

Article

Facile Fabrication of Mixed-Cation $\text{FA}_{1-x}\text{Cs}_x\text{PbI}_3$ Perovskites Thin Films for Photodetector Applications

Fenyun Wang¹, Pachaiyappan Murugan¹ , Shunhong Dong¹, Xiaolu Zheng¹, Jiaxiu Man¹, Zhiyong Liu^{1,2}, Weibin Zhang^{1,2}, Ting Zhu^{1,2} , and Hong-En Wang^{1,2,*}

¹ Yunnan Key Laboratory of Optoelectronic Information Technology, College of Physics and Electronic Information, Yunnan Normal University, Kunming 650500, China; p.kumu29@gmail.com (P.M.); shunhong.dong@outlook.com (S.D.); zhengxiaolu@ynnu.edu.cn (X.Z.); manjiaxiu@ynnu.edu.cn (J.M.); liuzhiyong@ynnu.edu.cn (Z.L.); 220001@ynnu.edu.cn (W.Z.); zhut0002@ynnu.edu.cn (T.Z.)

² Key Laboratory of Advanced Technique & Preparation for Renewable Energy Materials, Ministry of Education, Yunnan Normal University, Kunming 650500, China

* Correspondence: honggen.wang@ynnu.edu.cn or honggen.wang@outlook.com

Abstract: Formamidinium lead triiodide (FAPbI₃) perovskite has received great attention because of its distinct optoelectronic property, smaller band gap (~1.5 eV), and higher thermal stability than methylammonium lead triiodide (MAPbI₃). However, the efficient synthesis of such perovskite materials on a large scale at a low cost remains a challenge. In this work, mixed-cation $\text{FA}_{1-x}\text{Cs}_x\text{PbI}_3$ thin films were directly prepared in an atmospheric environment with a high film formation rate, low material loss, low cost, and low requirements for experimental instruments and environment. The as-obtained FAPbI₃ films exhibited excellent optoelectronic properties, showing promising applications in the photodetection field.

Keywords: mixed-cation $\text{FA}_{1-x}\text{Cs}_x\text{PbI}_3$ thin film; perovskites; optoelectronic properties; photodetectors



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1. Introduction

In recent years, organic–inorganic hybrid perovskite materials have attracted much attention in electronics and optoelectronic fields such as solar cells [1–3], light-emitting diodes [4,5], lasers [6], and photodetectors [7] due to their excellent optoelectronic properties. The device structure and mechanism of photodetectors have been widely studied. Specifically, the semiconductor material absorbs the incident light; generates photogenerated electrons/holes through the absorption and transit regions; and finally, the transmitted carriers are effectively collected to generate photocurrent. In particular, effective separation and collection of electron–hole pairs can only be achieved when the photon energy is greater than the semiconductor bandgap width ($h\nu \geq E_g$). Compared with metal oxide semiconductors, metal nitrides, and 2D semiconductor materials, perovskites are widely used in optoelectronic devices due to their high light absorption coefficient, carrier mobility, and defect tolerance. In addition, perovskite materials can be synthesized by a simple solution method and integrated with other materials to form composites for better optoelectronic performances [8–11].

Generally, organometal halide perovskites adopt a chemical formula of ABX_3 , where A is a monovalent cation (CH_3NH_3^+ , $\text{CH}_2(\text{NH}_2)_2^+$, Cs^+ , etc.), and B stands for Pb^{2+} or Sn^{2+} , while X is a halide anion (Cl^- , Br^- , and I^-). Early research mainly focused on methylammonium lead triiodide (MAPbI₃). However, due to the volatile nature of MA [12], MAPbI₃ has poor environmental stability and is easily degraded under the conditions of oxygen, moisture, and high temperature [13]. These undesirable intrinsic attributes of MAPbI₃ largely impeded its wide application [14]. At present, the environmental stability of perovskite has been extensively studied. For example, Tai et al. [15] achieved a conversion efficiency of 15% based on proper humidity to promote the nucleation and

growth of perovskite. Moreover, Ivy M. et al. [16] combined the chemical synthesis method and solvent engineering technique to obtain pinhole-free thin-film perovskite composed of large crystalline grains and high crystalline quality. Sanjay et al. [17] used a one-step deposition technique, two-step deposition technique, and vapor deposition technique under the atmospheric atmosphere to obtain high crystalline quality, low defect density, and large-size perovskite thin film.

In comparison, black-phase formamidinium lead triiodide (α -FAPbI₃) exhibits relatively superior atmospheric stability with a slightly smaller bandgap (1.45~1.51 eV) more suitable for optoelectronic applications, which has become a major research avenue in the community [18,19]. Typically, FAPbI₃ can be prepared from organic and inorganic halide precursors by either a one-step or two-step method [20,21]. Snaith et al. reported the preparation of less uniform and flat α -FAPbI₃ perovskite film by adding a certain amount of hydriodic acid (HI) [3]. Zhao et al. [22] introduced HPbI₃ into perovskite precursors and prepared relatively flat FAPbI₃ thin films by the one-step spin coating method. However, the as-prepared single FAPbI₃ films can still have many defects due to the larger FA⁺ cation (2.53 Å) than that of MA⁺ cation (2.17 Å) and the symmetry difference of FA⁺ and MA⁺ [23–25]. In addition, compared with MAPbI₃, α -FAPbI₃ is difficult to maintain its phase stability. Note that the phase stability/transition can be estimated by the Goldschmidt tolerance factor calculated from the ionic radius using the following expression [26]:

$$t = \frac{r_A + r_x}{\sqrt{2}(r_B + r_X)} \quad (1)$$

where r_A is the radius of the A-site cation, r_B is the radius of the B-site cation, and r_X is the radius of the anion. The calculated tolerance factor of FAPbI₃ is about 1, suggesting that it ideally has a (pseudo)cubic structure. When the default tolerance factor is higher than 1 or lower than 0.71, non-perovskite structures are formed [27].

Doping other cations or halide anions can improve the phase stability of FAPbI₃ [28]. For example, some cations (e.g., MA⁺, Cs⁺, Rb⁺, etc.) with an ionic radius smaller than FA⁺ can be used to partially replace FA⁺. Among them, the intrinsically stable inorganic cation Cs⁺ has a small ionic radius of 1.81 Å. By substituting part of FA⁺ in pure FAPbI₃ with Cs⁺, the volume of the cuboctahedron motifs can be reduced so that metal cations and halogens can achieve stronger interaction to form highly crystalline perovskite materials. Himchan et al. [29] found that after doping Cs⁺, the resultant FA_{1-x}Cs_xPbBr₃ perovskite thin film underwent a lattice shrinkage as reflected by the shift of XRD diffraction peak position towards a larger angle direction. Therefore, by effectively adjusting the tolerance factor of the desired cubic structure, the expansion or contraction of the perovskite lattice can be achieved, and its crystal growth can be regulated. Based on previous reported work, Cs_{0.15}FA_{0.85}PbI₃ perovskite was nucleated and grown mostly in N₂ atmosphere (glove box). However, the lack of a proper humidity environment for Cs_{0.15}FA_{0.85}PbI₃ synthesis leads to the formation of high defect density, small size grains, and the increase in non-radiative complexes severely limits the application of perovskite optoelectronic devices [30]. Therefore, it is essential to develop a novel method (atmospheric atmosphere) for the preparation of Cs_{0.15}FA_{0.85}PbI₃ perovskite.

Nevertheless, due to the strong hygroscopic nature of FAI, most reported high-efficiency FAPbI₃ perovskites have been fabricated under some specific conditions, usually with the protection of inert gases such as Ar or N₂ in a glovebox [12]. Such synthetic routes can potentially increase the processing cost and difficulty of large-scale industrialization. Therefore, it is of great significance to explore a facile and low-cost method to prepare FAPbI₃ perovskite thin films on a large scale (the best is directly in an atmospheric environment). However, research in this area is still in its infancy. Herein, we report on the facile and fast fabrication of FA_{1-x}Cs_xPbI₃ thin films with tunable Cs⁺ concentration (varied x values) in the atmosphere. The morphology, phase, microstructure, and composition of the as-prepared FA_{1-x}Cs_xPbI₃ thin films were carefully characterized. The results revealed that the optical properties of the as-prepared FA_{1-x}Cs_xPbI₃ thin films varied as a function

of the Cs⁺ concentrations, and an excellent optical property can be achieved with a Cs⁺ doping concentration of 15%. Further, the photodetection properties of the FA_{0.85}Cs_{0.15}PbI₃ thin film were investigated.

2. Experimental Section

2.1. Synthesis of Perovskite Precursor Solution

A 2 mol mL⁻¹ mixed solution was prepared by dissolving 0.461 g PbI₂ (Aldrich, Shanghai, China, 99.99%), as well as appropriate amounts of FAI (Aldrich, 99.5%) and CsI (Aldrich, 99.9%) powders with defined composition ratios, into 200 μL dimethyl sulfoxide (AR) and 800 μL N,N-dimethylformamide (AR), in that order. The resulting solution was heated in a water bath to 70 °C while being stirred for an hour, then cooled to room temperature before storage.

2.2. Preparation of FA_{1-x}Cs_xPbI₃ Thin Films

Squares of 1.5 cm × 1.5 cm were cut from a 4-inch SiO₂/Si substrate (Zhejiang Lijing Optoelectronics Technology, Hangzhou, China). To make the SiO₂/Si substrates more hydrophilic, they were sonicated in acetone, ethanol, and deionized water for 15 min in a squeegee, then dried with a nitrogen gun and treated with oxygen plasma for 10 min. The FA_{1-x}Cs_xPbI₃ thin films were prepared in an atmospheric environment using a method called spin coating. After the SiO₂/Si substrate was cleaned, 30 μL of the aforementioned precursor solution was deposited on it. Afterward, the SiO₂/Si substrate was put on a spin coater at 4000 rpm for 10 s, then 500 μL of diethyl ether was added dropwise and after 50 s of spin coating, in order to obtain the FA_{1-x}Cs_xPbI₃ samples. In order to obtain FA_{1-x}Cs_xPbI₃ thin films, the resulting films were annealed at 140 °C for 20 min.

2.3. Characterizations

The elemental distribution of the samples was investigated using energy-dispersive X-ray spectroscopy (EDX), while the morphology of the samples was observed using a scanning electron microscope (SEM, Quanta FEG 250). Steady-state photoluminescence (PL) spectra of the samples were taken using IK3301 spectroscopy and an excitation wavelength of 532 nm. X-ray diffraction experiments of the FA_{1-x}Cs_xPbI₃ thin film were carried out on a DX-2700 X-ray diffractometer. The Scientific Escalab 250 XPS spectrometer was used to conduct the X-ray photoelectron spectroscopy (XPS) on the samples. The ultraviolet–visible (UV–vis) light absorption spectra of the samples were obtained using a spectrometer model number UV-4100 (Hitachi). On a semiconductor integrated test system, the current–voltage (*I*-*V*) and current–time (*I*-*t*) curves of the devices as they were initially fabricated were recorded (Keithley 4200SCS, USA). The current and time of a periodically switched light source were tested by the Optical Chopper (New Focus 3502). The lamp used was Xenon Light (67005), a monochromatic light source at the wavelength of 790 nm, and the model was 918D-918D; additionally, an incandescent lamp with a wavelength in the visible light range with the model of MLC-150C was used.

2.4. Fabrication of FA_{1-x}Cs_xPbI₃ Thin-Film Photodetectors

Figure 1 provides a schematic representation of the fabrication process for an FA_{1-x}Cs_xPbI₃ thin-film photodetector. After the FA_{1-x}Cs_xPbI₃-coated SiO₂/Si substrate was secured with a mask (wound with a tungsten wire with a diameter of 10 μm), it was placed in an electron beam evaporator. To protect the perovskite film, an Au layer was deposited on top with a thickness of 80–100 nm. In the end, the SiO₂/Si substrate was removed, and for the purpose of the subsequent electrical measurements, the two ends of the perovskite sample that were in contact with the Au electrodes were chosen.

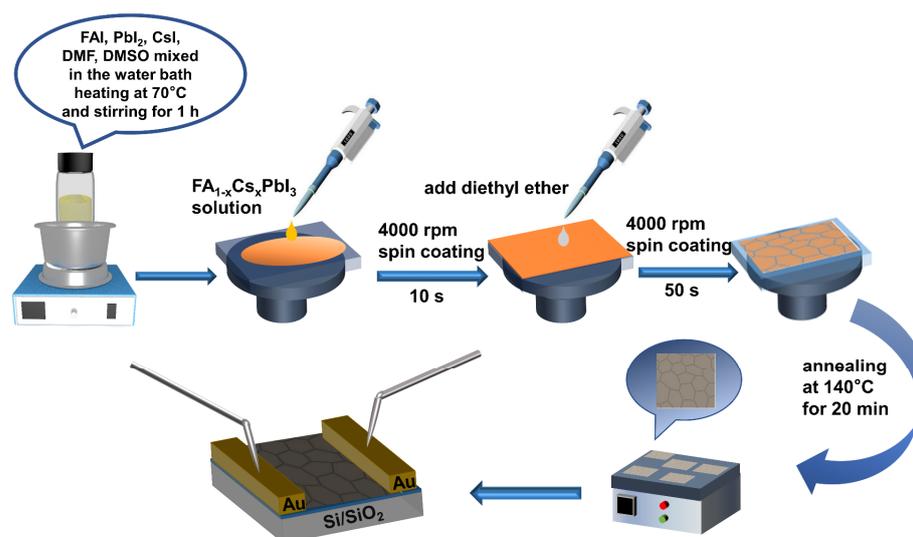


Figure 1. Flow chart of $\text{FA}_{1-x}\text{Cs}_x\text{PbI}_3$ thin-film device preparation.

3. Results and Discussion

Figure 2a–c shows SEM images of as-prepared $\text{FA}_{1-x}\text{Cs}_x\text{PbI}_3$ thin films with three different compositions, where x is equal to 0.10, 0.15, and 0.20, respectively. It is evident that a thin perovskite film can be manufactured with a large grain size when x is equal to 0.15, as this results in a film that is smooth, flat, and compact. Figure S1 is a statistical diagram and summary of the relevant SEM grain size data (Supporting Information, SI). A cross-sectional SEM image reveals that $\text{FA}_{0.85}\text{Cs}_{0.15}\text{PbI}_3$ films have a uniformly thick epilayer and a clearly defined film-substrate interface (Figure 2d–f). The reason for the difference in film thickness can be ascribed to the varied concentration of precursor solution with the Cs^+ doping. The corresponding effect of various Cs^+ contents on the evolution of film morphology is depicted in Figure S2, which can be found in reference [19]. When x is equal to 0, 0.1, 0.2, 0.25, or 1, it is easy to discover that discontinuous films with obvious holes or defects will be formed. This result stands in striking contrast to the one that was obtained when x was equal to 0.15, in which a perovskite with a continuous film of relatively high quality was discovered. The $\text{FA}_{0.85}\text{Cs}_{0.15}\text{PbI}_3$ thin film also has a smoother surface and more uniform element distribution, as seen in the SEM image of the $\text{FA}_{1-x}\text{Cs}_x\text{PbI}_3$ thin film and the corresponding element mapping in Figure S3. This is indicative of higher crystallinity and fewer defects in the $\text{FA}_{0.85}\text{Cs}_{0.15}\text{PbI}_3$ thin film. Therefore, the Cs^+ contents play an important role in the evolution of the film's morphology [19].

The X-ray diffraction (XRD) patterns of $\text{FA}_{1-x}\text{Cs}_x\text{PbI}_3$ samples with various Cs ratios ($x = 0, 0.1, 0.15, \text{ and } 0.2$) are being researched to shed light on the effect that the concentration of Cs^+ has on the perovskite structure. It is clear from Figure 3a that the δ -FAPbI₃ phase exists at a diffraction angle of 11.8° when $x = 0$ and 0.1 and that this phase is responsible for the bulk of the $x = 0$ case. This is consistent with reports in the literature [12,31,32] and is the result of moisture-induced perovskite crystallization, which is unpredictable and randomly oriented. At $x = 0.1$, however, the δ -FAPbI₃ phase begins to weaken, and by $x = 0.15$, it has almost completely disappeared. The results of which show that the formation of the δ -FAPbI₃ phase can be promoted even at a Cs doping concentration of 15%. Moreover, the characteristic peaks of the (001), (110), (111), (002), (012), (211), (022), and (003) for α -phase can be seen at diffraction angles of $14^\circ, 19.8^\circ, 24.2^\circ, 28^\circ, 31.5^\circ, 40^\circ, \text{ and } 42^\circ$, respectively. The cubic structure is characterized by the diffraction peaks and their characteristic shapes. The XRD pattern of CsPbI_3 ($x = 1$) is depicted in Figure 3b, and we can see that the characteristic diffraction peaks correspond very closely to those on the standard card (PDF#74-1970). Figure S5 displays the XRD patterns for the other individual $\text{FA}_{1-x}\text{Cs}_x\text{PbI}_3$ thin films with the following values for x : 0, 0.1, 0.15, and 0.2. In the cases of $x = 0$ and 0.1, the diffraction peaks at 12.7° corresponding to PbI_2 residue are observed

in Figure S5a,b. This is likely due to the FAI depletion and suppressed FAI intercalation into the underneath PbI_2 [12]. In contrast, when the value of x was equal to 0.15, the PbI_2 diffraction peak disappeared, illustrating the high-purity $\text{FA}_{0.85}\text{Cs}_{0.15}\text{PbI}_3$ thin film.

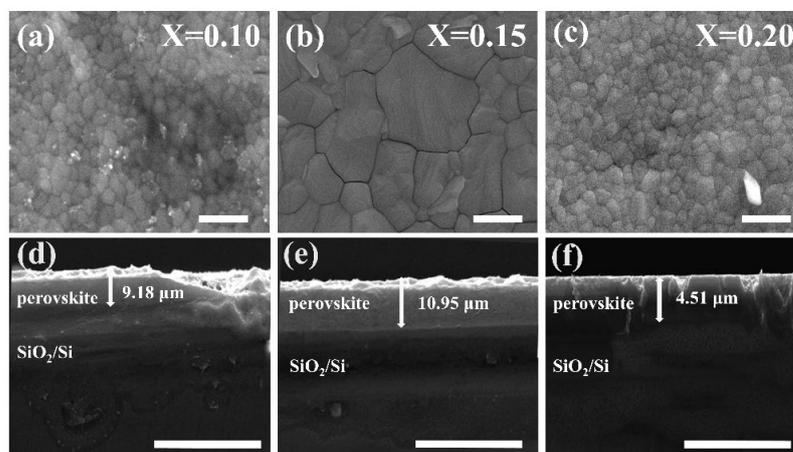


Figure 2. (a–c) SEM images of $\text{FA}_{1-x}\text{Cs}_x\text{PbI}_3$ thin films with varying compositions ($x = 0.10, 0.15,$ and $0.20,$ respectively), scale bar, $2 \mu\text{m}$. (d–f) show the corresponding ($x = 0.10, 0.15,$ and $0.20,$ respectively) cross-section SEM image of the $\text{FA}_{1-x}\text{Cs}_x\text{PbI}_3$ thin films; the thickness is $9.18 \mu\text{m}, 10.95 \mu\text{m}, 4.51 \mu\text{m},$ respectively, scale bar, $100 \mu\text{m}$.

To further illustrate, Figure 3c displays the photoluminescence (PL) spectra of five $\text{FA}_{1-x}\text{Cs}_x\text{PbI}_3$ samples with varying Cs ratios ($x = 0, 1, 0.1, 0.15,$ and 0.2). At approximately $750\text{--}830 \text{ nm}$, it was discovered that each and every $\text{FA}_{1-x}\text{Cs}_x\text{PbI}_3$ thin film exhibited a distinctive luminescence peak. According to the results of the normalized PL peaks, as the value of x increases from 0 to 0.1, 0.15 to 0.2, and 1, respectively, the peak of the $\text{FA}_{1-x}\text{Cs}_x\text{PbI}_3$ thin film has a blue shift from 801 to 790, 789, 788, and 760 nm. The blue shift in the PL peak can be caused by the slightly increased band gap of the $\text{FA}_{1-x}\text{Cs}_x\text{PbI}_3$ perovskites along with the increase in “ x ” values. This phenomenon is consistent with the findings of an earlier study [28]. Moreover, in terms of peak intensity, wavelength position, and FWHM, when compared to thin films with other concentrations of Cs^+ ($x = 0, 1, 0.1,$ and 0.2), our results showed that our films had the best characteristics (Table S1). For $x = 0, 1, 0.10, 0.15,$ and $0.20,$ the calculated FWHM values are 44.15, 42.31, 42.58, 36.18, and 42.42 nm. When CsI is added, the FWHM decreases, which is consistent with larger crystallite size according to the Scherrer equation ($D = K\lambda/\beta\cos\theta$), while an increase in FWHM above the value of $x = 0.20$ is probably attributable to the formation of an impurity [28]. In accordance with the XRD results and in agreement with a previous study [28], the highest purity of the $\alpha\text{-FAPbI}_3$ phase formed at $x = 0.15$ is found in $\text{FA}_{0.85}\text{Cs}_{0.15}\text{PbI}_3$, indicating that when the Cs ratio is 15%, a suppressed non-radiative recombination induced by reduced traps and defects within the perovskite [12] supports the formation of the phase. The intensity decrease in PL can be ascribed to the presence of lattice defects and increased grain boundaries in the $\text{FA}_{1-x}\text{Cs}_x\text{PbI}_3$ ($x = 0, 1, 0.1,$ and 0.2) material with non-uniform film morphology. The presence of lattice defects and grain boundaries can increase the non-irradiation recombination of photogenerated charge carriers, giving rise to decreased PL intensity. In addition to this, the half width of the luminescence peak is at its narrowest when x is equal to 0.15, which indicates that the quality of the perovskite film is higher when this ratio is used. These results provide further confirmation of the important role that the Cs^+ content plays in initiating the morphological evolution of the films.

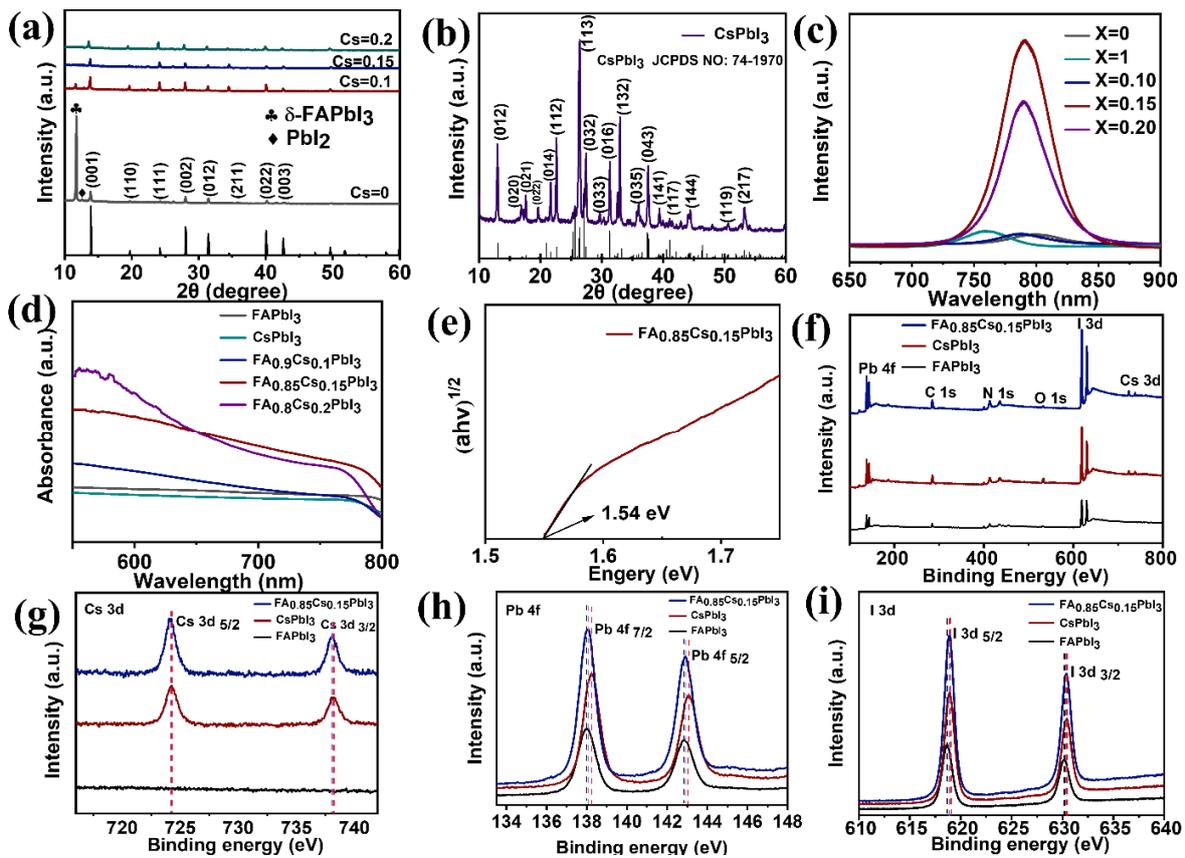


Figure 3. (a) XRD patterns of the FA_{1-x}Cs_xPbI₃ thin film ($x = 0, 0.10, 0.15,$ and $0.20,$ respectively); (b) XRD patterns of the CsPbI₃ thin film; (c) photoluminescence (PL) spectra of FA_{1-x}Cs_xPbI₃ thin film ($x = 0, 1, 0.10, 0.15,$ and $0.20,$ respectively); (d) the UV-vis absorbance spectra of FA_{1-x}Cs_xPbI₃ thin film ($x = 0, 1, 0.10, 0.15,$ and $0.20,$ respectively); (e) the relationship between $(ahv)^{1/2}$ and photon energy of FA_{0.85}Cs_{0.15}PbI₃ thin film; (f) XPS spectra of FAPbI₃ (black), CsPbI₃ (red) and FA_{0.85}Cs_{0.15}PbI₃ (blue) thin film; (g–i) the corresponding Cs 3d, Pb 4f and I 3d spectra, respectively.

Figure 3d shows the corresponding ultraviolet–visible (UV-vis) absorbance spectra of the FA_{1-x}Cs_xPbI₃ thin films; we can see the FA_{0.85}Cs_{0.15}PbI₃ thin film exhibits the strongest absorbance. The UV-vis spectra of FA_{1-x}Cs_xPbI₃ thin films ($x = 0, 0.1, 0.2,$ and 1) are blue-shifted compared to that of FA_{0.85}Cs_{0.15}PbI₃ thin film. The combined characterizations of PL, XRD, and SEM suggest that FA_{0.85}Cs_{0.15}PbI₃ thin film has large grain sizes, low defect density, and a small band gap. Compared to FA_{0.85}Cs_{0.15}PbI₃ thin film, other FA_{1-x}Cs_xPbI₃ ($x = 0, 0.1, 0.2,$ and 1) thin films showed blue shift due to their larger band gaps. Then the band gap of FA_{0.85}Cs_{0.15}PbI₃ thin film, as shown in Figure 3e, was calculated via the transformed Kubelka–Munk formula [33]:

$$\alpha(hv) = A(hv - E_g)^{1/2} \tag{2}$$

where α signifies the absorption coefficient, hv is the incident photon energy, A represents the constant depending on transition probability, and E_g is the optical bandgap. Accordingly, the band gap of 1.54 eV for FA_{0.85}Cs_{0.15}PbI₃ thin film is obtained, which is similar to the previous study [19].

In order to investigate the effect that doping with Cs had on the chemical composition of perovskite films, X-ray photoelectron spectroscopy (XPS) was utilized. For FAPbI₃, CsPbI₃, and FA_{0.85}Cs_{0.15}PbI₃, the core level peaks assigned to C, N, O, Cs (except for FAPbI₃), Pb, and I are shown in Figure 3f. Several sets of results for various Cs⁺ concentrations are shown in Figure S4. Figure 3g is an XPS spectrum of the Cd 3d_{5/2} and Cd 3d_{3/2} peaks, showing that the peaks in FA_{0.85}Cs_{0.15}PbI₃ are at 724.1 eV and 738.1 eV, while

the peaks in CsPbI₃ are at 724.2 eV and 738.2 eV. These results indicate that there is no Cs signal characteristic in FAPbI₃ thin film. Since the bond energy between Cs⁺ and [PbI₆]⁴⁻ is stronger than that between FA⁺ and [PbI₆] [34], both Cd 3d_{5/2} and Cd 3d_{3/2} of CsPbI₃ move 0.1 eV towards higher binding energy compared to FA_{0.85}Cs_{0.15}PbI₃.

Figure 3h displays the Pb 4f spectrum of FAPbI₃, which has two peaks at 138.0 eV and 142.8 eV, which correspond to Pb 4f_{7/2} and Pb 4f_{5/2}, respectively. When comparing FA_{0.85}Cs_{0.15}PbI₃ to FAPbI₃, the binding energies of both Pb 4f_{5/2} and Pb 4f_{7/2} move up by 0.1 eV. The shift of Pb 4f peaks towards higher binding energy is indicative of an increase in the cationic charge of Pb ions, which is responsible for the change in the chemical bonding nature between Pb and I [35]. This change in bonding nature is responsible for the fact that the Pb 4f peaks shifted towards higher binding energy. It is clear that the bond energy between Cs⁺ and [PbI₆]⁴⁻ is stronger than that between FA⁺ and [PbI₆]⁴⁻ because the binding energies of Pb 4f_{7/2} and Pb 4f_{5/2} of CsPbI₃ are higher than those of FA_{0.85}Cs_{0.15}PbI₃, respectively (by 0.1 eV and 0.2 eV, respectively). In addition, there was some variation in the I elements representing the formamidine building blocks (Figure 3i). Table 1 presents the corresponding values for the binding energies. These findings provide additional evidence that Cs was able to be successfully incorporated into the FAPbI₃ perovskite lattice to produce the FA_{0.85}Cs_{0.15}PbI₃ perovskite.

Table 1. The XPS data comparison of FAPbI₃, CsPbI₃, and FA_{0.85}Cs_{0.15}PbI₃ for Cs 3d, Pb 4f, and I 3d core levels.

Binding Energy (eV)	FAPbI ₃	CsPbI ₃	FA _{0.85} Cs _{0.15} PbI ₃
I 3d _{3/2}	630.2	630.5	630.4
I 3d _{5/2}	618.7	619.0	618.9
Pb 4f _{5/2}	142.8	143.1	142.9
Pb 4f _{7/2}	138.0	138.2	138.1
Cs 3d _{3/2}	–	738.2	738.1
Cs 3d _{5/2}	–	724.2	724.1

We fabricated FA_{1-x}Cs_xPbI₃-based optoelectronic devices by depositing an Au electrode on the surface of FA_{1-x}Cs_xPbI₃ thin film. This allowed us to study the optoelectronic properties of the FA_{1-x}Cs_xPbI₃ thin film. Figure 4 depicts the current–voltage (*I*-*V*) characteristics of FA_{1-x}Cs_xPbI₃ thin-film photodetectors doped with various concentrations of Cs⁺ at room temperature and atmospheric pressure and under illumination from an incandescent lamp with a power density of 21.57 mW/cm² in the dark. The on/off ratios of the photodetectors of FAPbI₃, CsPbI₃, FA_{0.9}Cs_{0.1}PbI₃, FA_{0.85}Cs_{0.15}PbI₃, and FA_{0.8}Cs_{0.2}PbI₃ samples were calculated as 1.32, 0.77 × 10³, 0.66 × 10², 1.58 × 10³, and 0.43 × 10², respectively. The variation in current that occurs when the bias voltage changes from −3 V to 3 V is shown, and all of the Cs⁺ concentration results for doping indicate that the photocurrent is significantly higher than the dark current. It is likely that the surface state (such as surface defects and vacancies) at the FAPbI₃/Au interface [36] is responsible for the asymmetrical behavior of the *I*-*V* curves observed for pure FAPbI₃, as shown in Figure 4a,b. However, when doped with varying concentrations of Cs⁺ (*x* = 1, 0.1, 0.15, and 0.2, respectively), as shown in Figure 4c–j, there is an ohmic contact formed between the FA_{1-x}Cs_xPbI₃ thin film and the Au electrode because the *I*-*V* curves are almost symmetric. Under a bias voltage of 3 V, the photocurrent in the FA_{0.85}Cs_{0.15}PbI₃ thin-film photodetector is 1.51 × 10⁻⁸ A, the dark current is 9.54 × 10⁻¹² A, and the ratio of photocurrent to dark current (*I*_{light}/*I*_{dark}) is 1.58 × 10³, as shown in Figure 4g,h. As a result of the fact that the ratio of photocurrent to dark current in the other Cs⁺ doping concentrations (*x* = 0, 0.1, 0.2, 1) is relatively smaller in comparison to the FA_{0.85}Cs_{0.15}PbI₃ thin-film device, it is not conducive to the preparation and research of photodetectors. As a result, the photoconductive characteristics of the FA_{0.85}Cs_{0.15}PbI₃ thin-film device is studied in the majority of this research.

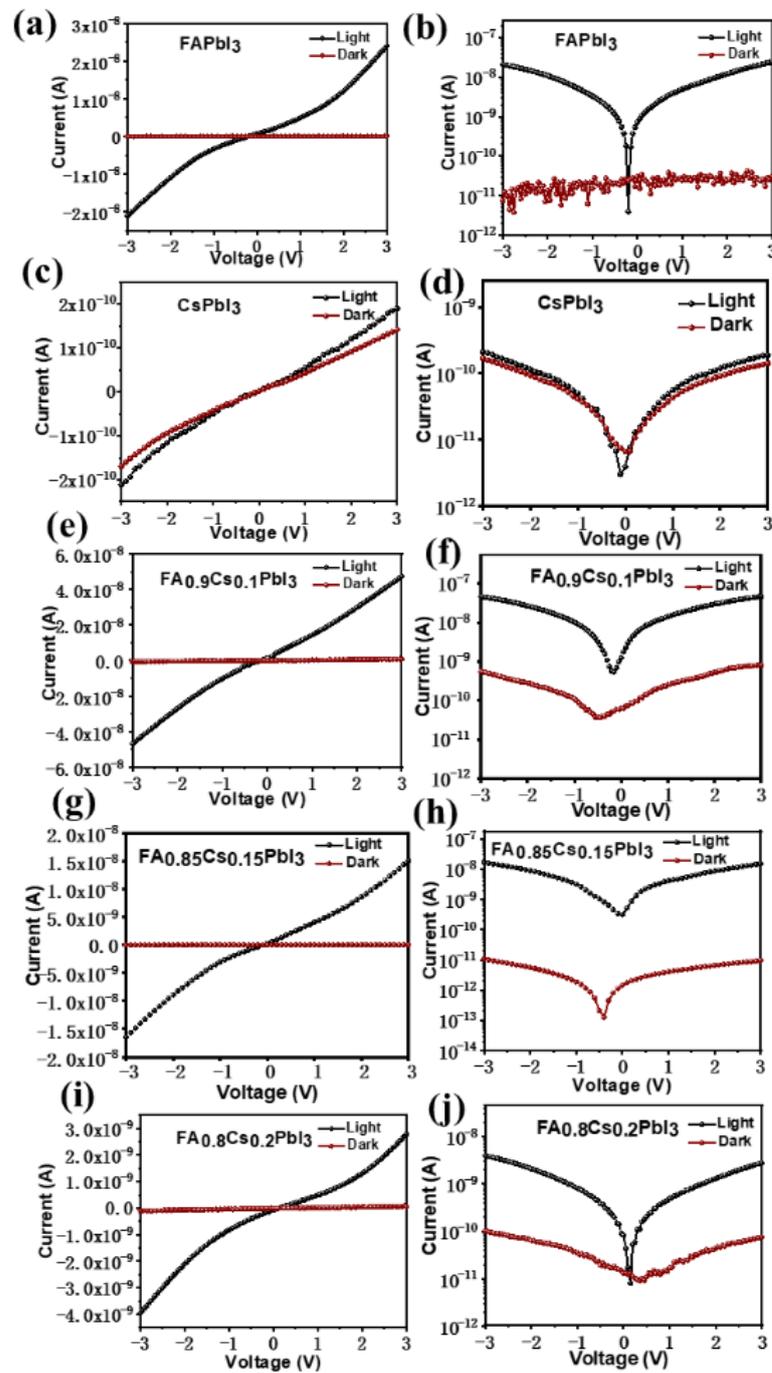


Figure 4. (a,c,e,g,i) *I-V* curve of the FA_{1-x}Cs_xPbI₃ thin-film device in light (black) and dark (red) conditions, respectively; (b,d,f,h,j) correspond to the (a,c,e,g,i) after logarithmic processing, respectively.

We measured the spectral response curves of the FA_{0.85}Cs_{0.15}PbI₃ thin-film device in the range of 530–830 nm in order to gain more insights into the optimal spectra of the FA_{0.85}Cs_{0.15}PbI₃ thin film. These curves are shown in Figure 5b, and they are elucidated in more detail below. The spectral response of the FA_{0.85}Cs_{0.15}PbI₃ thin film exhibits a wide photoresponse range, which extends from 560 to 790 nm. However, the photoresponse decreases dramatically at approximately 790 nm. The device’s best wavelength selectivity is demonstrated by the fact that its largest photoresponse is at 790 nm. As a result, we intend to investigate the photoelectric characteristics of a thin-film device made from FA_{0.85}Cs_{0.15}PbI₃ while exposed to 790 nm light.

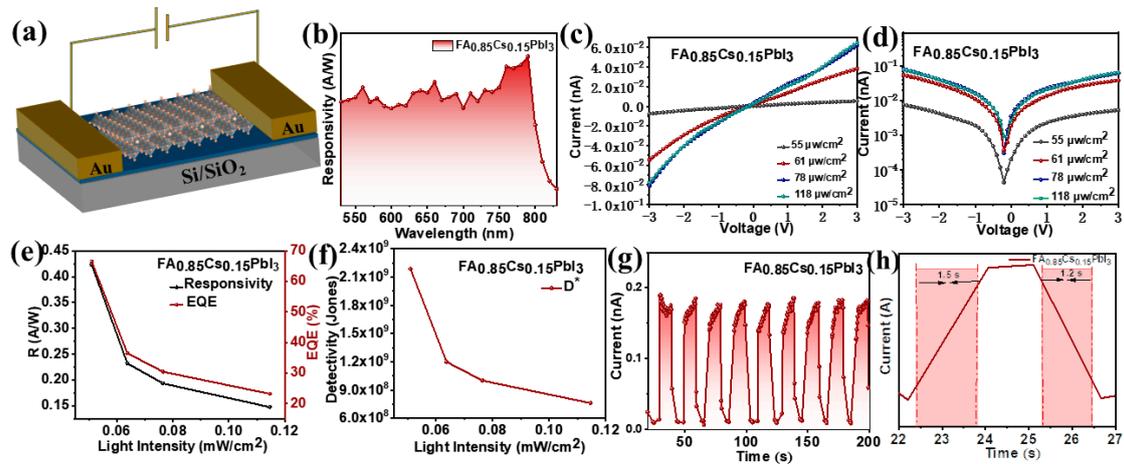


Figure 5. (a) Schematic illustration of the $FA_{1-x}Cs_xPbI_3$ photodetector; (b) spectral responsivity of the $FA_{0.85}Cs_{0.15}PbI_3$ thin-film photodetector at 3 V bias; (c) I - V curves of the $FA_{0.85}Cs_{0.15}PbI_3$ thin-film device at different light power density; (d) I - V curves of (c) after logarithmic processing; (e) diagrams of responsivity and optical power density; (f) relationship between detectivity and optical power density; (g) the $FA_{0.85}Cs_{0.15}PbI_3$ thin-film device relationship between the current and time of a periodically switched light source under 790 nm light illumination at a bias of 3 V; (h) voltage rise and decay edge of pulse response.

The I - V curves at varying light intensities for the prepared $FA_{0.85}Cs_{0.15}PbI_3$ thin-film photodetector are shown in Figure 5c. From the I - V curves, one can see that the photocurrent increases dramatically with an increase in light intensity, suggesting that the number of photogenerated carriers is related to the absorbed photon fluxes [37]. As shown in Figure 5d, for the I - V curve of (c) after logarithmic processing, the logarithmic I - V plot displays near symmetry at voltage biases of (-3 V– 3 V), indicating that the ohmic contacts between the $FA_{0.85}Cs_{0.15}PbI_3$ thin-film surfaces and the deposited Au electrodes are strong.

In order to conduct a more in-depth analysis of the performance of the $FA_{0.85}Cs_{0.15}PbI_3$ thin-film device, important parameters such as spectral responsivity (R), external quantum efficiency (EQE), and detection rate (D^*) were computed by making use of the following equations [38–40]:

$$R_\lambda = \frac{I_p - I_d}{P_\lambda A} \quad (3)$$

$$EQE = R_\lambda \left(\frac{hc}{q\lambda} \right) \frac{1}{\eta} \quad (4)$$

$$D^* = R_\lambda \sqrt{\frac{A}{2qI_d}} \quad (5)$$

where I_p is the photocurrent, I_d is the dark current, P is the light power density, A is the detector’s valid area, h is the Planck constant, c is the speed of light in a vacuum, q is the charge of an electron, λ is the wavelength of the incident light, and EQE is the quantum efficiency. In our work, the distance between the source light and the photodetector is 1.8 cm, and the effective area of illumination is $3.634 \times 10^{-5} \text{ cm}^2$. According to the information presented above, it was determined that the R , EQE , and D^* values of the devices when exposed to light with a wavelength of 790 nm are, respectively, 0.42 A/W, 66.5%, and 2.2×10^9 Jones. As shown in Figure 5e,f, the decrease in response can be attributed to the deterioration of the $FA_{0.85}Cs_{0.15}PbI_3$ thin film, which was influenced by the light and the air around it. In addition, from the curves of R , EQE , and D^* corresponding to the $FA_{0.85}Cs_{0.15}PbI_3$ thin-film device with light intensity, we can see that R , EQE , and D^* decrease with the increase in light intensity, indicating that the recombination loss in the device cannot be ignored.

In Figure 5g, the findings demonstrate that chopper illumination can efficiently and reproducibly alter the FA_{0.85}Cs_{0.15}PbI₃ thin-film device’s low and high current conduction states. In Figure 5h, we see a single cycle of FA_{0.85}Cs_{0.15}PbI₃ thin film’s response, which reflects the response time, are, respectively, 1.5 and 1.2 s, which is defined as the time it takes for the value to rise from 10% to 90% of its maximum and fall back down to 10% of its maximum value. This is the rise time and decay time, respectively [41]. The FA_{0.85}Cs_{0.15}PbI₃ thin film deterioration may be related to its slow degradation rate. This indicates that the performance of FA_{0.85}Cs_{0.15}PbI₃ thin film photodetector is still inadequate. As can be seen in Table 2, we compared the performance of the reported results. In addition, Figure 6 exhibits the *I-V* curves of the as-fabricated device after being stored in the air for five days (red curve). It was found that the photocurrent was 2.17 nA under 3 V bias; the device dropped to 14.3% of its initial value after being stored in the air for 5 days (black curve). In summary, the performance of formamidine-based perovskites is impacted by their level of stability. Next, we discuss the factors that affect stability.

Table 2. Performance comparison of different photodetectors.

Device Structure	Method	Wavelength (nm)	I_{light}/I_{dark}	R_{λ} (A W ⁻¹)	EQE (%)	D* (Jones)	Rise/Decay (ms)	Ref
Au/(BA) ₂ FAPb ₂ I ₇ /	-	405	-	0.95	-	-	62/57	[42]
ITO/MA _{1-x} FA _x (Br _{0.65} C _{10.35}) ₃ thin film/Au	A-site compositional	450	5.72×10^5	0.28	77.4	5.08×10^{12}	585/531	[43]
ITO/SnO ₂ /FAPbI ₃ /Spiro-OMeTAD/Ag	Additive engineering	700	-	0.48	95	2×10^{11}	0.00394/0.00476	[44]
FTO/Cs _{0.05} MA _{0.16} FA _{0.79} Pb(I _{0.9} Br _{0.1}) ₃ /Spiro/Au	-	-	7.3×10^5	0.52	-	8.8×10^{12}	0.019/0.021	[45]
PET/ITO/SnO ₂ /Active layer/CuI/Au Active layer: MBI, MBIB, MBIC films	chemical-vapor-deposited	382	-	0.30(MBI) 0.63(MBIB) 0.92(MBIC)	-	0.9×10^{13} 2×10^{13} 2.9×10^{13}	-	[46]
Pt NP@TiO ₂ /Ga ₂ N NRs	-	382	-	44.6	8.65×10^3	1.57×10^{14}	180/200	[47]
Au NPs@ZnO NWs	hydrothermal	325	-	0.000485	-	27.49×10^{10}	-	[48]
SiO ₂ /FA _{0.85} Cs _{0.15} PbI ₃ thin film/Au	solution	790	1.58×10^3	0.42	66.5	2.2×10^9	1500/1200	This work

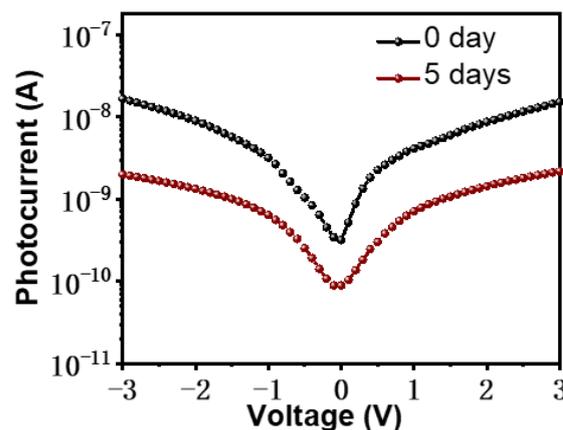


Figure 6. *I-V* curve of the initial photocurrent (black curve) of FA_{0.85}Cs_{0.15}PbI₃ thin film and after five days (red curve).

The stability of a perovskite based on formamidinium can be broken down into two categories: intrinsic properties and environmental influences, considering the influence of ambient air oxygen and moisture levels. For example, in the mapping characterization of FA_{0.85}Cs_{0.15}PbI₃ thin film, we can observe the rich oxygen element part from the oxygen component that is possible from the oxygen in the air that has been adsorbed on its surface, which is also the reason why its possible degradation is a possibility. It has been reported that oxygen molecules that are adsorbed on perovskite films can obtain photogenerated

electrons to form superoxide ions when the film is illuminated. These superoxide ions are then easily dehydrogenated with organic cations in perovskite, which leads to the decomposition of perovskite crystals (photo-oxygen-induced decomposition). It has been discovered that the incorporation of moderate Cs^+ ions into MAPbI_3 or formamidinium-based perovskite acts as a powerful stabilizer, preventing the decomposition of the perovskite in the presence of oxygen and light [49]. It has also been shown that perovskite crystalline materials such as MAPbI_3 tend to decompose to PbI_2 when exposed to moisture because of the bonding interactions between MA^+ and H_2O molecules. Niu et al. [50] proposed that perovskite degradation starts with the deprotonation of methylammonium cations by water to produce methylamine, hydrogen iodide, and lead iodide, which breaks down the bonding. On the other hand, the same bond is present between FAPbI_3 molecules and H_2O molecules. To prevent moisture from penetrating and increase device stability, Chen et al. [51] introduced trace amounts of hydrophobic molecules from outside the perovskite layers. In addition, light and electric fields, etc., can also have an effect on its performance. For example, Liu et al. [52] prepared an innovative resistive memory based on CsPbBr_3 QDs:GO hybrid film by controlling the light and electric fields of the device, which exhibited good performance. Meng et al. [48] reported outstanding SPUVPD performances of the Pt NP@ TiO_2 /GaN NRs hybrid heterojunction, which was due to the abundant light absorption and better charge collection (hot electrons) by the enhanced LSPR effect and the adequate interfacial charge separation of photogenerated e/h pairs by its enhanced built-in field and the effective charge transport via the appropriate energy band alignment. As a result, the effective coupling effect of the LSPR effect of Pt NP with TiO_2 /GaN NRs heterojunction significantly enhances the optoelectrical properties.

A number of intrinsic factors, such as ion migration [53,54], phase instability [55,56], metal-perovskite reactions [57], residual strain [57], photoinduced strain [58], etc., contribute to the instability of perovskite devices [59]. Once ion migration has taken place in perovskite materials, the loss of perovskite ions causes the perovskite lattice to collapse, which results in changes to the composition and morphology of perovskite films. Perovskite materials are doomed to destruction if a process known as dynamic ion migration is allowed to take place [57]. Xia et al. [60] demonstrated strong photoinduced polarization strain in triple-cation mixed-halide perovskite CsFAMA by examining the concurrent evolution of ionic distribution and spontaneous polarization of CsFAMA under light illumination using dynamic-strain-based scanning probe microscopy. Strong linear piezoelectricity arising from photo-enhanced polarization was observed, while ionic migration was found to be not significantly increased by lightening. Their research proved that ionic migration, polarization, and photocurrent hysteresis are directly correlated at the nanoscale.

It has been found that the phenomenon of ion migration in the MAPbI_3 thin film can make the process of photo-oxygen-induced decomposition inside the perovskite even more severe. This is the case due to the fact that the movement of iodide ions, while they are subject to an electric field, can result in the formation of iodine vacancies (defects), and the accumulation of iodine vacancies can increase the generation rate of superoxide ions and speed up the process of photo-oxygen-induced decomposition of perovskites [49]. Additionally, Li et al. [58] observed that the photoinduced strain-promoted variations in mechanical properties were caused by the reversible migration of MA^+ cations. However, FAPbI_3 is prone to phase transition at room temperature ($\alpha \rightarrow \delta$ phase transition), and pure α -phase FAPbI_3 perovskite generally requires high annealing temperature, both of which degrade the stability of the device. It has been shown that Au atoms/ions can diffuse through organic hole transport layers into the perovskite layer and react with the perovskite [61], and such Au-perovskite reactions can be promoted by continuous light illumination and high thermal stress. A systematic investigation into the mechanism of Au electrode degradation due to reaction with iodine-based perovskites was reported by Tarasov et al. [62]. At room temperature, they discovered that the reactive MAI-nI₂ tends to oxidize the Au electrodes, leading to the formation of a new $(\text{MA})_2\text{Au}_2\text{I}_6$ phase at the perovskite/Au interface. This demonstrates that the metal-perovskite reaction has

an effect on the stability of the device's performance. Because of their polycrystalline structure, organometallic perovskites are also subject to the detrimental effects of lattice strain on the residual strain. It has been shown that during film formation in perovskite, residual strain can be generated in the lattice via thermal annealing [63]. Specifically, lattice strain within the thin film would induce chemical degradation of the perovskite after it has been cooled down from a thermal annealing state because the substrate would prevent the perovskite from shrinking. It is also possible for the hybrid perovskites to experience material inhomogeneity as a result of component separation [64,65] and/or thermal stress, which may result from chemical mismatches between the components and/or from non-equilibrium growth conditions during film fabrication [66]. Furthermore, phase separation is thought to be a serious material inhomogeneity that deviates from the initially expected material properties and reduces device performance (efficiency and operational stability) [67,68]. There is a correlation between emerging residual strain and local lattice mismatch in thin films, which indicates a moderate level of material inhomogeneity. The crystal microstructure of the perovskite thin film can be distorted by this residual strain, which can have an effect on the film's properties [66,69–73].

4. Conclusions

In conclusion, $\text{FA}_{1-x}\text{Cs}_x\text{PbI}_3$ thin films were successfully synthesized in the atmospheric environment using the simple solution method. It was demonstrated, on the basis of a number of characterization results, that the Cs^+ doping concentration is relatively ideal when set at 15%. Furthermore, $\text{FA}_{0.85}\text{Cs}_{0.15}\text{PbI}_3$ thin film was prepared into an optoelectronic device for the purpose of research, and it was discovered that the photoelectric characteristics are affected by degradation factors; consequently, the possible degradation factors were discussed. Our results highlight the significance of controlling doped Cs concentrations and gaining insight into their potential degradation factors, which serve as a benchmark for the systematic optimization of FA-based perovskite devices, paving the way for their use in photovoltaics and other fields.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/photonics10030312/s1>, Figure S1: (a–e) SEM images of $\text{FA}_{1-x}\text{Cs}_x\text{PbI}_3$ thin films with different Cs^+ contents ($x = 0, 0.10, 0.15, 0.20$ and 1 , respectively). (f) Statistical diagram of the grain sizes of the $\text{FA}_{1-x}\text{Cs}_x\text{PbI}_3$ thin films; Figure S2: (a–f) SEM images of $\text{FA}_{1-x}\text{Cs}_x\text{PbI}_3$ thin films with different Cs^+ contents ($x = 0, 0.10, 0.15, 0.20, 0.25$, and 1.0 , respectively); Figure S3: EDX elemental mapping of $\text{FA}_{0.85}\text{Cs}_{0.15}\text{PbI}_3$ thin film; Figure S4: Survey XPS spectra of (a) $\text{FA}_{0.9}\text{Cs}_{0.1}\text{PbI}_3$ and (b) $\text{FA}_{0.8}\text{Cs}_{0.2}\text{PbI}_3$, respectively; Figure S5: (a–d) XRD patterns of FAPbI_3 , $\text{FA}_{0.9}\text{Cs}_{0.1}\text{PbI}_3$, $\text{FA}_{0.85}\text{Cs}_{0.15}\text{PbI}_3$ and $\text{FA}_{0.8}\text{Cs}_{0.2}\text{PbI}_3$ thin films, respectively; Table S1: The PL data of $\text{FA}_{1-x}\text{Cs}_x\text{PbI}_3$ thin films ($x = 0, 1, 0.1, 0.15$ and 0.2 , respectively) with peak intensity, wavelength position, and FWHM.

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