

Epitaxial Stabilization of Tetragonal Cesium Tin Iodide

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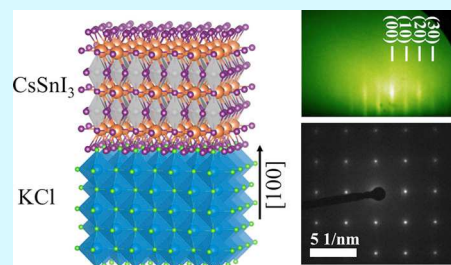
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Supporting Information

ABSTRACT: A full range of optoelectronic devices has been demonstrated incorporating hybrid organic–inorganic halide perovskites including high-performance photovoltaics, light emitting diodes, and lasers. Tin-based inorganic halide perovskites, such as CsSnX_3 ($X = \text{Cl, Br, I}$), have been studied as promising candidates that avoid toxic lead halide compositions. One of the main obstacles for improving the properties of all-inorganic perovskites and transitioning their use to high-end electronic applications is obtaining crystalline thin films with minimal crystal defects, despite their reputation for defect tolerance in photovoltaic applications. In this study, the single-domain epitaxial growth of cesium tin iodide (CsSnI_3) on closely lattice matched single-crystal potassium chloride (KCl) substrates is demonstrated. Using in situ real-time diffraction techniques, we find a new epitaxially-stabilized tetragonal phase at room temperature that expands the possibility for controlling electronic properties. We also exploit controllable epitaxy to grow multilayer two-dimensional quantum wells and demonstrate epitaxial films in a lateral photodetector architecture. This work provides insight into the phase control during halide perovskite epitaxy and expands the selection of epitaxially accessible materials from this exciting class of compounds.

KEYWORDS: halide perovskite, epitaxy, vapor-deposition, 2D quantum well, photodetector



INTRODUCTION

Halide perovskites have shown great potential for a wide range of applications in solar harvesting,^{1–4} light emission,^{5–8} lasing,^{9–12} quantum dots,^{13–17} water splitting,^{18–20} and thin-film electronics.^{21–29} Despite the incredibly fast development of their applications in energy conversion,³⁰ particularly with lead-based compositions, the main hindrances of structural defects,^{31,32} trap states,³³ toxicity of lead,^{34,35} and the instability of organic components^{35–39} remain a challenge. CsSnX_3 perovskites ($X = \text{Cl, Br, I}$) have been investigated as inorganic and lead-free alternatives.^{40–44} However, compared with lead halide perovskites, the crystalline thin-film fabrication of CsSnX_3 has been more challenging and has limited development in high-performance photovoltaics and optoelectronics due to a lower defect tolerance.

Another critical challenge for improving the optoelectronic performance of CsSnX_3 -based devices is controlling the phase during film growth. For cesium tin iodide (CsSnI_3), four different phases can form depending on the temperature including cubic ($B-\alpha$), tetragonal ($B-\beta$), orthorhombic (black, $B-\gamma$), and orthorhombic (yellow, Y) phases where only the orthorhombic (black) and orthorhombic (yellow) phases are stable at room temperature.^{45,46} These phases have different optical and electronic properties, which impact carrier transport. To date, most research on CsSnI_3 focuses on the orthorhombic (black, $B-\gamma$) phase as the absorber layer.⁴⁷ However, there has been little work on the cubic and

tetragonal phases since they are both unstable at room temperature.

Epitaxial growth has long been utilized to achieve the lowest defect densities and highest performance for applications in lasers, thin-film transistors, two-dimensional (2D) electron gases, sensors, and high-power devices. The development of inorganic materials such as III–V semiconductors has been extensively accelerated by epitaxial growth. Moreover, studies of epitaxial oxide perovskites have shown that unique properties can occur at the interfaces of different materials including superconductivity, ferroelectricity, and magnetism. These functional properties can be tuned by engineering the symmetries and degrees of freedom of correlated electrons at the interfaces of oxide perovskites, which is associated with the atomic arrangement at the interface.^{48–51} Thus, epitaxial growth provides precise interface control and correspondingly yields the potential for interesting new systems such as magnetic superconductors, noncentrosymmetric superconductors, and multiferroics.^{52–56} These successes have driven a new focus to control film quality, defect density, strain, and phases of new semiconducting materials that should be applicable to halide perovskites. Recently, the demonstration of controllable epitaxial growth of CsSnBr_3 on metal halide salts,⁵⁷ thick

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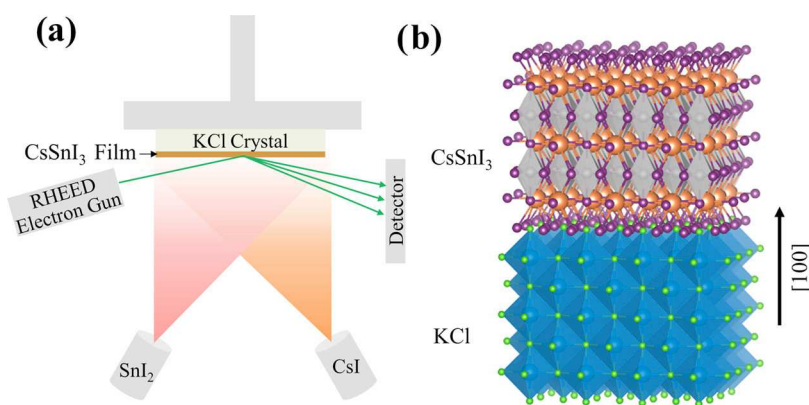


Figure 1. (A) Thin-film CsSnI_3 is grown epitaxially on a single crystalline $\text{KCl}(100)$ substrate with two precursors, CsI and SnI_2 (1:1) monitored by RHEED in situ and real time. (B) A schematic of the epitaxial structure of the CsSnI_3 film on $\text{KCl}(100)$ (Cs: orange; Sn: gray; I: purple; K: blue; Cl: light green).

quasiepitaxial growth of CsPbBr_3 ,⁵⁸ and epitaxial nanoplatelets of CsPbBr_3 on strontium titanate^{59,60} has confirmed the feasibility of vapor-phase epitaxial growth methods for this group of materials.

In this study, the room-temperature epitaxial growth of CsSnI_3 on single crystalline alkali halide salt substrate KCl is demonstrated. The substrate was chosen to closely match the high-temperature cubic phase lattice constants and maintain similar ionic bonding character of the film. However, we find that the epitaxial growths lead to a new stable tetragonal phase at room temperature that has a and b lattice constants similar to the high-temperature cubic phase. This “epitaxial stabilization” method provides an approach to stabilize a metastable phase. The impact of strain is explored by tuning substrate lattice constants via alloyed interlayer deposition. Exploiting the precise growth enabled by vapor-phase epitaxy, we also explore the quantum confinement effect in this material and determine a surprisingly small effective Bohr radius. Finally, epitaxial films of CsSnI_3 are integrated into a lateral photodetector application with good photoresponse. This work provides new insight into the stabilization of halide perovskite crystal phases and expands the selection of epitaxial halide perovskites.

RESULTS AND DISCUSSION

Epitaxial Growth and Structure Analysis. The epitaxial growth of CsSnI_3 films on single crystalline $\text{KCl}(100)$ substrates is achieved using reactive thermal deposition of CsI and SnI_2 with a molar ratio of 1:1, which was monitored in situ and real-time using reflection high-energy electron diffraction (RHEED) with ultralow currents (nanoampere range) to prevent charging and beam damage (Figure 1a). A schematic of the epitaxial growth is shown in Figure 1b. The freshly cleaved KCl substrate exhibits sharp streaky peaks along the $[100]$ direction along with Kikuchi lines indicative of the single crystalline (single domain) and thick nature of the KCl substrates. After growing one monolayer (ML) of CsSnI_3 , the pattern changes, and the KCl Kikuchi patterns disappear. A new set of streaky lines emerges overlapping with the (20) streaks of KCl , along with (10) streaks between the (20) streaks (Figure 2a). These additional streaks are expected as there is a structural change from the face-centered cubic substrate to the primitive cell of the halide perovskite film. These patterns are observed without any substrate rotation, indicating good lattice matching and alignment between the

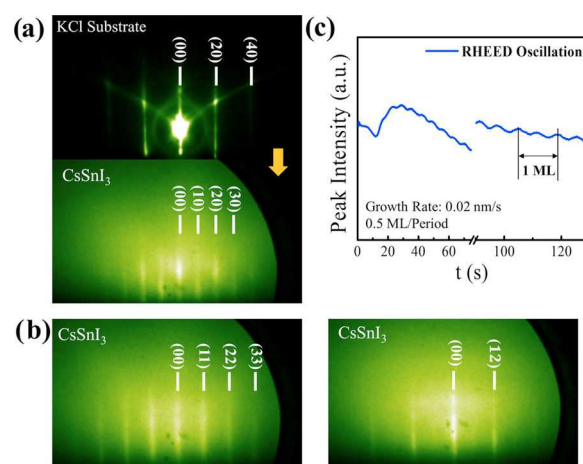


Figure 2. (A) RHEED pattern of the bare KCl substrate and 20 nm of CsSnI_3 . (B) Rotation-dependent RHEED patterns of the smooth CsSnI_3 epitaxial film. (C) RHEED oscillations monitored by capturing the peak intensity change of the central streak of the pattern as a function of time. The observation of 0.5 ML/period is consistent with the epitaxial growth of CsSnI_3 (note that the growth rate 0.02 nm/s is for the reacted film not the sources).

film and the substrate. The streaky RHEED patterns remain essentially unchanged up to and beyond thicknesses of ~ 20 nm. The streakiness of the pattern is an indication of a smooth crystalline layer, which is consistent with the morphology shown in the scanning electron microscope (SEM) (Figure S1a). To further understand the crystal structure of the CsSnI_3 epitaxial film, RHEED patterns were collected at various azimuthal angles (Figure 2b). The patterns vary as expected for a single crystal, indicating that single-domain growth is achieved across the KCl substrate. From the d -spacing obtained at various azimuthal angles, we obtained the lattice constant of the epitaxial film: $a = b = 0.622 \pm 0.007$ nm.

During the epitaxial growth, low source deposition rates (< 0.02 nm/s) are found to aid in the formation of smoother films and streakier patterns. If the sources are deposited with a much higher growth rate, spotty patterns quickly replace the streaky patterns from the KCl substrate, indicating that a rough crystalline film is formed (Figure S2b). The growth mode was also studied by monitoring the intensity of the RHEED patterns (Figure 2c). When using low source deposition rates, RHEED oscillations are observed indicating Frank–van der

Merwe (layer-by-layer) growth mode. Two full cycles of the oscillation are found to correspond to the growth of one ML (half of a complete unit cell) of the CsSnI_3 film as confirmed from ex situ thickness measurements (Figure 2c). This is similar to the observation for epitaxial CsSnBr_3 growth on NaCl .⁵⁷

Under certain growth conditions (e.g., high-rate growth), half-order RHEED streaks sometimes appear, as seen in Figure S3. This indicates the formation of surface reconstruction. In these cases, the half-order streaks fade as the film growth proceeded to higher thickness. Because these streaks are only observed under high growth rates, it is unlikely to be indicative of the underlying growth front mechanism. That is, the growth front does not typically proceed via a surface reconstruction.

Out-of-plane X-ray diffraction (XRD) data was collected to confirm the crystal structure of the epitaxial film (Figure 3a).

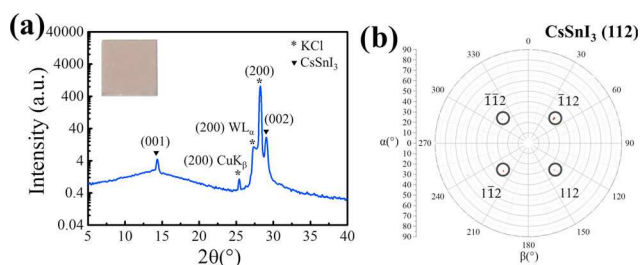


Figure 3. (A) Out-of-plane XRD scan of 40 nm of CsSnI_3 on the KCl substrate and photograph of the film on a 1 cm $\times$ 1 cm substrate. The KCl(200) peak is at 28.35° ($\text{Cu K}\beta$ and $\text{W L}\alpha$ peaks are seen at 25.50 and 27.42°), and the CsSnI_3 (001) and (002) peaks are at 14.46 and 29.16° . (B) The (112) pole figure scan of 40 nm of CsSnI_3 on KCl. α and β are the tilt angle and rotation angle, respectively, around the sample surface normal direction. Note that the (112) is not observable for KCl. Additional pole figures of both the film and substrate are provided in the Supporting Information.

The peaks observed at 14.46 and 29.16° are the (001) and (002) of the epitaxial phase, respectively, which gives a lattice constant $c = 0.612 \pm 0.002$ nm. Combined with the RHEED data, we determine that this is an epitaxial tetragonal (referred to as “epi-tetragonal”) phase ($a = b = 0.622 \pm 0.007$ nm, $c = 0.612 \pm 0.002$ nm) stabilized by lattice matching with the KCl substrate ($a = 0.629$ nm) that has a significantly different structure and atomic arrangement from the bulk high-temperature tetragonal phase.⁴⁵ The d spacings are well matched with the substrate in the early growth stage (within error) and remain nearly unchanged as the growth proceeds to higher thickness indicating that the growth is pseudomorphic. The (112), (021), and (211) pole figure scans of the film are

shown in Figures 3b and S4b–d. These were chosen as they are clearly distinguishable from any substrate peaks and are not allowed for KCl. The fixed diffraction angles for each pole figure scan are calculated from the lattice constant of the epi-tetragonal phase. The (112) and (021) pole figures show the expected fourfold symmetry, whereas the (211) scan shows the expected eightfold symmetry (see Figure S4e,f for the simulated pole figures for both KCl and epi-tetragonal CsSnI_3). The a/c ratio obtained from the transmission electron microscopy (TEM) high-resolution images of the epitaxial interface is 1.03, which clearly emphasizes the tetragonal nature of the structure and is close to 1.02 obtained from diffraction data (Figure 4). The TEM also clearly confirms the pseudomorphic nature of the film. To further verify the crystal structure, the film was removed from the substrate and folded to obtain a pseudopowder (textured powder) for synchrotron X-ray characterization. This data confirms that the epitaxial film is a new tetragonal phase, as shown in Figure S5. An obvious peak split is seen at 11.28 and 11.39° that corresponds to the (200) and (002) planes of the tetragonal phase. From the synchrotron X-ray data fitting (Figure S6), we obtain lattice constants of the epitaxial film of $a = b = 0.6240$ nm and $c = 0.6178$ nm, which are close to and consistent with the XRD and RHEED analysis. The slight difference from the substrate lattice is due to the temperature difference of the scan conditions. Extrapolating the lattice constant from room temperature to 100 K for comparison to the synchrotron data, the lattice constant of the cubic KCl substrate would be 0.625 ± 0.001 nm at 100 K, assuming a thermal expansion coefficient of $3.2 \times 10^{-5}/\text{K}$,⁶¹ which is within the error of the in-plane lattice constant measured with the synchrotron data ($a = b = 0.6240$ nm). This further confirms the pseudomorphic nature of the film and agrees with the findings from TEM.

When determining the crystal structure and phases of these compounds, it is important to consider the oxidation states. For example, Sn^{2+} and Sn^{4+} oxidation states have been observed in this class of materials, which leads to other analogues such as Cs_2SnI_6 (cubic, $a = 1.165$ nm⁶²). This phase is ruled out from the simulated diffraction patterns (Figure S7). Furthermore, we confirm the chemical state of Sn and the ratio of these three elements with X-ray photoelectron spectroscopy (XPS). The ratio matches the stoichiometry of CsSnI_3 , and the Sn is found to have a +2 valence state in the epitaxial film (Figure S8). We note that we do observe a phase transformation from CsSnI_3 to Cs_2SnI_6 when epitaxial films are exposed to air for more than 20 h (Figure S9a,b). This is consistent with other reports for the B- γ and Y phases of CsSnI_3 .⁶³ However, we do not observe this transformation for

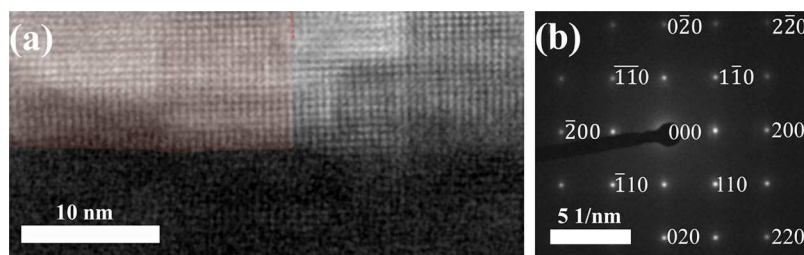


Figure 4. (A) Cross-sectional high-resolution TEM (HRTEM) image at the interface. The film is shaded in red on the left side of the image. Note a substrate step can be observed just to the bottom right of the shading. (B) Selected area electron diffraction (SAED) pattern of the film clearly indicating the tetragonal nature of the crystal structure.

films kept in a N_2 environment under dark conditions or under illumination (~ 1 sun) (Figure S9c–e).

Both the high-temperature tetragonal and cubic phases are unstable at room temperature.⁶⁴ Epitaxy has been commonly deployed to grow metastable phases at a lower temperature.⁶⁵ The mechanism for stabilization can include pseudomorphism (strain accommodating lattice matching) or superstructures, whereas relaxation past a critical thickness would result in a bulk structure. In our case, pseudomorphism is the dominant mechanism (seen directly in the high-resolution TEM and synchrotron data) where lattice matching constraints result in a phase that looks similar to the high-temperature cubic phase but exhibits tetragonal distortion to accommodate the tensile strain and perovskite octahedra.

We subsequently utilized the growth on other halide crystal salts with much larger lattice misfit ($>10\%$) to emphasize the control over the resulting phase. When changing the substrate to KBr ($a = 0.660$ nm),⁴⁵ growth of the orthorhombic phase was observed from RHEED and XRD (Figure S10). The RHEED pattern of the film grown on KBr substrate shows the formation of rotated microdomains. The increase in misfit strain to a value where the critical thickness is less than a monolayer results in unstrained incommensurate (quasiepitaxial) film growth that then exhibits the expected room-temperature orthorhombic phase.

As we have shown previously, misfit strain between the substrate and the film can be reduced using lattice engineering by alloying epitaxial metal halide interlayer films.⁵⁷ For $CsSnI_3$ growth, a thin alloyed layer (6 nm) of KCl and NaCl with a ratio of 6.7:1 is grown homoepitaxially on the KCl substrate to provide a near-ideal lattice match to the halide perovskite. Streaky RHEED patterns of the alloyed layer and the epitaxial $CsSnI_3$ layer are shown in Figure S11. By adding a tuned pseudomorphic interlayer of alloyed alkali halide salts, the misfit defect concentration is likely to be reduced even further.

Optical Properties and Quantum Well Fabrication. The optical properties of the $CsSnI_3$ epi-tetragonal phase on KCl were studied (Figure 5). The band gap energies were

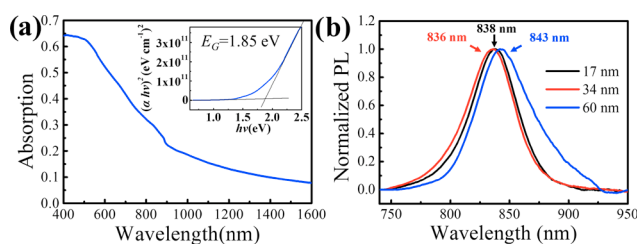


Figure 5. (A) Absorption spectrum of 40 nm $CsSnI_3$ grown on the KCl substrate. The absolute absorption from the film is plotted. The Tauc plot shows the extrapolation of a direct bandgap of 1.85 eV (inset). (B) PL spectra of quantum wells with well widths of 17, 34, and 60 nm showing peaks at 838, 836, and 843 nm, respectively.

extracted with a Tauc plot, giving a direct band gap of 1.85 eV (Figure 5a, inset). This value is consistent with the photoluminescence (PL) peak emission and onset emission at 1.47 and 1.60 eV. The simulated bandgap of all of the relevant phases is shown in Table S1 using the B3LYP hybrid functional. The epi-tetragonal bandgap is calculated to be 2.07 eV. This overestimation from the simulation is consistent with slight overestimation for the orthorhombic phase (1.40 eV from simulation and 1.31 eV from experiment⁶⁶). This

bandgap is notably distinct from the high-temperature tetragonal phase of 0.41 eV. As discussed above, the epitaxial growth allows the stabilization of a new epi-tetragonal $CsSnI_3$ phase. Thus, the observation of a larger bandgap is not surprising.

Quantum wells were fabricated with the halide perovskite as the well, and KCl was used as a barrier to study the quantum confinement effect. KCl was grown using a similar method to the homoepitaxy of NaCl reported previously.⁶⁷ RHEED was used during growth to confirm that each layer was crystalline and smooth as indicated by streaky patterns. PL spectra of the quantum wells show that by varying well width from 60 to 34 nm, the PL peak shifts modestly from 843 to 836 nm. This indicates that the Bohr radius of $CsSnI_3$ is relatively small (<10 nm). A similarly small quantum confinement effect has been reported for $CsSnBr_3$ nanocrystals and $CsSnBr_3$ quantum wells.^{40,57}

Photodetector Fabrication with Epitaxial $CsSnI_3$ Thin Film. Single crystalline $CsSnI_3$ thin-film-based photodetectors were fabricated with the architecture shown in Figure 6a (see

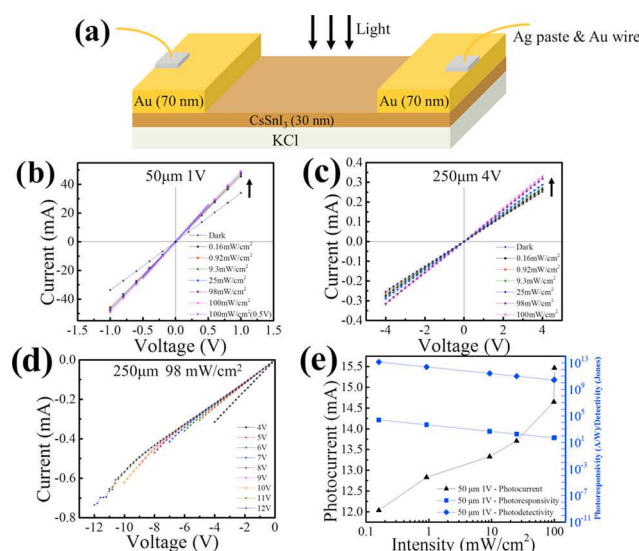


Figure 6. (A) Architecture of single crystalline $CsSnI_3$ thin-film-based photodetector. Devices with 50 and 250 μm channel width are fabricated and tested using simulated AM1.5 G solar illumination. (B) I – V characteristics of the device with 50 μm -wide channel width under different illuminations. The arrows indicate the increase in the current when increasing the light intensity. (C) I – V characteristics of the device with 250 μm -wide channel width under different illuminations. (D) I – V characteristics of the device with 250 μm -wide channel width under different testing voltages. (E) Photocurrent (black triangles), photoresponsivity (blue squares), and specific detectivity (blue diamonds) of the device with 50 μm -wide channel at 1 V.

the Materials and Methods section for fabrication details). The $CsSnI_3$ film serves as the photosensitive material to absorb light, and Au electrodes were vapor-deposited on the epitaxial $CsSnI_3$ layer to collect photogenerated charge carriers. The symmetrical and linear characteristics of the current–voltage (I – V) curve indicate the ohmic contact between the Au electrode and $CsSnI_3$. When the channel width between the two Au electrodes is 50 μm , the photocurrent is over 2 magnitudes higher than the photocurrent obtained with 250 μm -wide channel. This indicates that the width of the depletion region is less than 250 μm . In Figure 6e, the

photocurrent is shown to continuously increase with increasing illumination intensity. It is noted that the photocurrent increases significantly faster at the lower range of illumination intensity. The responsivity (R) is a key parameter commonly utilized to evaluate the performance of a photodetector. The responsivity is calculated as

$$R = \frac{I_{\text{light}} - I_{\text{dark}}}{P_{\text{incident}} \times A} \quad (1)$$

where I_{light} and I_{dark} represent the current measured with or without light illumination, respectively, P_{incident} is the incident light power density, and A is the active area. R is typically reported as a function of wavelength but can also be reported for broadband light sources. For this proof-of-principle demonstration, we utilize the average incident white-light power since we were better able to characterize the incident power density of white light versus monochromatic light in this configuration. As shown in Figure 6e, the responsivity exhibits different trends from the photocurrent. As the responsivity is closely correlated to quantum efficiency, the quantum efficiency then decreases with increasing intensity. This reduction is likely due to an accumulation of space charge that creates additional carrier scattering and has been shown to turn off halide perovskite solar cells.⁶⁸ Nonetheless, the photocurrent is significantly higher than in the solution-processed lead-based hybrid halide perovskite $\text{CH}_3\text{NH}_3\text{PbI}_3$ incorporated in similar device configurations.⁶⁹ For the photodetector under an applied bias, the specific detectivity (D^*) is limited by Shot noise as

$$D^* = \frac{R}{\sqrt{2qJ_{\text{dark}}}} \quad (2)$$

where q is the electron charge and J_{dark} is the dark current density.⁷⁰ The average white-light detectivity gives a value of 1.32×10^{13} Jones ($\text{cm Hz}^{1/2}/\text{W}$).

CONCLUSIONS

In summary, the room-temperature epitaxial growth of CsSnI_3 on low-cost metal halide crystals is achieved via reactive thermal deposition and characterized by in situ and ex situ diffraction techniques. This growth is investigated on $\text{KCl}(100)$, $\text{KBr}(100)$, and alloyed (NaCl/KCl) interlayers on KCl . The growth on $\text{KCl}(100)$ reveals a new room-temperature epitaxial tetragonal phase of CsSnI_3 that is closely lattice matched (pseudomorphic) to the KCl . In contrast, the growth observed on KBr (with large misfit) results in quasiepitaxial films with the orthorhombic phase (common room-temperature phase) and rotated microdomains. The epitaxial growth of CsSnI_3 is further exploited to demonstrate multilayer epitaxial quantum wells and lateral photodetectors. This work provides insight into the control over phase and ordering during halide perovskite epitaxial growth and expands the selection of photoactive materials for growing epitaxial halide perovskites that can be exploited in high-performance electronic applications.

MATERIALS AND METHODS

Epitaxial Film and Quantum Well Growth. The epitaxial growth of CsSnI_3 was carried out by co-evaporating the precursors CsI and SnI_2 in a customized multisource thermal evaporator (Angstrom Engineering). Prior to growth, KCl single-crystal substrates were cleaved to expose the fresh (100) surfaces in a

glovebox. The growth method as well as the in situ and real-time characterization techniques have been discussed in detail in our previous report.⁵⁷ The capability of performing low-current RHEED on insulating halide crystals has also been demonstrated in our previous studies.⁶⁷ Similar growth conditions are used for the fabrication of quantum well multilayers. Epitaxial KCl (barrier layer) was vapor-deposited from a KCl powder source with a rate of 0.002 nm/s and a barrier thickness of 1.5 nm .

Material Characterization. Details on cross-sectional TEM, SEM, XPS, PL, and UV–Vis measurements have been discussed in detail in our previous report.⁵⁷ Note that nitrogen gas was purged during both PL and UV–Vis measurements to protect the sample during the scan.

Out-of-plane XRD and pole figures were obtained using an XRD instrument with a Cu K_α source at 40 kV and 44 mA and using a Ni filter (Rigaku SmartLab). The sample was placed in a nitrogen-sealed dome to protect it from oxygen and moisture during the scan but also reduces the intensity of the film peaks. Synchrotron XRD data were collected at the NE-CAT beamline 24-ID-C, Advanced Photon Source (wavelength: 0.0619870 nm). The sample was prepared by carefully cleaving the single crystalline epitaxial film from the substrate and mounting/folding the film onto a copper holder stored at liquid nitrogen during transferring. The data were processed with XDS as implemented in rapid automated processing of X-ray data (<https://github.com/RAPD/RAPD>).

Photodetector Fabrication. Lateral photodetectors were fabricated by depositing Au film (70 nm) onto the epitaxial CsSnI_3 single crystalline film by e-beam deposition. The channel between the two Au electrode was fabricated by placing an Au wire (diameter $50 \mu\text{m}$, Alfa Aesar) or a Cu wire (diameter $250 \mu\text{m}$, Alfa Aesar) over the CsSnI_3 film as the mask to form the channel region.

Photocurrent Measurement. Silver paste (Ted Pella) was used to fix a gold wire onto each Au electrode for better electrical connection. The gold wires of both electrodes were connected to a customized photocurrent set-up, which has been described in details in our previous report.⁵⁷

Band gap Simulation. Band structures and bandgap calculations were performed using the CASTEP module in Material Studio 7.0 with the B3LYP functional (300 eV cutoff energy with the k-points set to $2 \times 2 \times 2$ for the Brillouin zone integration).

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsami.9b05592.

Summary of CsSnI_3 phases (Table S1); scanning electron microscope (SEM) image of epi-tetragonal CsSnI_3 (Figure S1); reflection high-energy electron diffraction (RHEED) patterns of high-rate CsSnI_3 epitaxial growth (Figure S2); RHEED patterns for surface reconstruction (Figure S3); pole figure scans of KCl and epi-tetragonal CsSnI_3 (Figure S4); synchrotron X-ray diffraction (XRD) patterns of epi-tetragonal CsSnI_3 (Figures S5 and S6); simulated diffraction patterns of Cs_2SnI_6 (Figure S7); X-ray photoelectron spectroscopy (XPS) scans of epi-tetragonal CsSnI_3 (Figure S8), epi-tetragonal CsSnI_3 film stability test (Figure S9), CsSnI_3 growth on KBr (Figure S10), and CsSnI_3 growth on a pseudomorphic buffer layer (Figure S11) (PDF)

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Author Contributions

L.W. and P.C. contributed equally to this work. R.R.L., L.W., and P.C. conceived the project and wrote the manuscript. L.W. and P.C. performed the epitaxial growth, RHEED, XRD, 2D quantum well fabrication, UV-Vis and PL measurements. P.C. performed the pole figure scans. I.K. helped with the film thickness calibration and growth. L.W. fabricated the photo-detector and performed measurements. P.S.K. helped with PL measurements. K.S. performed the TEM. R.S. prepared the synchrotron sample and aided in the analysis.

Notes

The authors declare no competing financial interest.

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SUPPLEMENTARY INFORMATION

Epitaxial Stabilization of Tetragonal Cesium Tin Iodide

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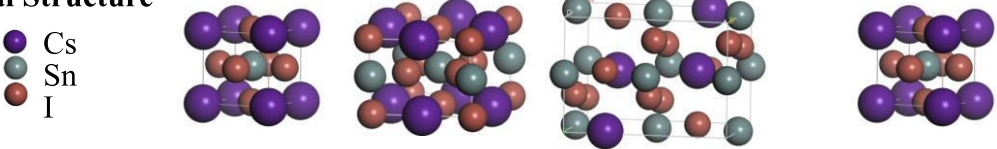
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Table S1. Crystal structures, lattice parameters, experimental and simulated bandgaps of the cubic, tetragonal, orthorhombic and the epi-tetragonal phase from this work.¹ Band structure and

bandgap calculations were performing using the CASTEP module in Material Studio 7.0 with the B3LYP functional.

Phase	Cubic (High T)	Tetragonal (High T)	Orthorhombic (Room T)	Epi-tetragonal (Room T , this work)
Crystal Structure				
Lattice Parameters(nm)	$a=0.62057$	$a=b=0.87182$, $c=0.61908$	$a=0.86885$, $b=1.23775$, $c=0.86384$	$a=b=0.622\pm0.007$, $c=0.612\pm0.002$
Experimental Bandgap (eV)	-	-	1.31^2	1.85
Simulated Bandgap (eV)	0.76	0.41	1.40	2.07

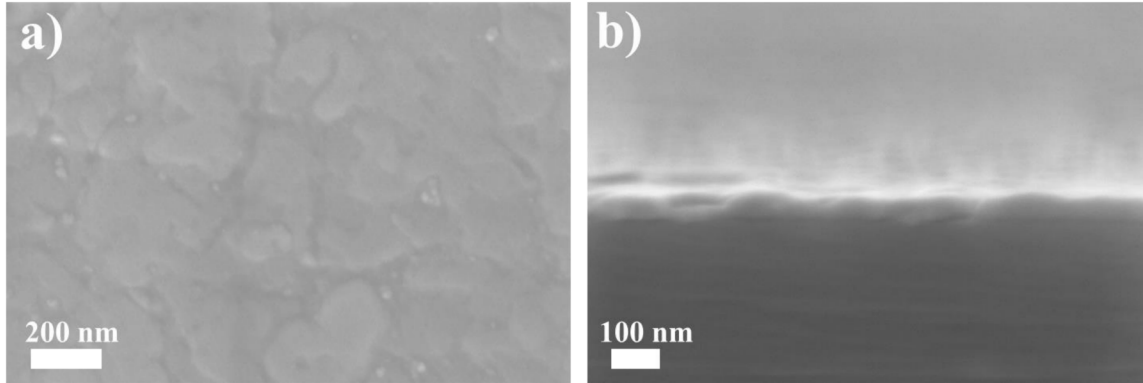


Figure S1. (A) Scanning electron microscope (SEM) and (B) cross-section SEM image of 40nm epitaxial CsSnI₃ on KCl.

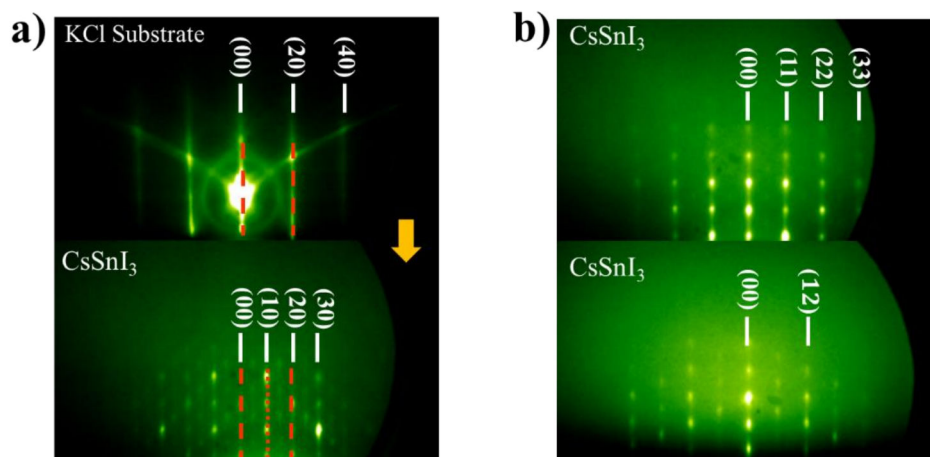


Figure S2. (A) Reflection high-energy electron diffraction (RHEED) pattern of the bare KCl substrate and 20nm of CsSnI₃ grown at high rate. The spotty pattern indicates the film is crystalline and rough. (B) Rotation dependent RHEED patterns of the rough CsSnI₃ epitaxial film.

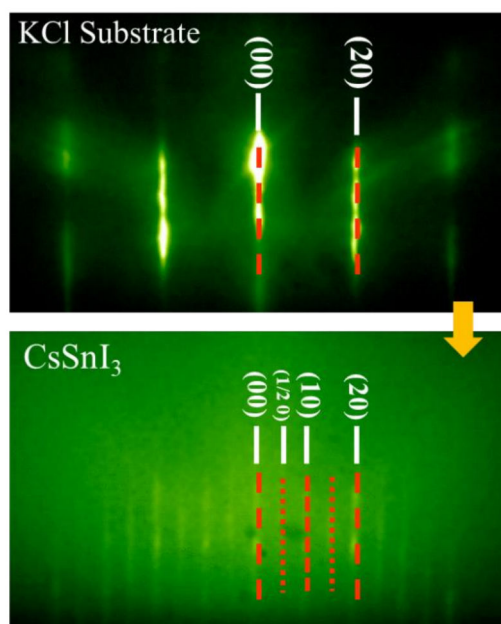


Figure S3. RHEED pattern of the bare KCl substrate and 20nm of CsSnI₃. Half-order streaks are occasionally observed at high growth rate indicating a surface reconstruction of the perovskite monolayer.

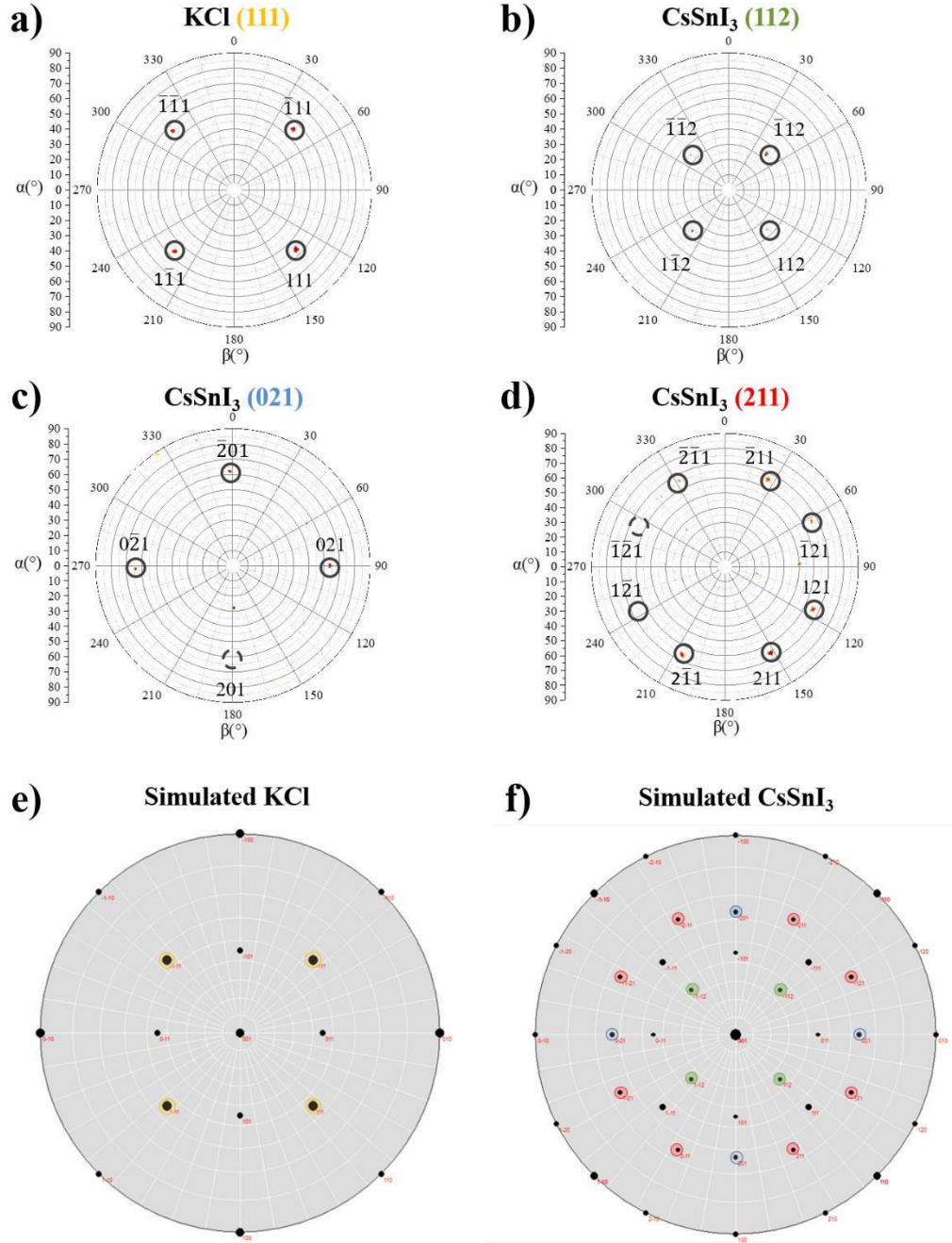


Figure S4. (A) The (111) pole figure scan of KCl substrate. (B-D) The (112) (021) (112) pole figure scan of 40nm of CsSnI₃ on KCl substrate. α and β are tilt and rotation angles around the sample surface normal direction. (E-F) Simulated pole figure of KCl and epi-tetragonal CsSnI₃, which are in good agreement with the experimental scans. Note that a couple of the (211) are missing due to slight tilt of the crystal. The (112) (021) (112) poles for epi-tetragonal CsSnI₃ are clearly distinguishable from the KCl substrate.

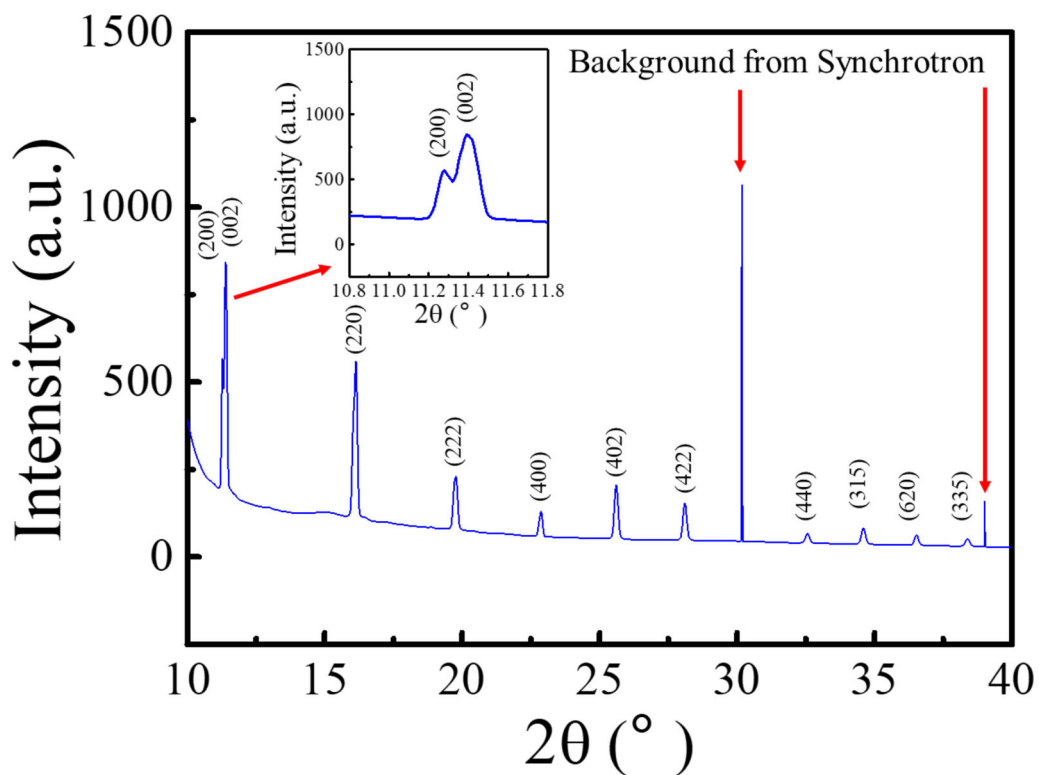


Figure S5. Synchrotron X-ray diffraction (XRD) patterns of 20nm of CsSnI_3 removed from the substrate and formed into a folded (textured pseudo-powder) film. An obvious peak split is seen at 11.28° and 11.39° (inset), which corresponds to the (200) and (002) planes of the epi-tetragonal phase respectively.

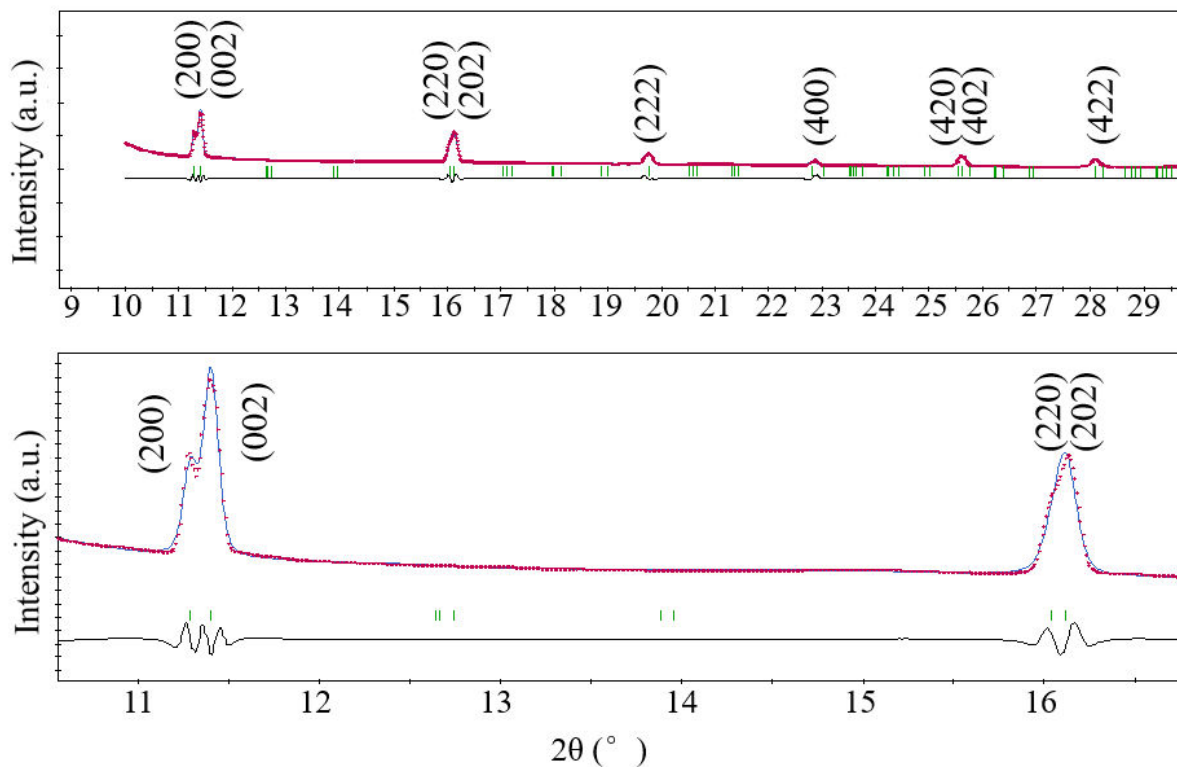


Figure S6. (top) The refinement and fitting of the synchrotron ($\lambda = 0.0619870\text{nm}$) XRD pattern using the Pawley method in Materials Studio. Lattice constants of the epitaxial CsSnI_3 film obtained from the fitting are $a = b = 0.6240\text{nm}$, $c = 0.6178\text{nm}$. Note the blue line is the fit, red dots are the data, and the black line is the difference between the experimental data and the fit. (bottom) Zoom-in of the plot on top highlighted the region around the (200)/(002) and (220)/(202) peaks.

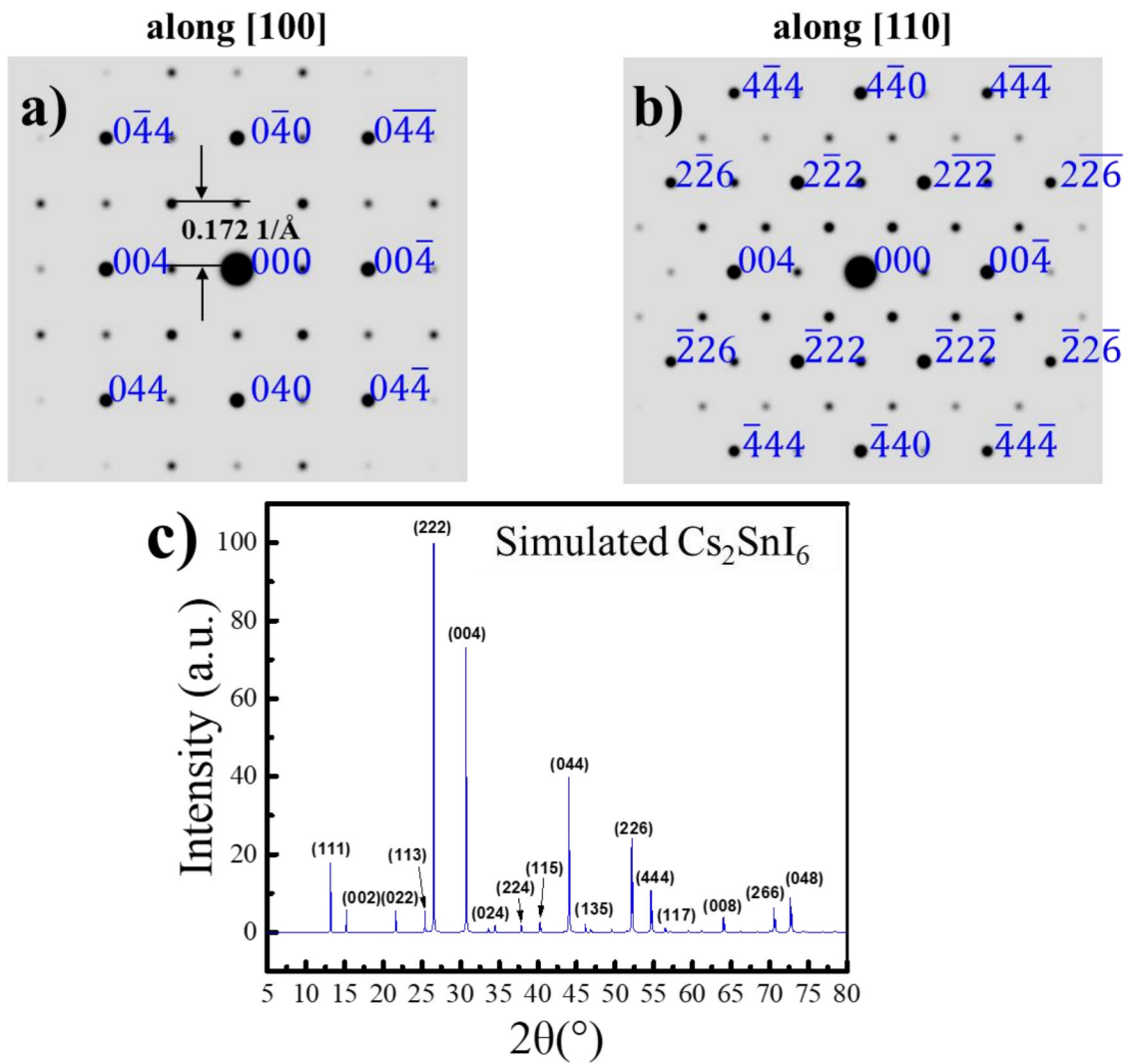


Figure S7. (A-B) Simulated selected area electron diffraction (SAED) patterns of Cs_2SnI_6 . (C) Simulated XRD pattern of Cs_2SnI_6 .

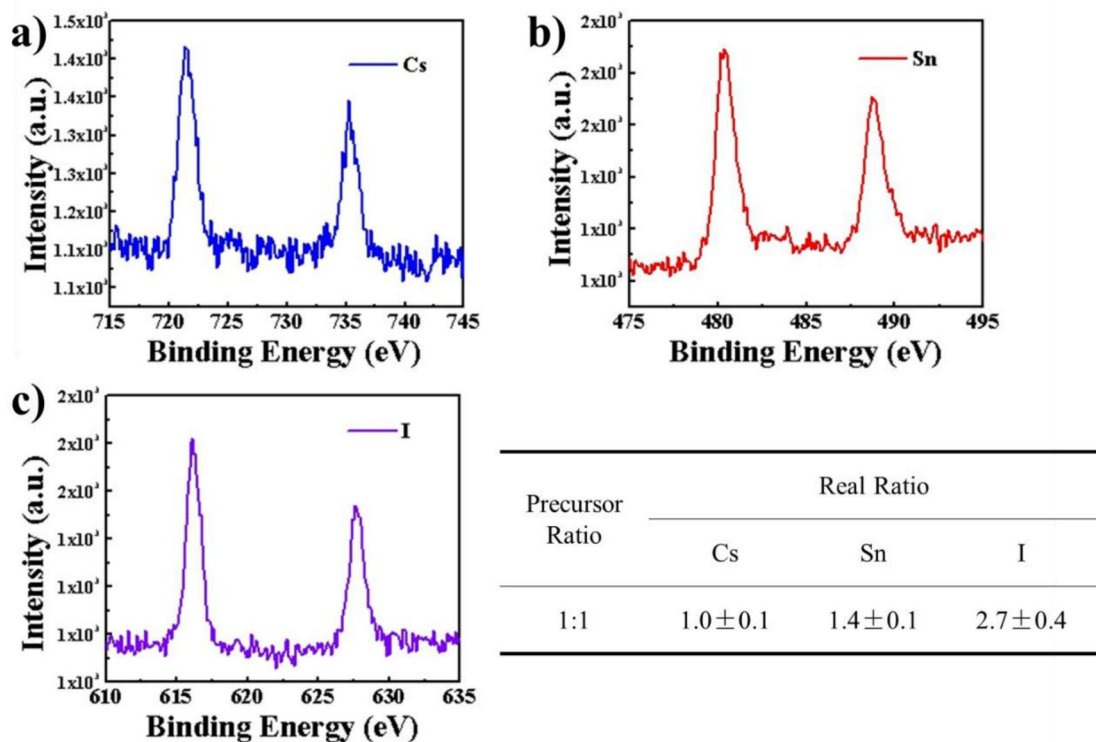


Figure S8. X-ray Photoelectron Spectroscopy (XPS) spectra of (A) Cs (B) Sn and (C) I for the epitaxial CsSnI₃ film. The ratio matches with the stoichiometry of CsSnI₃ and the Sn is found to have a +2 valence state in the epitaxial film.

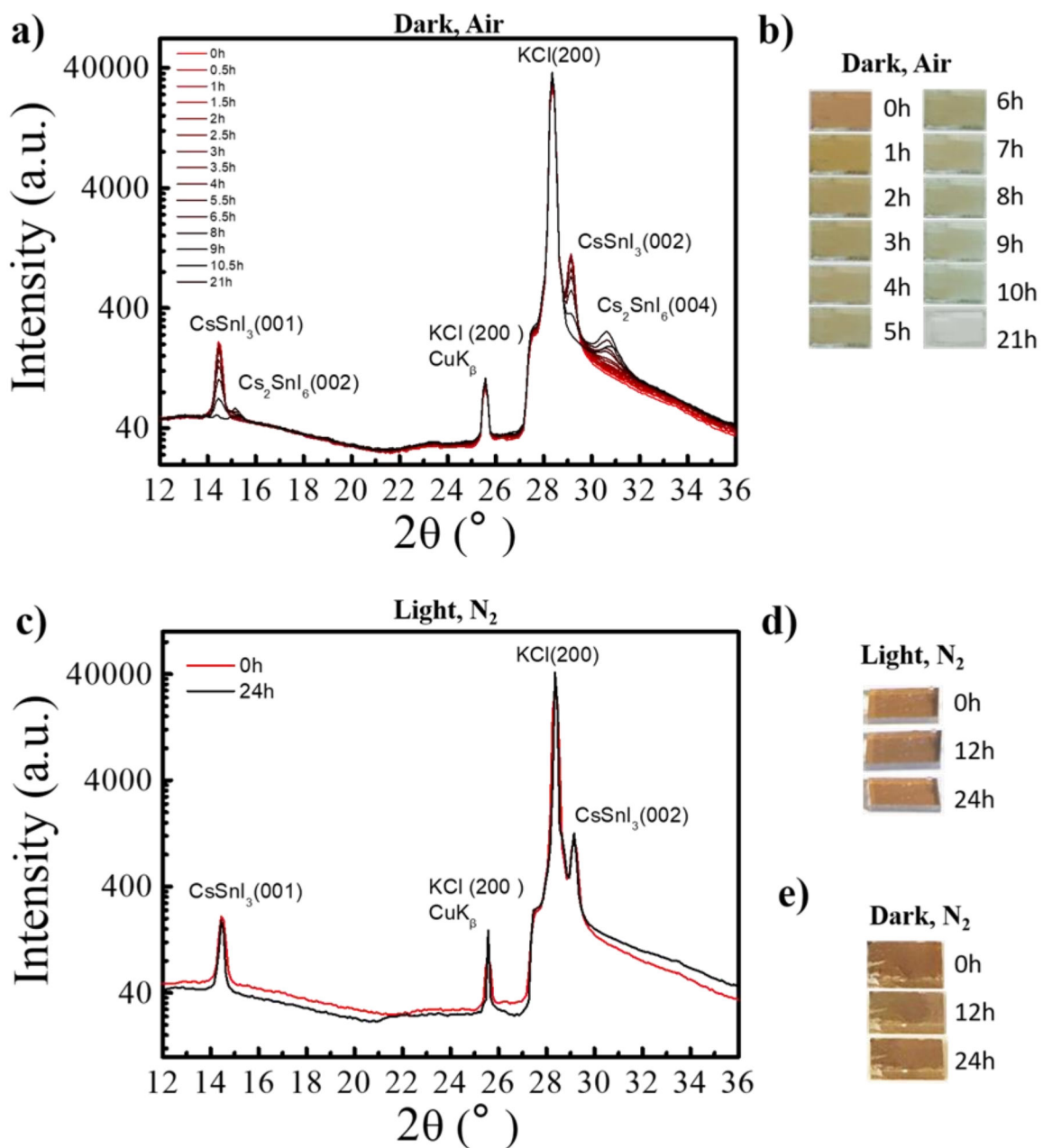


Figure S9. (A) XRD patterns and (B) color change of an epitaxial CsSnI_3 film (40nm) on KCl as a function of time in the dark and exposed to air. (C) XRD patterns and (D) color change of an epitaxial CsSnI_3 film (40nm) on KCl as a function of time under light soaking and in N_2 . (E) Color change of an epitaxial CsSnI_3 film (40nm) on KCl as a function of time in dark and in N_2 .

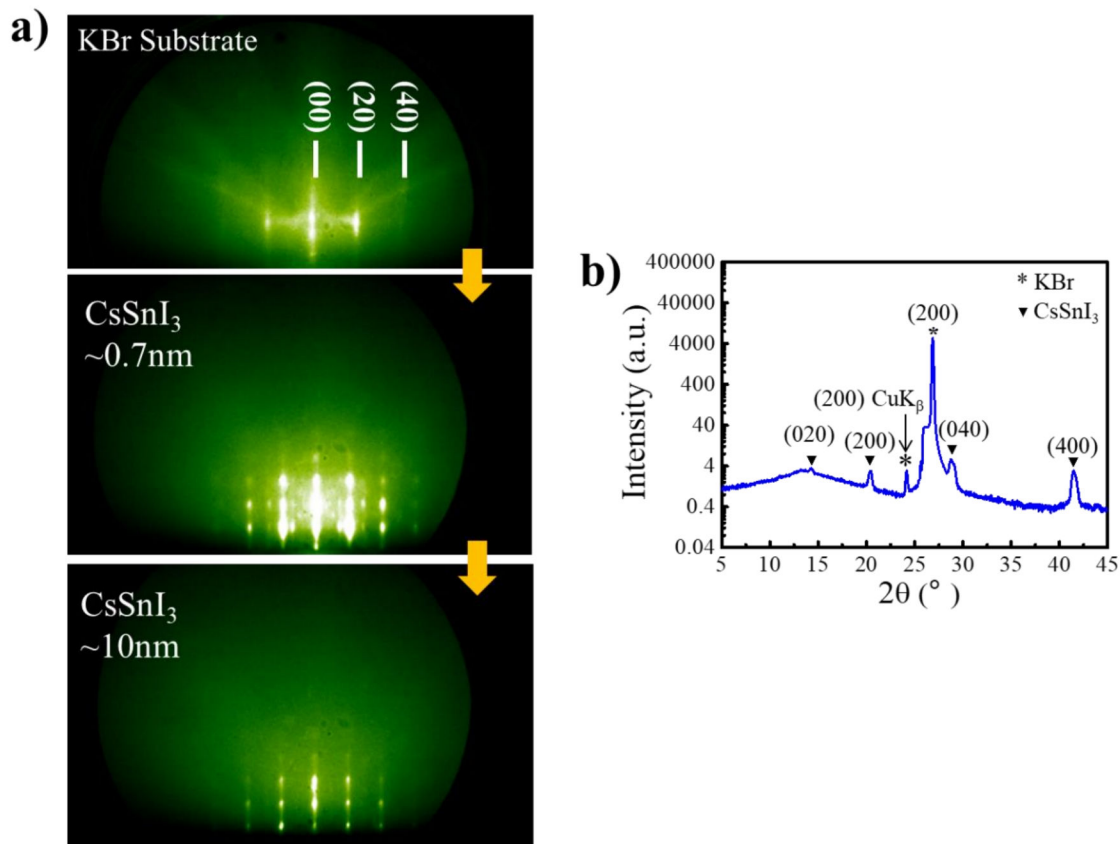


Figure S10. (A) RHEED pattern of the bare KBr substrate and CsSnI₃ at low and high thickness. Multiple rotational domains are seen during the initial growth. (B) Out-of-plane XRD scan of 40nm of CsSnI₃ on KBr. Both the XRD and RHEED data are consistent with the typical room-temperature orthorhombic phase.

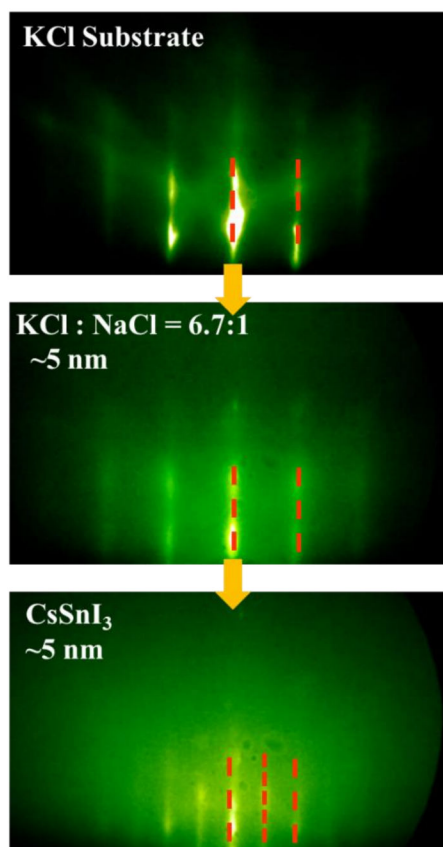


Figure S11. RHEED pattern of the bare KCl substrate, the alloyed growth of 5nm of KCl and NaCl (6.7:1) and 5 nm of CsSnI₃.

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