show pinholes and cracks around grain boundaries, probably resulting from the volatilization of excess solvents from thick precursor films during the high-temperature annealing treatment (Figure S3, Supporting Information). Promisingly, thick films prepared by DSCT exhibit dense and crack-free morphologies, as well as present larger grain sizes (Figure 2c and Figure S4, Supporting Information), which could potentially suppress the pinhole- and crack-induced leakage current. The significantly morphological differences can be

found in the cross-sectional images of Figure 2d–f. Notably, thick films produced by Method 1 and Method 2 show large voids located at the surface of ITO substrates (i.e., the bottom of perovskite films). Besides, the films produced by Method 2 achieve the decreased void size compared with films by Method 1, which indicates that more amount of residual solvents volatilize in Method 2 and thus leave relatively small-size voids after high-temperature annealing treats precursor films. Surprisingly, DSCT growth provides void-free and compact thick films, which could avoid detrimental current leakage caused by voids, benefiting efficient photodetection.^[32,37]

High surface roughness of thick active layers could potentially increase non-radiative recombination and thus increase dark current as well as undesirable noise current of PDs. We found that thick Sn–Pb perovskite films prepared by Method 1 and Method 2 show the large root mean square (r.m.s.) roughness of 74.7 and 60.5 nm (Figures 2g,h), respectively. Distinctively, DSCT-grown thick films shown in Figure 2i have the r.m.s. roughness of 29.6 nm, less than half of that of films

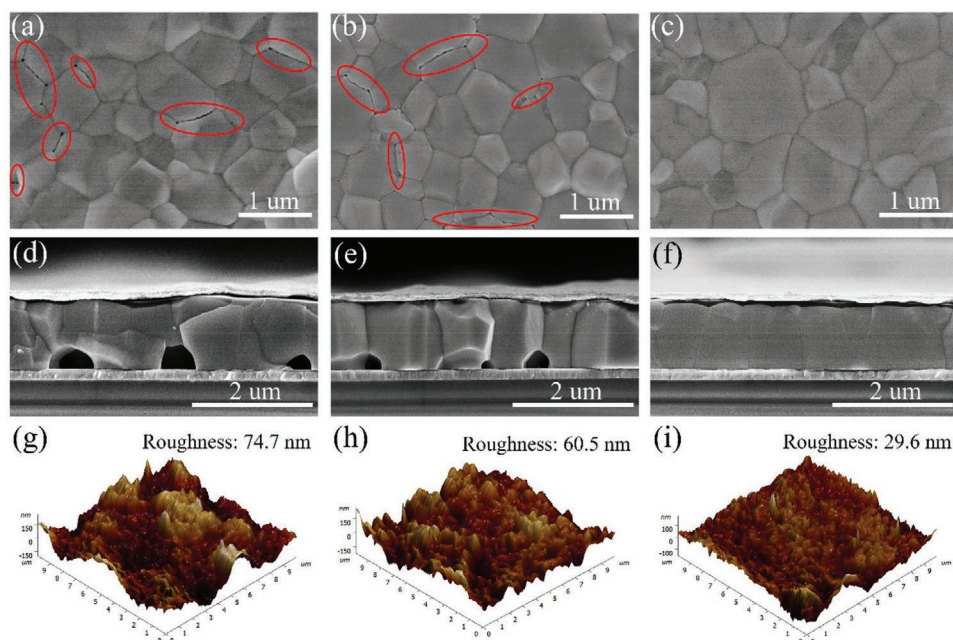


Figure 2. a–c) SEM images, d–f) cross-sectional SEM images, and g–i) 3D AFM images of thick $\text{FA}_{0.85}\text{Cs}_{0.15}\text{Sn}_{0.5}\text{Pb}_{0.5}\text{I}_3$ perovskite films prepared by Method 1, Method 2, and DSCT, respectively.

prepared by Method 1 and Method 2. Therefore, we can conclude that thick Sn–Pb perovskite films produced by DSCT achieve dense, compact, pinhole-free, and void-free morphologies, and low r.m.s. roughness, which beneficially contribute to the reduced dark current of PDs.

We attempt to explain the underlying crystallization mechanism of DSCT which facilitates high-quality film formation and thus beneficially contributes to the low dark current as discussed later. Notably, we find that Sn–Pb perovskite precursor films could achieve spontaneous nucleation and growth at room temperature, probably owing to the nature of Sn-based complexes with the strong I–Sn ionic bonding between MAI and tin iodide (SnI_2).^[37] Interestingly, FA–Cs cation-based precursor films also show room-temperature spontaneous nucleation and growth, and achieve polycrystalline films (Figure S5, Supporting Information). The room-temperature spontaneous crystallization will affect the process of thick film growth. Different from widely used Method 1 employed to treat thin precursor films, thick precursor films after freshly treated by antisolvent washing (Figure 3, Process i) might have different crystallization phases between the top surface and the bottom surface. The top region of thick precursor films experiences the direct antisolvent washing and thus have the lower amount of residual solvents which will result to the higher supersaturated precursors, favoring room-temperature spontaneous crystallization and thus facilitating the fast crystal growth. Distinctively, the bottom of thick precursor films might have more amount of residual solvents and thus harbor a concentration of precursors relatively lower than that on the top region, potentially impeding spontaneous crystallization. Therefore, the immediate high-temperature annealing will induce the vigorous crystallization happened on the top and thus cause the rough surface (Figure 2g). Meanwhile, the rapid volatilization of residual solvents potentially passes through grain boundaries of the top and thus induce pinholes and cracks around grains (Figure 2a).^[38] More importantly, the rapid removal of residual solvents leaves voids near the bottom of thick perovskite films (Figure 2d). All these features (i.e., rough surfaces, pinholes, cracks and voids) would induce detrimental shorting, poor carrier extraction, and large electron/hole non-radiative

recombination that reduce photocurrent and increase dark current.

In order to reduce the volatilization speed of residual solvents, instead of direct high-temperature annealing (i.e., Method 1), low-temperature free-space annealing (i.e., Method 2) was employed. The bottom of thick precursor films with pre-existed nuclei (Figure 3, Process ii) composed of soft complexes of organic components coordinated with inorganic ones prefer to consume dimethyl sulfoxide (DMSO)-based intermediates and slowly grow to Sn–Pb perovskite crystal grains (Figure S4, Supporting Information).^[37,39,40] Meanwhile, although the top of precursor films prefers to quickly complete the crystal growth, residual solvents released from the bulk of thick Sn–Pb perovskite precursors will repeatedly dissolve the top nanocrystals or nuclei until residual solvents are completely removed. The repeated crystallization and dissolution happened at the top of thick precursor films (Figure 3, Process iii) would result in the small-size grains (Figure S4, Supporting Information) and rough surfaces. Given the limited crystallization time (6 min, as shown in Figure 3), related lower amount of residual solvents (compared with Method 1) will lead to smaller voids and reduced pinholes and cracks, evidenced by Figure 2b,e. Therefore, it can be concluded that Method 2 (even though improve from Method 1) is still not a suitable method for growing dense, smooth, pinhole-free, and void-free thick Sn–Pb perovskite films.

Importantly, we first propose and demonstrate the low-temperature space-restricted annealing to effectively tune crystallization of the top and bottom of thick perovskite precursor films (i.e., DSCT), and thus successfully grow high-quality thick Sn–Pb perovskite films (Figure 2c,f). DSCT can preserve the escaped residual solvents and offer the solvent atmosphere to form the thick precursor films, which significantly retard the crystallization of the top of precursor films (Figure 3, Process iv). The solvent atmosphere can provide a pathway that facilitates the release of residual solvents from the bulk of thick Sn–Pb perovskite precursor films, and at the same time, promote the growth of larger grain size crystals. Therefore, as shown in Figure S4, Supporting Information, the precursor films show increased grain sizes for the top (compared with precursor films by Method 2) and even achieve single grains between the

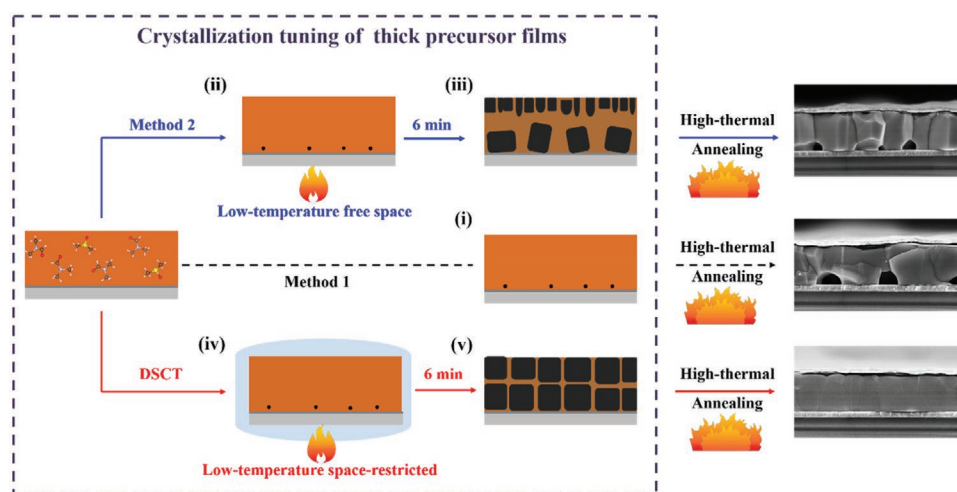


Figure 3. The schematic diagram of thick film formation of Sn–Pb perovskites prepared by Method 1, Method 2, and DSCT, respectively.

top and the bottom. Ultimately, the optimized DSCT-prepared precursor films (with the annealing time of 6 min shown in Figure 3 Process v) were further treated by the high-temperature annealing, which enables small grains to coalesce with each other to form thick film with large grain sizes and well-aligned block-like crystals (Figure 2c,f). We can thus conclude that DSCT is an effective method for successfully growing high-quality and well-aligned block-like Sn–Pb perovskite thick crystalline films, exhibiting smooth, pinhole-free, and void-free properties, which are beneficial for efficient PDs.

2.3. Crystallinity, Orientation, and Trap Density of Thick Sn–Pb Perovskites

To understand the film crystallinity and orientation, X-ray diffraction (XRD) patterns of Sn–Pb perovskite films prepared by Method 1, Method 2, and DSCT are investigated (shown in Figure 4a). Manifestly, the Sn–Pb perovskite thick film produced by DSCT shows significantly enhanced intensities of reflection peaks compared with that of Method 1- and Method 2-formed films, especially for the (100) plane, indicating

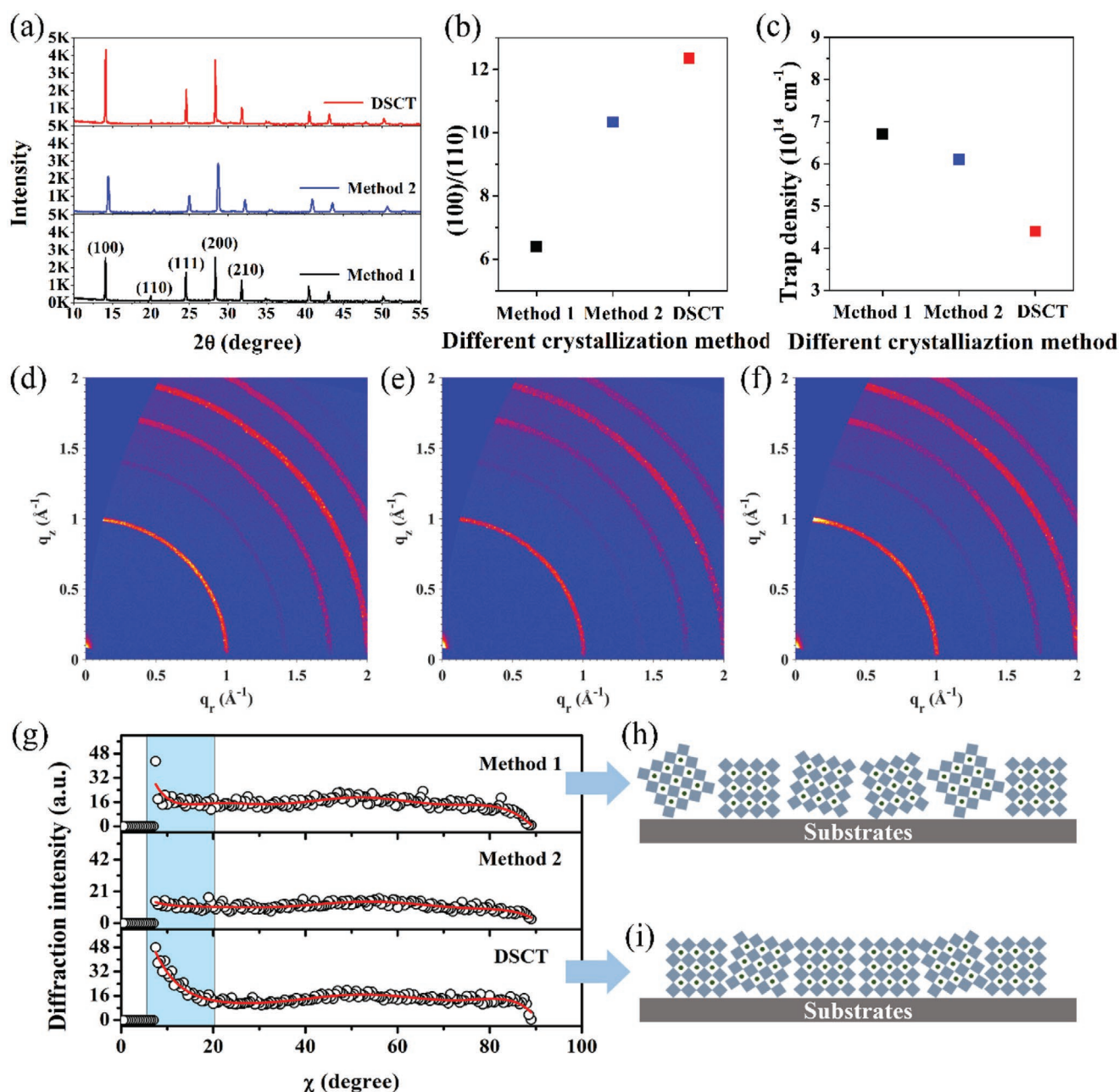


Figure 4. a) XRD patterns, b) (100)/(110) peak intensity ratios, and c) trap density of perovskite films against different crystallization methods. GIWAXS patterns of Sn–Pb perovskites formed by d) Method 1, e) Method 2, and f) DSCT. g) Integrated intensities of GIWAXS patterns along the ring at $q = 1.0 \text{ \AA}^{-1}$ of Sn–Pb perovskites formed by different crystallization methods. Schematic diagrams depict preferred stacking patterns of thick Sn–Pb perovskite films produced by h) Method 1 and i) DSCT.

increased crystallinity and phase purity.^[41] This improved crystallinity could favor charge transport in thick perovskite films, and finally help achieve the high photocurrent of NIR PDs.^[42] Meanwhile, Figure 4b clearly shows that the highest peak ratio of (100)/(110) is achieved by DSCT-prepared Sn–Pb perovskite films, suggesting the intensified preferred orientation. The findings indicate that our proposed DSCT can facilitate the (100) plane growth and simultaneously suppress the growth of other competing planes, that is, achieving Sn–Pb perovskite thick films with strengthened preferred orientation and enhanced crystallinity.

Moreover, grazing incidence wide-angle X-ray scattering (GIWAXS) is used to gain deep insights on the preferred orientation evolution of Sn–Pb perovskite thick films (Figure S6, Supporting Information). Figure 4d–f depicts the GIWAXS patterns of different perovskite films produced by Method 1, Method 2, and DSCT. For the total momentum transfer q , q_r is the in-plane component (i.e., parallel to the substrate plane) and q_z is the out-of-plane component (i.e., perpendicular to the substrate plane). The diffraction pattern of perovskite films produced by Method 1 and Method 2 (Figure 4d,e) along $q = 1.0 \text{ \AA}^{-1}$ (corresponding to the (100) lattice plane of the Sn–Pb perovskites) exhibit isotropic intensity distribution, indicating the random orientation of (100) planes of resultant Sn–Pb nanocrystals. In contrast, the diffraction pattern of optimized DSCT-prepared perovskite film (Figure 4f) shows significantly enhanced diffraction intensity along the q_z axis, suggesting the preferred orientation of (100) plane of resultant Sn–Pb nanocrystals. Consequently, we plot the intensity profile of GIWAXS patterns along the (100) ring at $q = 1.0 \text{ \AA}^{-1}$ versus the polar angle (χ) with respect to the q_z axis. The missing data (i.e., the wedge in Figure 4d–f) from 0° to 7° in Figure 4g originates from the grazing incidence geometry.^[43] As shown in Figure 4g, compared with Sn–Pb thick perovskite films produced by Method 1 and Method 2 with the relatively flat diffraction intensity across the polar angle from 7° to $\approx 85^\circ$, DSCT-prepared perovskite thick films present the unique intensity enhancement along the q_z direction, indicating that the preferred stacking patterns of nanocrystals are along the out-of-plane direction.

To intuitively show the facet orientation, the schematics of preferred stacking patterns of Sn–Pb thick perovskites are shown in Figures 4h (Method 1) and 4i (DSCT). Due to the rapid volatilization of residual solvents and the abrupt crystallization in high-temperature annealing-treated Sn–Pb perovskite precursor films, the uncontrollable crystallization in Method 1 would lead to relatively random stacking patterns, as shown in Figure 4h. The random stacking patterns can be experimentally confirmed in Figure 2d. Although the volatilization speed of residual solvents is reduced and relatively slow crystallization is introduced in Method 2, the repeated crystallization and dissolution happened at the top of thick precursor films would also result in random stacking patterns of resultant perovskite films (Figure 2e). Distinctively, the proposed DSCT could provide more controllable crystallization in the space-restricted residual solvent atmosphere through the formation of solvent-coordinated intermediate phases (e.g., FAI–PbI₂–DMSO, FAI–PbI₂–DMF, and SnI₂–DMSO).^[44–46] Nuclei in thick precursor films would gradually consume these solvent-based intermediate phases and thus grow into high-quality Sn–Pb thick perovskite films

(Figure 2c,f). More importantly, DSCT-produced perovskite films also achieve preferred stacking patterns along the out-of-plane direction (Figure 4i), beneficially contributing to the high mobility, the low trap density, and efficient photocurrent extraction.^[47]

We further fabricated hole-only devices with the structure of ITO/PEDOT:PSS/perovskites/MoO₃/Ag to study the trap density of Sn–Pb perovskite films. Derived by the dark current density (J)–voltage (V) curves of hole-only devices (Figure S7, Supporting Information), the values of trap-filled limited voltages (V_{TFL}) can be obtained. The trap density can then be determined from V_{TFL} according to the equation of $V_{\text{TFL}} = n_t q L / 2 \epsilon \epsilon_0$, where n_t is the trap density, q is the elementary charge, L is the thickness of Sn–Pb perovskite films, ϵ is the relative dielectric constant, and ϵ_0 is the vacuum permittivity. The trap density of three different Sn–Pb perovskite films are summarized in Figure 4c. V_{TFL} values of perovskite devices based on Method 1 and Method 2 are 0.23 and 0.21 V, corresponding to a trap density of 6.7×10^{14} and $6.1 \times 10^{14} \text{ cm}^{-3}$, respectively. It is found that the V_{TFL} value of DSCT-based perovskite devices substantially decreases to 0.15 V, corresponding to the lowest trap density of $4.4 \times 10^{14} \text{ cm}^{-3}$. Clearly, comparing with Method 1 and Method 2, DSCT can effectively favor the formation of Sn–Pb perovskite thick films with lower trap densities, which greatly contribute to the lower dark current and noise level for Sn–Pb perovskite NIR PDs.^[48]

2.4. Performances of Optimized Sn–Pb Perovskite Near-Infrared Photodetectors

Since we have studied the underlying crystallization mechanism of the three different methods (i.e., Method 1, Method 2, and DSCT) and their effects on film morphologies, crystallinity, orientation, and trap densities, we further investigate their influence on photocurrent and dark current by J – V measurements and EQE tests. As shown in Figure 5a, DSCT-based Sn–Pb perovskite NIR PDs simultaneously achieve decreased dark current and enhanced photocurrent. Specifically, compared with NIR PDs using perovskite thick films prepared by Method 1 and Method 2, DSCT-based NIR PDs enable the photocurrent density up to 31.5 mA cm^{-2} in the photovoltaic mode. This implies the efficient charge extraction in such thick Sn–Pb perovskite films. The high photocurrent should be resulted from the improved crystallinity (Figure 4a), strengthened preferred orientation (Figure 4b,d–f), and low trap density (Figure 4c) of dense, smooth, and pinhole-free Sn–Pb perovskite thick films (Figure 2c,f). Meanwhile, the dark current of DSCT-based NIR PDs is about one order of magnitude lower than that of the two methods and at a value as low as $2.8 \times 10^{-4} \text{ mA cm}^{-2}$ at -0.4 V . The suppressed dark current is potentially originated from the reduction of charge recombination, which can be confirmed by the decreased saturation current density of perovskite PDs (Figure S8, Supporting Information).^[49,50] EQE spectra of PDs are measured in the photovoltaic mode, as shown in Figure 5b. Notably, due to DSCT-produced high-quality thick Sn–Pb perovskite films, PDs can efficiently operate as self-powered devices. EQE values of Sn–Pb perovskite PDs prepared by DSCT are significantly increased in the NIR region, reaching

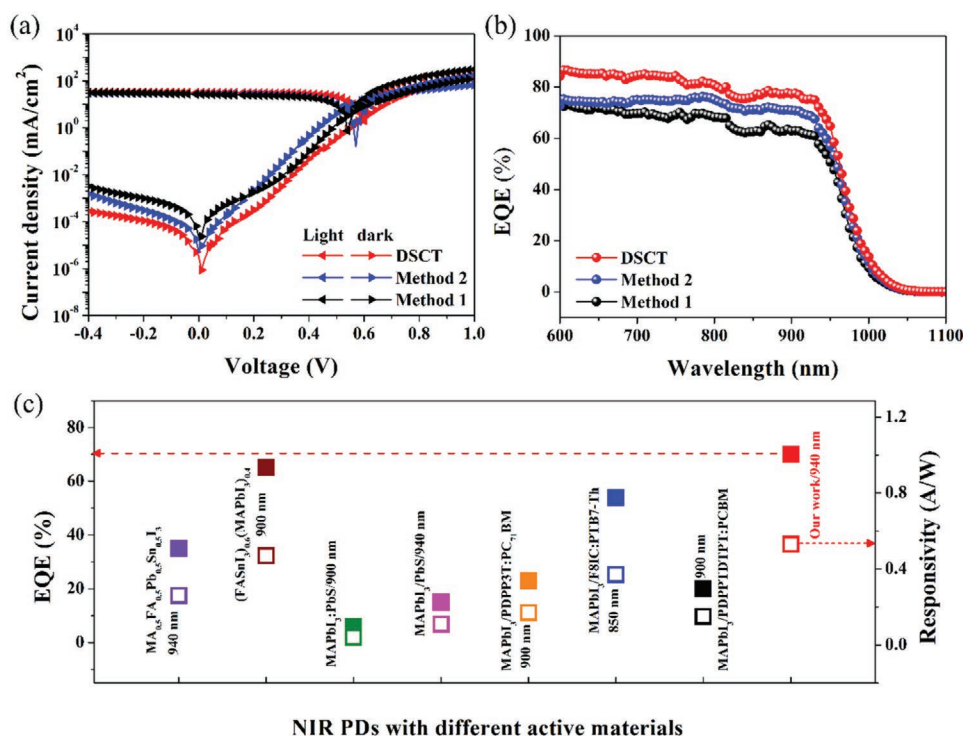


Figure 5. a) *J*–*V* curves of NIR PDs under dark and light irradiation, b) the EQE spectra of Sn–Pb perovskite PDs in the photovoltaic mode. c) EQE and responsivity values of NIR PDs based on different active materials.

≈80% from 760–900 nm, and a desirable value of 70% at 940 nm wavelength. It should be pointed out that the high EQE value at 940 nm is considerably higher than that of commercial silicon-based image sensors (less than 10%). These results show the convincing potential of the Sn–Pb perovskite PDs for the imaging applications.^[51] Moreover, the EQE value of optimized Sn–Pb perovskite PDs in the NIR region is higher than that of other types of perovskite-based PD including MA-based Sn–Pb perovskite PDs,^[29,32] hybrid perovskite:PbS quantum dot PDs,^[27,52] and perovskite/organic bulk heterojunction PDs.^[24,53,54] The detailed comparison is shown in Figure 5c. The high NIR EQE further suggests the efficient charge carrier collection inside NIR PDs prepared by DSCT.

We have also made further exploration on other key figures of merit of the optimized Sn–Pb perovskite NIR PDs, including *R*, noise current, detectivity, linear dynamic range (LDR), and transient photocurrent response. *R* is the ratio of photocurrent to the incident light intensity, and it is usually directly related to EQE values as presented by the equation of $R = EQE \cdot e/h\nu$, where *e*, *h*, and *ν* are the elementary charge, Planck's constant, and frequency of optical signal, respectively. As shown in Figure 6a, the optimized Sn–Pb perovskite PDs present the wide NIR response from 760–1000 nm, and obtain a high responsivity of 0.53 A W^{−1} at 940 nm, which is largely superior to that of perovskite/narrow-bandgap polymers or perovskite/quantum dots-based NIR PDs.^[24,27]

Figure 6b depicts the noise current of optimized Sn–Pb perovskite NIR PDs. Generally, noise current comprises thermal noise, shot noise, and flicker noise.^[32] Intriguingly, the noise current of optimized Sn–Pb perovskite NIR PDs is as low

as 2.54×10^{-14} A Hz^{−1/2} and is almost frequency independent, which indicates flicker noise is negligible and the noise current is dominated by white noise. The largely decreased dark current of optimized PDs finally leads to a low shot noise of 4.73×10^{-15} A Hz^{−1/2} following the equation $i_s = \sqrt{2qI_d\Delta f}$, where *I_d* is the dark current and Δf is the response bandwidth. Meanwhile, the thermal noise *i_t* is calculated to be 1.6×10^{-14} A Hz^{−1/2} given by $(4kT\Delta f/R)^{1/2}$, where *k* is Boltzmann's constant, *T* is temperature, and *R* is the shunt resistance of PDs. Thus, the total white noise current is 1.67×10^{-14} A Hz^{−1/2} by the equation of $i_w = \sqrt{i_s^2 + i_t^2}$. The measured value of noise current match well the theoretical white noise. Additionally, noise equivalent power (NEP) exhibits the minimum incident optical power that PDs can distinguish from noise current, calculated following the equation $NEP = I_{noise}/R$, where *I_{noise}* is the noise current. Figure S9, Supporting Information, shows that DSCT-produced Sn–Pb perovskite NIR PDs can achieve a NEP as low as 4.79×10^{-14} W Hz^{−1/2} at 940 nm, which is lower than inorganic, perovskite/quantum dots- and organic semiconductor-based NIR PDs.^[55–57]

*D** is one of the most critical parameters for PDs. It can be obtained by the following equation

$$D^* = \frac{R\sqrt{A\Delta f}}{I_{noise}} = \frac{\sqrt{A\Delta f}}{NEP} \quad (1)$$

where *A* is the detection area of PDs. According to this equation, enhanced responsivity and decreased noise current are intuitive elements for improving the detectivity of Sn–Pb perovskite NIR PDs. Apparently, as shown in Figure 6c, the optimized Sn–Pb

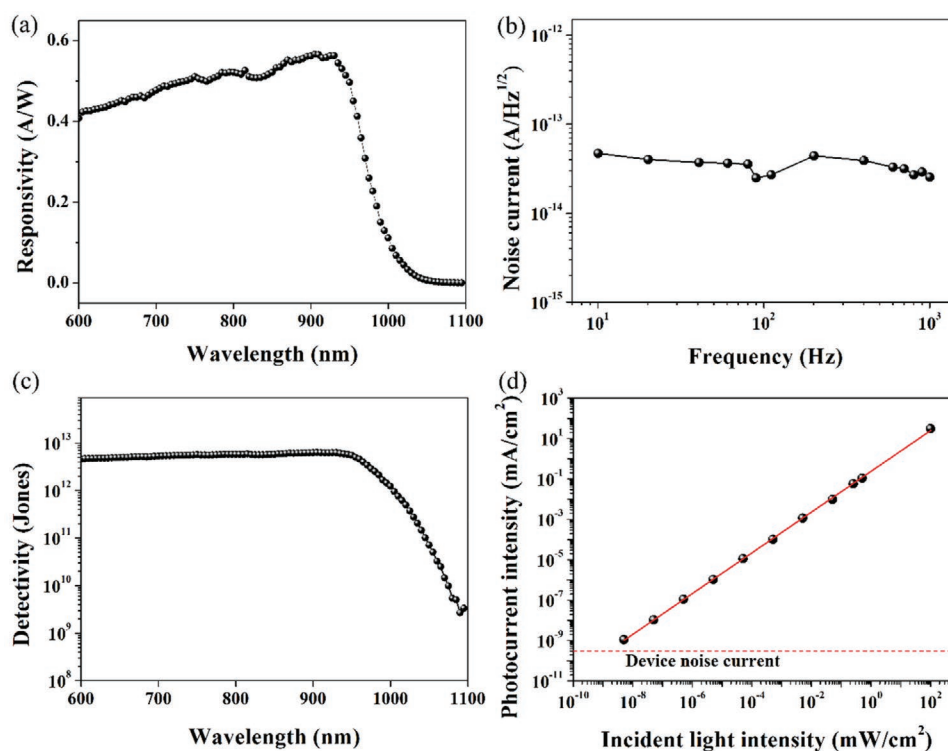


Figure 6. a) Responsivity, b) noise current versus signal frequency, c) specific detectivity as a function of spectral wavelengths, and d) the linear dynamic range plot of optimized Sn–Pb perovskite NIR PDs.

perovskite NIR PDs achieve a high D^* exceeding 10^{12} Jones in the NIR region from 760–1000 nm, and reach 6×10^{12} Jones at 940 nm. The high specific detectivity of optimized Sn–Pb perovskite NIR PDs largely suppress commercial inorganic PDs, which show the great potential of the Sn–Pb perovskite for future NIR detection applications.^[8]

LDR is the region where photocurrent has a linear relationship with different incident light intensities. It can be calculated by the equation $LDR = 10 \times \log(P_{\max}/P_{\min})$, where $P_{\max}$ and $P_{\min}$ are the maximum and minimum incident light intensity limits deviated from the linearity. The LDR is measured through changing various light intensities of the monochromatic light of 940 nm. For the optimized Sn–Pb perovskite NIR PDs, the minimum incident light intensity, $P_{\min}$, that can be detected is 5.08 pW cm^{-2} (Figure 6d), which is limited by the device noise current. Notably, the lowest linearly detectable intensity of DSCT-based perovskite NIR PDs is lower than that of hybrid perovskite/organic-, organic semiconductor heterojunction-, and inorganic quantum dots-based PDs, and is even almost two orders of magnitude lower than that of perovskite/quantum dots-based NIR PDs.^[52,54,58,59] The maximum linearly detectable intensity is limited by the saturation current when the incident light intensity reaches a certain level, and then photocurrent cannot be efficiently extracted due to the space charge buildup.^[60] In our case, the measured maximum incident light intensity $P_{\max}$ is 100 mW cm^{-2} . Hence, optimized Sn–Pb perovskite NIR PDs can achieve the high LDR of $\approx 103 \text{ dB}$, which is greater than most lead perovskite/polymer- and lead perovskite/PbS-based NIR PDs and comparable with MA-based Sn–Pb perovskite NIR PDs.^[28,52,54]

The transient photocurrent response is conducted to estimate the response speed of optimized Sn–Pb perovskite NIR PDs by using a 532 nm 6 ps pulse laser. The ability to truthfully record an incident light signal turning on and off can be exhibited by the speed of rise and fall processes. The rise and fall time are defined as the time when transient photocurrent changes between 10% and 90% of the maximum photocurrent, as shown in the Figure S10, Supporting Information. The self-powered optimized PDs present the fast response speed with the rise time (t_{rise}) of 58.3 ns and the fall time (t_{fall}) of 0.86 μs , suggesting it can offer fast detection and imaging applications.^[61] This result indicates the efficient photocurrent extraction within DSCT-produced perovskite NIR PDs contributed by the high-quality Sn–Pb thick perovskite films.

3. Conclusion

We propose and demonstrate the DSCT via low-temperature space-restricted annealing to effectively optimize the perovskite crystallization at the top and bottom region of the thick precursor films, and ultimately realize the high-quality thick Sn–Pb perovskite films. The thick FA–Cs perovskite films are featured with smooth, pinhole-free, and void-free morphologies and show improved crystallinity with preferred out-of-plane stacking patterns, and decreased trap density. With these excellent features, the optimized self-powered FA–Cs Sn–Pb perovskite NIR PDs show several remarkable figures of merit including a high flat EQE of $\approx 80\%$ at 760–900 nm, a recorded responsivity of 0.53 A W^{-1} , a high specific detectivity

of 6×10^{12} Jones at 940 nm, a low NEP of $479 \text{ fW Hz}^{-1/2}$, and a fast fall time of $0.86 \mu\text{s}$. The work not only offers the fundamental understanding of the crystallization kinetics of thick perovskite films but also high-efficiency perovskite NIR PDs for the emerging NIR applications in autonomous vehicles, biometric identification, and biomedical imaging.

4. Experimental Section

Preparation of Sn–Pb Perovskite Precursor Solutions: 2 M and 1.4 M $\text{FA}_{0.85}\text{Cs}_{0.15}\text{Sn}_{0.5}\text{Pb}_{0.5}\text{I}_3$ precursor solutions were prepared by dissolving stoichiometric amounts of formamidinium iodide (FAI, GreatCell Solar Limited, 99.99%), cesium iodide (Sigma Aldrich, 99.999%), SnI_2 (Alfa Aesar, 99.999%), lead iodide (PbI_2 , TCI, 99.99%), and tin fluoride (Sigma Aldrich, 99%) into 1 mL mixed solution of *N,N*-dimethylformamide (DMF, Acros, 99.8%, extra dry) and DMSO (Acros, 99.7+%, extra dry) in the nitrogen (N_2) filled glove box. Before depositing, precursor solutions were shaken to totally dissolve, and then were filtered using $0.22 \mu\text{m}$ PTFE filters.

Formation of Sn–Pb Perovskite Films: Preparing Sn–Pb perovskite films with over $1 \mu\text{m}$ thickness by three different crystallization methods (i.e., Method 1, Method 2, and DSCT): First, for all these three methods, 2 M precursor solutions were spun at 2000 rpm and then were washed by $300 \mu\text{L}$ toluene at the 25th s. Then, antisolvent washed thick precursor films were treated by different processes according to Method 1, Method 2, and DSCT. Specifically, for Method 1, precursor films were directly annealed at 120°C for 5 min; for Method 2, before annealing at 120°C for 5 min, precursor films were first treated at 60°C for 6 min under a free space; for the proposed DSCT, precursor films were treated at 60°C for 6 min under a condition of the restricted space (i.e., determined by a 9 cm diameter Petri dish) and then annealed at 120°C for 5 min. In addition, preparing different thickness perovskite films: For 1100 nm thickness perovskite films, as described above, 2 M precursor solution was spun at 2000 rpm and then was washed by toluene; For 700 and 500 nm thickness perovskite films, 1.4 M precursor solutions were used and the spin-coating speeds were 2000 and 4000 rpm, respectively. Finally, perovskite precursor films with different thicknesses experience the same DSCT-based crystallization process.

Device Fabrication: Sn–Pb perovskite NIR PDs were fabricated with the structure of ITO/PEDOT:PSS/Sn–Pb perovskite films/ $\text{PC}_{61}\text{BM}/\text{ZrAcac}/\text{Ag}$. First, ITO-coated glass substrates were cleaned with detergent, deionized water, acetone, and ethanol, successively. After that, clean ITO substrates were dried by industrial nitrogen gas and sequentially exposed in the ultraviolet-induced ozone atmosphere for 24 min. Then, PEDOT:PSS (Clevios P VP Al 4083) solution was spin-coated in air at 4000 rpm for 30 s, followed by annealing at 140°C for 20 min. After transferring all the prepared samples into the N_2 -filled glove box, Sn–Pb perovskite active layers were deposited on PEDOT:PSS substrates with the revised antisolvent method. Subsequently, 20 mg mL^{-1} PC_{61}BM in chlorobenzene was spun on resultant perovskite films at 1200 rpm, and then 2 mg mL^{-1} ZrAcac in isopropanol was dynamically spin-coated at 3000 rpm. Finally, 140 nm Ag electrode was thermally deposited under a vacuum of 10^{-6} Torr. The active area of Sn–Pb perovskite PDs was 0.08 cm^2 .

Film Characterization: Perovskite top-view morphology and cross-sectional images were characterized by Hitachi S4800 field-emission SEM. Roughness was measured by NT-MDT AFM. XRD patterns were characterized by Bruker D2 Phaser, and GIWAXS measurement was carried out with a Xeuss 2.0 SAXS/WAX laboratory beamline using a Cu X-ray source (8.05 keV $1.54 \text{ \AA}$, incidence angle is 0.3°) and a Pilatus 3R 300K detector.

Device Characterization: Current density as a function of voltage for Sn–Pb perovskite NIR PDs was recorded by a Keithley 2635 source meter. Simulated AM1.5 sunlight was generated by an Abet Class AAB AM1.5G solar simulator. EQE measurement was carried out by a home-built system with a light source setup of 1000 W xenon arc lamp.

LDR was measured under different light intensities using ThorLabs metallic-coated neutral density filters. Facility-calibrated (Newport) Si photodetector was used to measure the intensity of monochromatic light. Noise current against different frequency was recorded with Stanford Research SR830 lock-in amplifier. The transient photocurrent response was measured with a 532 nm pulse laser and an Agilent MSO9404A digital oscilloscope.

Device Absorption Simulation: First, the authors measured the realistic refractive indexes from ellipsometry (VASE, J.A. Woollam Co., Inc.). Then, the theoretical absorption was obtained with an optical model to simulate the field distribution inside the Sn–Pb perovskite NIR PDs by using the realistic refractive indexes. The optical model was solved with Maxwell's equation using a finite-difference method.^[62] In order to analyze the absorption capacities of the PDs, the illumination intensity of different light wavelengths ranging from 600 to 1000 nm were assumed to be uniform for the normalized absorption spectra simulation.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords

low-temperature space-restricted crystallization, near-infrared photodetectors, Sn–Pb perovskites, thick perovskites

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