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Effect of Polarization on Performance of Inverted Solar Cells Based on Molecular Ferroelectric 1,6-Hexanediamine Penta iodide Bismuth with PCBM as Electron Transport Layer

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Abstract: The depolarization field of ferroelectric photovoltaic materials can enhance the separation and transport of photogenerated carriers, which will improve the performance of photovoltaic devices, thus attracting the attention of researchers. In this paper, a narrow bandgap molecular ferroelectric Hexane-1,6-diammonium penta iodobismuth (HDA-BiI₅) was selected as the photo absorption layer for the fabrication of solar cells. After optimizing the ferroelectric thin film by the antisolvent process, the effect of different polarization voltages on the performance of ferroelectric devices was studied. The results showed that there was a significant increase in short-circuit current density, and the photoelectric conversion efficiency showed an overall increasing trend. Finally, we analyzed the internal mechanism of the effect of polarization on the device.

Keywords: ferroelectrics; solar energy materials; thin films

1. Introduction

Ferroelectric materials have come to the attention of researchers because of their ferroelectric photovoltaic effect, a phenomenon that modulates photovoltaic states through polarization [1–3]. Then, with the progress of film preparation technology and the gradual improvement of ferroelectric polarization theory, people found that compared with block material, ferroelectric film has more excellent photovoltaic properties [4].

The ideal band gap range for materials used in solar cells is 1 to 1.5 electron volts, while the band gap is wider for ferroelectric photovoltaic materials. Common ferroelectric materials, such as BiFeO₃, BaTiO₃ and Pb(Zr,Ti)O₃ (PZT), have band gaps greater than 2.5 eV and can only absorb the ultraviolet part of sunlight. Basu et al. obtained the short-circuit current of 13.4 μA/cm² in the device based on BiFeO₃, a ferroelectric material [5]. Dong et al. also obtained devices based on this material with short-circuit current density and open-circuit voltage of 0.13 × 10^{−3} A/cm² and 0.65 V, respectively [6]. There are not many ferroelectric materials that can be used as photovoltaic materials for energy, which cannot achieve high photoelectric conversion efficiency (PCE) [7]. Therefore, finding ferroelectric materials with appropriate band gaps is the key to improve the performance of ferroelectric photovoltaic devices.

As more and more people started to explore the synthesis of a narrow bandgap ferroelectric material, a new organic–inorganic hybrid molecular ferroelectric material Hexane-1,6-diammonium penta iodobismuth [C₆N₂H₁₈]BiI₅ (HDA-BiI₅) was reported by Zhang et al., who stated that this ferroelectric material not only possesses good stability and ferroelectricity, but also has the narrowest band system of 1.89 eV of the current molecular

ferroelectric material, which means that it can convert most of the visible light energy into electrical energy [8]. Liu et al. fabricated conventional photodetectors using this material, and the photocurrent density of the device was $17.5 \mu\text{A}/\text{cm}^2$. After polarization, the photocurrent generated by the ferroelectric photovoltaic device was significantly increased, reaching the maximum of $92.4 \mu\text{A}/\text{cm}^2$ [9]. In David M's work, the device exhibited a short-circuit photocurrent density (JSC) of $0.124 \text{ mA}/\text{cm}^2$, an open-circuit photovoltage of 403 mV, a fill factor of 0.43, and an photoelectric conversion efficiency of 0.027% [10]. Their work showed a significant increase in photogenerated current in ferroelectric photovoltaic devices after polarization. There are results proving that ferroelectric polarization is responsible for high photovoltage and effective separation of photoexcited electron-hole pairs [11,12].

Since the study of HDA-BiI₅ is still in its infancy, there are no reports on the photovoltaic performance of the polarized inverted devices based on this material. Since the inverted structure photovoltaic device is conducive to reducing hysteresis and the preparation process is simple [13], in this paper we have used this structure to prepare ITO/NiO_x/HDA-BiI₅/PCBM/Ag solar cells. Optimization of the film quality using the antisolvent process is also a very critical step to improve the device performance [14,15], therefore the effect of different polarization voltages on the device open circuit voltage, short circuit current density, fill factor and PCE before and after optimization using chlorobenzene as an antisolvent was investigated. The results of the study provide a reference value for the application of molecular ferroelectric materials as photo absorption layers in solar cells.

2. Experimental

2.1. Materials

Indium tin oxide (ITO), N, N-dimethylformamide (DMF, 99.8%), methyl ammonium iodide (CH₃NH₃I, > 99.5%), and dense nickel oxide spin coating solution (HT-NiO_x 99.98%) were obtained from Shanghai Mater Win New Materials Co., Ltd., Shanghai, China. Hydroiodic acid (HI $\geq 45\%$), bismuth iodide (BiI₃ 98%), and 1, 6-hexanediamine (H₂N(CH₂)₆NH₂ 99.5%) were purchased from Xi'an Polyme Light Technology Corp., Xi'an, China. Ethanol, and isopropyl alcohol and acetone were bought from Sinopharm Chemical Reagent Co., Ltd., Beijing, China.

2.2. Device Fabrication

2.2.1. ITO Substrate Cleaning

First, the ITO glass substrate was immersed in a Petri dish containing a mixture of cleaning agent and deionized water for 10 min, with the aim of removing impurities and grease from the surface of the substrate and improving the conductivity of the substrate. Then, we placed the cleaned ITO substrate glass conductive surface facing upward in the Petri dish. The washing solution (volume ratio of acetone isopropanol-deionized water = 1:1:1) was added to the Petri dish. Then, the Petri dish was put into the ultrasonic cleaner for 20 min and the ITO was washed with ethanol, referring to the above method. Finally, the dried ITO glass substrate was put into a drawer-type UV light washer and treated with UV ozone for 15 min to eliminate organic impurities and improve hydrophilicity.

2.2.2. Ferroelectric Materials Formation

BiI₃ (10.0 mmol, 5.90 g) powder was added to an excess of HI (45%, 100 mL) solution and heated and stirred for more than 4 h. The external heating temperature was maintained at about 90 °C until the powder was completely dissolved. Then, H₂N(CH₂)₆NH₂ (1,6-hexanediamine; 10.0 mmol, 1.16 g) was added to the completely dissolved solution and heated and stirred for 24 h. A thermometer was inserted inside to maintain its temperature at about 90 °C, at which time the external heating temperature was about 135 °C. After the solution was completely reacted, it was heated and dried on a hot plate at 90 °C until brick-red crystals were precipitated, at which time the ferroelectric material HDA-BiI₅

was obtained for this experiment. The crystals were ground into a powder and put into a glass jar.

2.2.3. Ferroelectric Thin Film Formation

The ground ferroelectric powder was dissolved in DMF solution at a ratio of 500 mg/0.4 mL and heated and stirred for 4 h or sonicated with ultrasonic equipment for 3 h until the powder was completely dissolved, at which point the solution turned dark brown. The completely dissolved solution was filtered through a 0.22 μm diameter filter to obtain the solution for spin coating. The cleaned and ozonated ITO substrate is placed in the center of the homogenizer and the vacuum pump is turned on so that the substrate is tightly attached to it. Before spin-coating, the possible dust was removed with a rubber suction bulb, 40 μL of the solution was taken by pipette gun and applied to the substrate uniformly in drops, and then spun at 6000 r.p.m. for 40 s. The finished spin-coating sample was placed on a hot plate at 150 $^{\circ}\text{C}$ and annealed for 30 min, which completed the preparation of the ferroelectric film.

In here, the anti-solvent process is annotated. The 40 μL ferroelectric solution was spin-coated on the Glass/ITO substrate at 1000 rpm (acceleration of 200 r/s) for 10 s, followed by 5000 rpm (acceleration of 1000 r/s) for 30 s. The first 10 s is referred to here as the first stage and the second 30 s as the second stage, while the dropwise addition of the counter-solvent occurred in the second stage of spin-coating.

2.2.4. Inverted Devices Fabrication

Next, 40 μL of the dense NiOx solution, stirred for 4 to 8 h and filtered with a 0.2 μm filter tip, was applied uniformly onto the UV-ozone treated ITO glass substrate with a pipette. The samples were spin-coated at a rate of 4000 r.p.m. for 30 s and placed on a hot plate at 100 $^{\circ}\text{C}$ for 10 min. After the solvent evaporated slowly, the samples were placed in a ceramic fiber muffle furnace and the annealing temperature was set to 300 $^{\circ}\text{C}$, where the rise time and annealing time were set to 30 min and 60 min, respectively. When the annealing was finished, the samples were spin coated with ferroelectric films according to the procedure in the supplementary material. Finally, the 80 nm silver counter electrode was vaporized on the samples.

2.3. Characterization

Scanning electron microscopy (SEM) (SIGMA, Zeiss, Jena, Germany) was used to measure the morphology of the organic–inorganic hybrid ferroelectric films. The x-ray diffraction data of the HDA-BiI₅ films deposited on the bottom of the ITO were measured with an x-ray diffractometer (D8 Focus, Bruker, Dresden, Germany). The absorption spectra were measured by an ultraviolet-visible (UV-Vis) absorption spectrometer (Avantes, Apeldoorn, the Netherlands), and the LabIRAW HR800 photoluminescence (PL) test system (HORIBA Jobin Yvon, Paris, France) was used to acquire Photoluminescence (PL) spectral data were acquired using a LabIRAW HR800 photoluminescence (PL) test system (HORIBA Jobin Yvon, Paris, France). J-V tests and polarization tests were performed on ferroelectric photovoltaic devices using Princeton Applied Research's electrochemical workstation and a standard sunlight simulator.

3. Results and Discussion

We prepared HDA-BiI₅ powder and HDA-BiI₅ ferroelectric films and characterized them. By comparing the XRD plots of Figure S1, the characteristic peak positions are consistent with a orthorhombic crystal structure of space group Pna21, which is consistent with the literature Ref. [8]. It has been reported that its crystal structure consists of one-dimensional zigzag chains of the corner-shared distorted BiI₆ octahedra and hexane-1,6-diammonium cations. The ferroelectric film absorbs light in the wavelength range of 450 nm to 600 nm, i.e., most of the sunlight, as shown in Figure S2. The ultraviolet photoelectron spectroscopy of the ferroelectric films were also measured, and the Fermi

energy level, valence band maximum and optical bandgap of this ferroelectric material were calculated from the processing of Figures S2 and S3 to be about 4.99 eV, 6.57 eV and 1.99 eV, respectively, which are similar to the energy band values reported by Zhang et al. This implies that this organic–inorganic hybrid material is an N-type semiconductor, so a P–N junction can be formed in the heterojunction interface between it as an optical absorber layer material and a P-type hole transport layer, thus accelerating the carrier separation and transport. Therefore, we use conventional inverted structure of solar cell as shown in Figure 1.

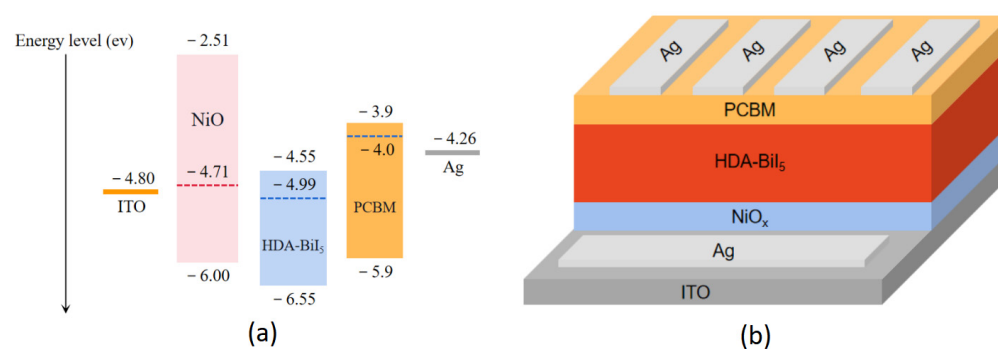


Figure 1. (a) Schematic diagram of work function of each functional layer material; (b) structure diagram of ITO/NiO_x/HDA-BiI₅//PCBM/Ag inverted device.

In this study, we used chlorobenzene as the anti-solvent to optimize the ferroelectric film, and after several experiments, we found that when chlorobenzene was added dropwise at the 10th second of the second stage of film spin coating, the film was more uniform and crack-free, but the overall film denseness was poor, as shown in Figure 2. Therefore, we adjusted the amount of counter-solvent and observed in Figure 3 that the surface of the film was the flattest and densest when 40 μ L of chlorobenzene was added in the 10th second, and there were almost no cracks and holes. The detailed performance parameters of the device are provided in Table 1. The forward scan test yields a PCE of 0.053% and the reverse scan of 0.040%, which are 152% and 74% higher, respectively, compared with the device without the anti-solvent process; the open-circuit voltage (V_{oc}) of the device is 0.69 V and 0.74 V under the forward scan and reverse-scan test conditions, respectively, which are 30% and 16% higher, respectively, compared with the device without the anti-solvent process. The short-circuit current densities of 0.41 mA/cm² and 0.20 mA/cm² under forward and reverse scan test conditions are shown in Table 1, which are improved by 105% and 43%, respectively. The flat and dense film structure facilitates the transport of photogenerated carriers and reduces carrier complexation at the interface, thus improving the performance of ferroelectric solar cells.

Table 1. Performance parameters of unpolarized devices before and after optimization.

Optimized Conditions	Scanning Direction	PCE (%)	V_{oc} (V)	J_{sc} (mA/cm ²)	FF (%)
No chlorobenzene adding	Forward scan	0.021	0.53	0.20	19.56
	Reverse scan	0.023	0.64	0.14	25.94
Chlorobenzene adding	Forward scan	0.053	0.69	0.41	18.26
	Reverse scan	0.040	0.74	0.20	27.26

For ferroelectric photovoltaic devices, polarization can improve its photovoltaic performance, so we conducted a study by polarizing one sample with structure ITO/NiO_x/HDA-BiI₅/PCBM/Ag at different voltages. The measured J–V curves of the ITO/NiO_x/HDA-BiI₅/PCBM/Ag structured device after polarization at different constant voltages are shown in Figure S4, where the maximum values of the forward and reverse scan ranges of each experiment are consistent with the polarization voltage values. The trends of each

performance parameter of this sample device after polarization at different voltages are shown in Figure 4. Where (0) represents the unpolarized state, (1), (2), (3), and (4) represent the conditions of polarization at 0.6 V, 0.8 V, 1.0 V, and 1.2 V for 30 s, respectively, while the solid dot plots represent the forward scan and the hollow ones represent the reverse sweep. From this figure, it can be found that under different voltage polarization conditions, the forward scan V_{oc} and fill factor of the device are lower than those of the reverse sweep, while the J_{sc} is higher than that of the reverse sweep. Both the PCE of forward scan and reverse scan show an increasing trend with the increase of polarization voltage, which achieves the expected effect. The highest PCE of 0.112% was obtained for the forward scan of the device when the constant polarization voltage was 1.2 V. This result is an improvement of about 41 times with respect to the 0.6 V polarized device and about five times with respect to the unpolarized device.

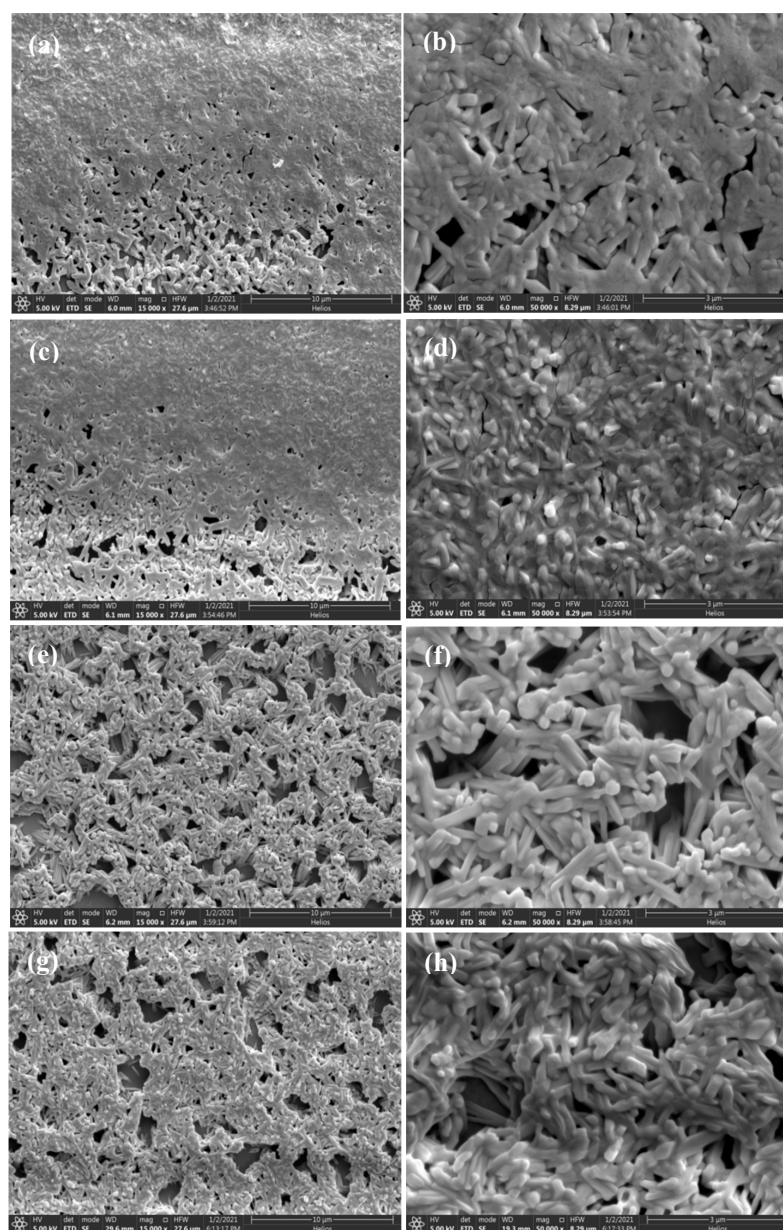


Figure 2. Different magnifications SEM top view of organic–inorganic hybrid ferroelectric thin films formed by different chlorobenzene dropping time. (a,b) 0 s in the second stage, (c,d) 5 s in the second stage, (e,f) 10 s in the second stage, and (g,h) 15 s in the second stage.

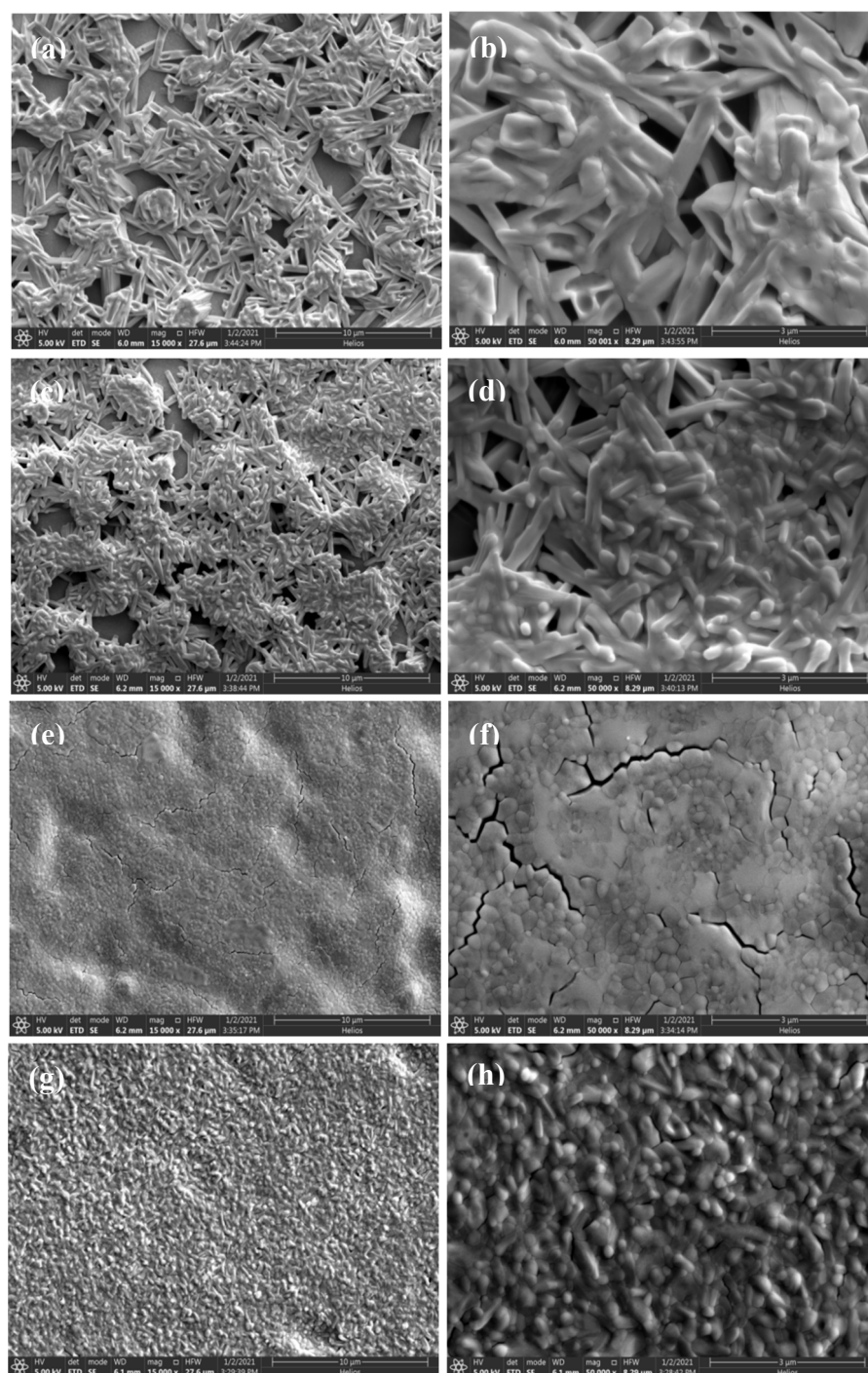


Figure 3. SEM top view of organic–inorganic hybrid ferroelectric thin films formed by different chlorobenzene drops. (a,b) 100 μL , (c,d) 80 μL , (e,f) 60 μL , and (g,h) 40 μL .

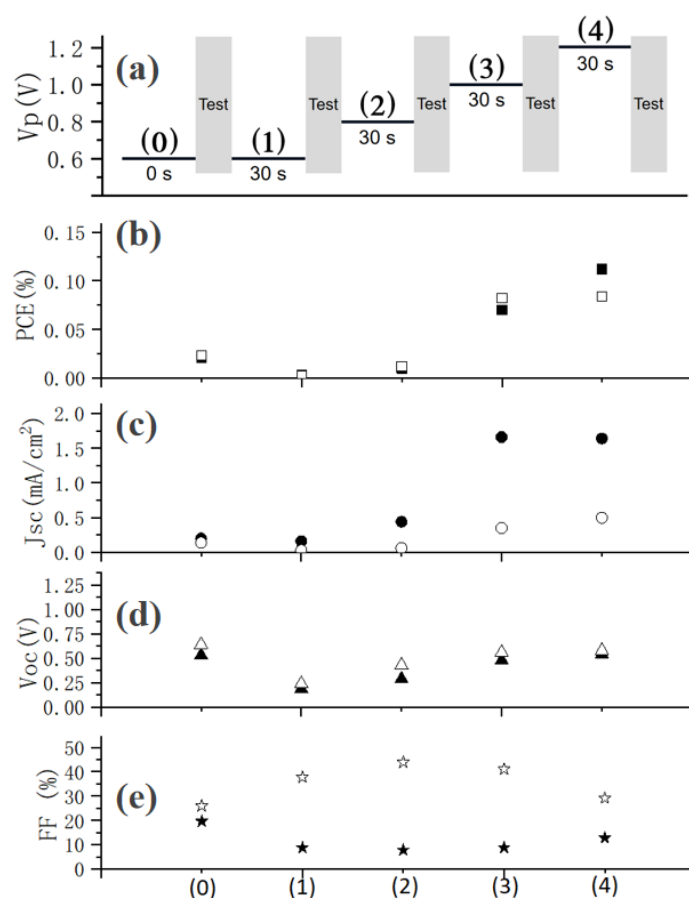


Figure 4. The performance parameters of unoptimized devices vary with the polarization conditions. (a) Different polarization conditions; (b) the variation trend of PCE with polarization conditions; (c) the variation trend of J_{sc} with polarization conditions; (d) variation trend of V_{oc} with polarization conditions; and (e) the variation trend of FF with polarization conditions.

To further investigate the effect of the ferroelectric films prepared by the anti-solvent process on the device performance, the devices with ITO/NiO_x/HDA-BiI₅ (anti-solvent process)/PCBM/Ag structure were also polarized and the device performance after polarization at different voltages was tested. The J-V curves tested after polarization at 0.6 V, 0.8 V, 1.0 V, and 1.2 V, as shown in Figure S5a–d. Figure 5 shows the trend of each performance parameter of the optimized device with the polarization voltage, indicating that the J_{sc}, both forward and reverse sweep, has a significant increase. The V_{oc} does not change much, or even decreases slightly, but the PCE still has a substantial increase, which is mainly attributed to the very large improvement in the photogenerated current obtained after polarization. The trend of the overall increase in fill factor also shows that the photovoltaic performance of the device has been really improved. In our experiments, the highest PCE was achieved at a polarization voltage of 1.2 V for both forward and reverse scan tests, with a forward scan of 0.084%, an improvement of 58.4% compared to the unpolarized device, and a reverse scan of 0.089%, an improvement of about 147.5%. By comparing with the device without the anti-solvent process, it can be found that the optimized device has a more stable performance change during the polarization process, the overall device performance is higher, and the J-V curves of forward and reverse scan are closer. In particular, after the lower voltage polarization, the performance is substantially improved compared to the unoptimized device. An increase in the short circuit current density can be related to polarization switching. However, in a DC poling field experiment, there is no way to distinguish between increased current density due to electrical leakage currents (conductivity) and polarization switching. The polarization switching has been

explored with present PFM investigation. It can be seen from the PFM image that HDA-BiI₅ has good ferroelectric property. When the polarization of positive and negative 10V voltage is applied, the domain has obvious inversion, as shown in Figure S6. Therefore, we could think that it is polarization that improves the performance of the device.

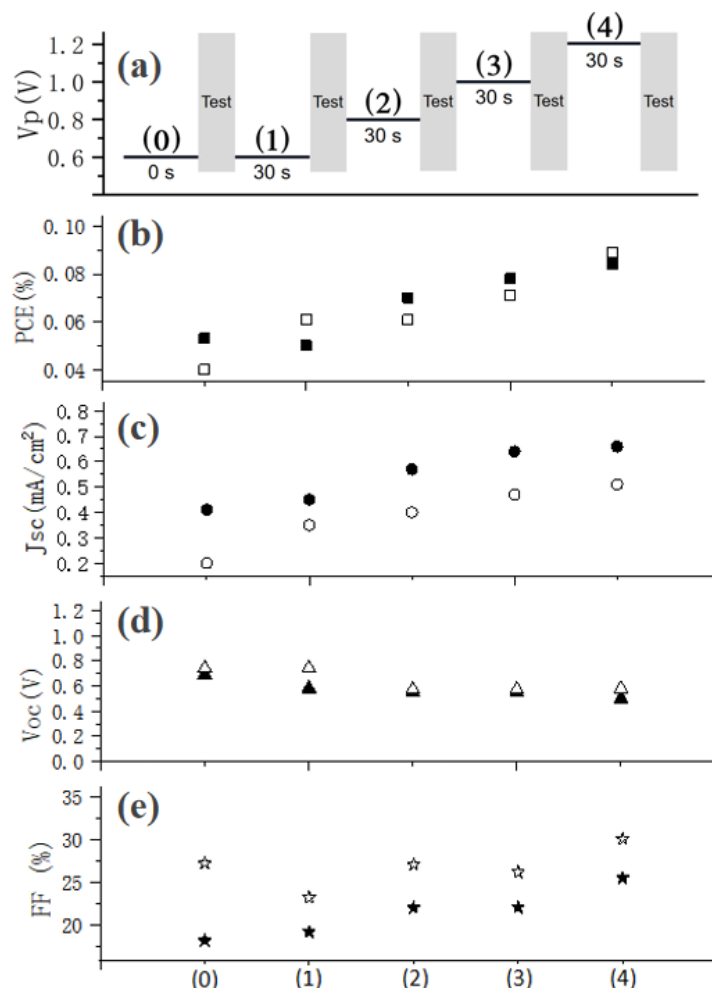


Figure 5. The performance parameters of the optimized device vary with the polarization condition. (a) Different polarization conditions; (b) the variation trend of PCE with polarization conditions; (c) the variation trend of J_{sc} with polarization conditions; (d) variation trend of V_{oc} with polarization conditions; (e) the variation trend of FF with polarization conditions.

The energy of sunlight excites electron hole pairs inside ferroelectrics, and it is the separation and transportation of these electron hole pairs that produce a photocurrent. As shown in Figure 6a, when no voltage polarization is applied to the inverted solar device, the built-in electric field generated mainly by the P-N junction formed at the interface between NiO_x/HDA-BiI₅ plays a role in the separation and transportation of electron hole pairs. After the addition of voltage polarization, a depolarization electric field is generated in the ferroelectric, and its direction is consistent with the direction of the built-in electric field formed on the heterogeneous interface. The superposition of these two electric fields greatly promotes the separation of light-generated carriers within the light absorption and accelerates the transport of carriers, thus reducing the recombination of carriers. As a result, the photocurrent short-circuit density is greatly enhanced after polarization, and the performance of photovoltaic devices is also significantly improved.

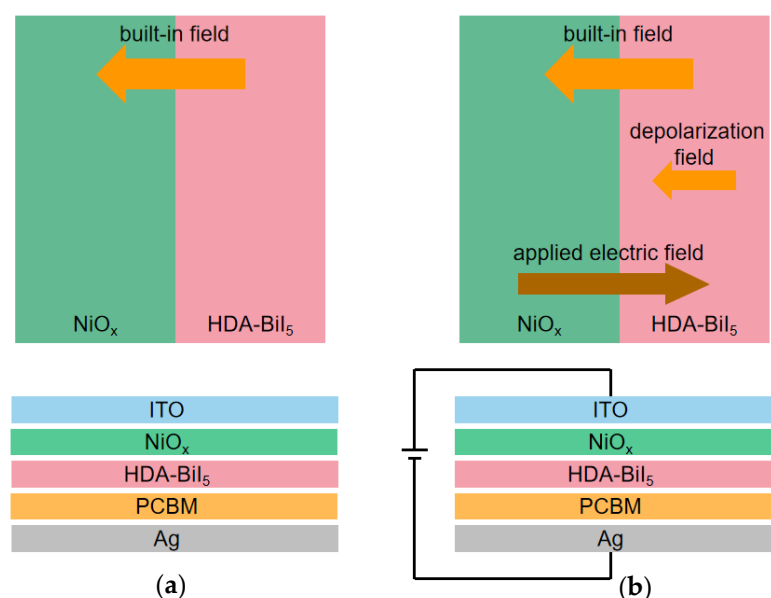


Figure 6. Schematic diagrams of (HDA-BiI₅)-based ferroelectric solar cells under different conditions: (a) no polarization, and (b) polarization.

4. Conclusions

In summary, before polarization, the chlorobenzene-optimized devices showed different degrees of improvement in V_{oc} and J_{sc} , regardless of forward or reverse sweep, which also led to a 152% improvement in the PCE of the devices compared to the unoptimized ones. The devices before and after chlorobenzene optimization showed an increase in J_{sc} and iron as a whole under different voltage polarizations, except for the V_{oc} , which did not change significantly, and the PCE was significantly improved. Although the maximum PCE with a value of 0.112% was obtained for the unoptimized device under 1.2 volts polarization, the optimized device showed a more stable performance change during polarization. The reason for the improved device performance due to polarization can also be attributed to the synergistic effect of the depolarizing electric field of the ferroelectric photoabsorption layer and the electric field built into the P-N junction. At present, it seems that ferroelectric materials have not yet become the mainstream of the solar cell photoabsorption layer, but we believe that with the unremitting efforts of researchers, ferroelectric photovoltaic cells are expected to become the best candidate for the next generation of solar cells.

Supplementary Materials: The following are available online at <https://www.mdpi.com/article/10.3390/app112110494/s1>, Figure S1: X-ray diffraction spectra of organic-inorganic hybrid ferroelectric materials, Figure S2. Ultraviolet-visible light (UV-vis) absorption spectra and photoemission spectra (PL) of organic-inorganic hybrid ferroelectric films, Figure S3. Ultraviolet Photoelectron Spectroscopy (UPS) of Organic-inorganic Hybrid Ferroelectric Material HDA-BiI₅, Figure S4. J-V curves of ITO/NiO_x/HDA-BiI₅/PCBM/Ag structure devices after different constant voltage polarization. (a) 0.6 V, (b) 0.8 V, (c) 1.0 V, (d) 1.2 V, Figure S5. J-V curves of the optimized device after different voltage polarization. (a) 0.6 V, (b) 0.8 V, (c) 1.0 V, (d) 1.2 V, Figure S6. The vertical PFM phase angles of ferroelectric films are (a) −10 V, (b) 10 V, (c) −10 V and the horizontal PFM phase angles are (d) −10 V, (e) 10 V, (f) −10 V.

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Conflicts of Interest: The authors declare no conflict of interest.

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