## **Supplementary Information**

Lead-Free Perovskite Cs<sub>2</sub>AgBiBr<sub>6</sub> Epitaxial Thin Films for Highperformance and Air-Stable Photodetectors

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$$\Delta = \frac{\mid a_e - 3a_s \mid}{a_e} * 100\%$$
 Formula

**S**1

In the process of growing high-quality films, the crystal symmetry compatibility and lattice mismatch between thin films and substrates are two important factors affecting the heteroepitaxial growth. The calculated lattice mismatch according to formula (1) is 3.9% for Cs<sub>2</sub>AgBiBr<sub>6</sub> (Fm3m, a=11.25 Å) to STO (Pm3m, a=3.905 Å), where  $a_e$  is the lattice constant of Cs<sub>2</sub>AgBiBr<sub>6</sub> and  $a_s$  is the lattice constant of STO (the lattice constants use is those of the bulk material). This meets the conditions for film heteroepitaxy, especially for pseudocrystal growth.



Figure Fig. S1. (a) XRD spectra of Cs<sub>2</sub>AgBiBr<sub>6</sub> target powder and (b) spin coated films.



Fig. S2. AFM image of Cs<sub>2</sub>AgBiBr<sub>6</sub> films prepared by PLD at different substrate temperatures.



Fig. S3. Atomic Force Microscope image of Cs<sub>2</sub>AgBiBr<sub>6</sub> films prepared by PLD at different laser

energy.



**Fig. S4.** (a) the light absorption and photoluminescence (PL) spectra of spin-coated  $Cs_2AgBiBr_6$  films. (b) the Tauc diagram for the spin-coated films



**Fig. S5.** Thickness of epitaxial films prepared using different numbers of pulses, measured with a step meter.



**Fig. S6.** Phi-scans of STO (110) and Cs<sub>2</sub>AgBiBr<sub>6</sub> (110) peaks. The Cs<sub>2</sub>AgBiBr<sub>6</sub> film has a thickness of 700 nm.



Fig. S7. Standard XRD rocking curve analysis at different epitaxial  $Cs_2AgBiBr_6$  films thicknesses. The results show that the FWHM of the rocking curves gradually increases with film thickness, indicating a decrease in the out-of-plane atomic ordering.



**Fig. S8.** (a) and (b) show the light absorption and photoluminescence (PL) spectra, respectively, of the epitaxial  $Cs_2AgBiBr_6$  film with varying thicknesses. (c) the FWHM of the PL spectra; (d) the indirect bandgap of epitaxial  $Cs_2AgBiBr_6$  films with varying thicknesses, determined using the Tauc plot method.

The results presented in Fig. S9 indicate that the thickness of the epitaxial films has almost no influence on the bandgap of  $Cs_2AgBiBr_6$  and the FWHM of the PL spectra.



**Fig. S9.** (a-e) Cross-sectional SEM images of epitaxial Cs<sub>2</sub>AgBiBr<sub>6</sub> films with different pulse number and (f) spin-coated Cs<sub>2</sub>AgBiBr<sub>6</sub> film.

	Cs	Ag	Bi	Br		
Cs <sub>2</sub> AgBiBr <sub>6</sub>				and the second second		
STO	Pulse Number 3	300				
	Cs	Ag	Bi	Br		
Cs <sub>2</sub> AgBiBr <sub>6</sub>						
sto	Pulse Number 2	2000				
	Cs	Ag	Bi	Br		
Cs2AgBiBr6				Statistics &		
1 Stevens						
STO	Pulse Number 4000					
	Cs		Bi	Br		
Cs2AgBiBr6						
STO	Pulse Number 6500					

Fig. S10. Cross-sectional EDX mapping of epitaxial Cs<sub>2</sub>AgBiBr<sub>6</sub> films deposited with different numbers of pulses.

TABLE I Summary of the relative atomic ratios (%) of Cs, Ag, Bi, and Br in  $Cs_2AgBiBr_6$  films

Pulse Number	Cs	Ag	Bi	Br
300	2.09	0.94	1	5.86
2000	2.01	0.93	1	5.90
4000	1.95	0.97	1	5.75
6500	2.03	0.95	1	5.93

fabricated with different pulse numbers, using the element Bi ratio as a measurement reference.



**Fig. S11.** (a-f) Atomic Force Microscope image of epitaxial Cs<sub>2</sub>AgBiBr<sub>6</sub> films; (g) AFM image of spin-coated Cs<sub>2</sub>AgBiBr<sub>6</sub> films.

Surface morphology studies using AFM reveal that, although the films exhibit low surface roughness at the initial growth stage, dense islands are observed on the surface (Fig. S11). This growth behavior differs from the layer-by-layer growth mode typically reported for PLD films.<sup>1</sup> While numerous studies have suggested that PLD films typically grow in a layer-by-layer mode, our PLD process operates at a significantly higher growth rate. Under these conditions, the film is more likely to grow via a Stranski–Krastanov three-dimensional (3D) island mode instead of the layer-by-layer mode, resulting in the observed formation of islands. As the film thickness increases and stress accumulates between the epitaxial film and the substrate, the surface roughness also escalates, often accompanied by a higher density of structural defects, including grain boundaries and dislocations. This observation is in accordance with our XRD rocking curve analysis, which reveals a gradual increase in the FWHM with increasing film thickness, indicating a decrease in out-of-plane atomic ordering.



**Fig. S12.** (a) Photos of epitaxial and spin-coated  $Cs_2AgBiBr_6$  film detector device; (b) Spectral responses of the epitaxially grown  $Cs_2AgBiBr_6$  film photodetector and the spin-coated  $Cs_2AgBiBr_6$  film photodetector were measured under various wavelengths at the same irradiation power densities.; (c) I–V curves of  $Cs_2AgBiBr_6$  photodetectors with various thicknesses in the dark state and (d) in light illumination with an irradiant power of  $10\mu$ W/cm<sup>2</sup>



Fig. S13. (a) (b) PL spectra of the epitaxial and spin-coated  $Cs_2AgBiBr_6$  films in the temperature range of room temperature to 100°C. (c) (d) Temperature dependence of the PL intensity.

The results from the temperature-dependent photoluminescence measurements presented in Fig. S14 show that, when heated to 100°C, the PL intensity of the epitaxial film decreased by only 15.3%, while that of the spin-coated film decreased by 28.7%. This indicates a significant reduction in non-radiative recombination channels in the epitaxial film, which is consistent with the lower defect density observed in the epitaxial film compared to the spin-coated film through SCLC measurements.<sup>2</sup> Additionally, the full width at half maximum of the epitaxial film broadened by only 18.2 meV from room temperature to 100°C, whereas that of the spin-coated film broadened by 37.3 meV, suggesting stronger defect scattering (e.g., grain boundaries or surface defects) and more pronounced carrier localization in the spin-coated film.<sup>3, 4</sup> By fitting the PL intensity thermal quenching curves with Arrhenius model, the defect activation energy  $(E_a)$  of the epitaxial film was determined to be 208 meV, which is comparable to that of single crystals and significantly higher than that of the spin-coated film ( $E_a = 87$ meV).<sup>5</sup> This suggests that the residual defects in the epitaxial film are primarily deeplevel defects (e.g., lattice vacancies),<sup>6</sup> from which carriers are less likely to escape via thermal excitation and participate in non-radiative recombination<sup>5</sup>. In contrast, the spincoated film is dominated by shallow-level defects (e.g., grain boundaries or surface states), which readily induce non-radiative recombination, leading to a rapid decrease in PL intensity.<sup>7</sup> Furthermore, the PL peak positions of both films showed no significant shift during heating, indicating excellent bandgap stability and the absence of additional lattice distortion introduced by the epitaxial process.



Fig. S14. Impedance graph of the spin-coated and epitaxial films device in the dark (1 V bias, 1 Hz to 1 MHz).

As shown in Fig. S14, compared to the device based on the spin-coated film, the device based on the epitaxial film exhibited a significantly larger semicircle in the Nyquist plot, corresponding to higher recombination resistance. This reflects the reduced charge recombination at defect sites within the epitaxial film, indicating superior crystallinity and fewer defects (e.g., grain boundaries or point defects).<sup>8,9</sup>



Fig. S15. (a) Temperature-dependent dark current versus voltage for epitaxial film device (b) Natural logarithm of dark current versus 1000/T for epitaxial film device. (c) Temperature-dependent dark current versus voltage for spin-coated film device. (d) Natural logarithm of dark current versus 1000/T for spin-coated film device.

As shown in Fig. S15, temperature-dependent I-V measurements were conducted on both devices. By analyzing the dark current at various temperatures, the activation energies for carrier transport were extracted using the equation  $\sigma = \sigma_0 exp(-E/2k_BT)$ , where  $\sigma$  is the conductivity,  $\sigma_0$  is the pre-exponential factor, E is the activation energy, and k<sub>B</sub> is the Boltzmann constant.<sup>10</sup> The epitaxial film device exhibited an activation energy of 0.87 eV, which suggests a conduction mechanism dominated by deep-level defect ionization or quasi-intrinsic transport. The low defect density and weak carrier localization in the epitaxial film contribute to its high  $\mu\tau$  product and suppressed Shockley-Read-Hall recombination.<sup>11</sup> In contrast, the spin-coated film device showed a lower activation energy of 0.3 eV, indicating a transport and recombination pathway dominated by shallow defects. This shallow defect-mediated mechanism leads to a significantly reduced  $\mu\tau$ product.<sup>12</sup>



**Fig. S16.** Photocurrent as a function of the incident light intensity for a spin-coated Cs<sub>2</sub>AgBiBr<sub>6</sub> film photodetector.



Fig. S17. (a) noise spectral density and (b) NEP of epitaxial  $Cs_2AgBiBr_6$  film photodetector under 530 nm light with different light intensities.



**Fig. S18.** (a) dark current and responsivity distribution of 20 devices; (b) NEP and D\*and distribution of 20 devices. This verified the reliable reproducibility of the devices fabricated through the epitaxial film process.



**Fig. S19.** A typical transient photocurrent response of spin coated Cs<sub>2</sub>AgBiBr<sub>6</sub> film photodetector.



**Fig. S20.** Long-term storage stability, the last six cycles correspond to the photoresponse after storage in air for 30 days (RH: ~85%).



Fig. S21. Comparison of the XRD patterns of the epitaxial  $Cs_2AgBiBr_6$  film before and after storage for 60 days in ambient air.



**Fig. S22.** (a) UPS spectra of epitaxial  $Cs_2AgBiBr_6$  films and (b) corresponding energy level diagram; (c) energy band diagram of the Au/Cs<sub>2</sub>AgBiBr<sub>6</sub>/Au structure showing the generation, transfer and collection processes of photogenerated carriers.

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