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Enhanced open voltage of BiFeO$_3$ polycrystalline film by surface modification of organolead halide perovskite

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Inorganic-organolead halide perovskite CH$_3$NH$_3$PbI$_3$ modified BiFeO$_3$ polycrystalline film has been established. The composite photoelectrode presents much larger open voltage and several magnitudes superior photoelectric conversion performance in comparison to the ordinary BiFeO$_3$ polycrystalline film. The I-V curve shows that the short-circuit current (J_{sc}) is 1.74 mA·cm^{-2} and open-circuit voltage (V_{oc}) is 1.62 V, the device's photon to current efficiency is over 1%. The large open voltage and high photovoltaic efficiency is believed to attributed to the spontaneous polarization of composite perovskite induced by BiFeO$_3$ lattice and modified reduced work function of the modified BiFeO$_3$ surface. Our results clearly show that the present BiFeO$_3$-CH$_3$NH$_3$PbI$_3$ planar device is capable to generate a large voltage in macro scale under visible light, leading an approach to further applications on photodetectors and optoelectronic switch. © 2014 AIP Publishing LLC. [http://dx.doi.org/10.1063/1.4888912]

For the conventional semiconductor photovoltaic devices, their open-voltage is limited to the Shockley-Queisser's law.[1,2] The photo-induced voltage is determined by the difference of the Fermi level at two sides of the interface region. Moreover, this value is usually even smaller than the semiconductor band gap in the actual measurement. In most cases, the open voltage is smaller than 1.0 V. However, in some practical applications, such as photodetector and optoelectronic switch, a large voltage is prerequisite to drive the downstream equipment.[3–5]

Owing to their bulk photovoltaic effect (BPVE), inorganic perovskites based ferroelectric semiconductor materials with the general formula of ABO$_3$ have been taken into account as one of the most promising candidates for next generation photoelectric devices. The BPVE always arises from crystals having no center of symmetry (LiNbO$_3$, BiFeO$_3$, BaTiO$_3$, etc.).[6] The excitation of free carriers from localized states will, in general, result in a bulk photovoltaic effect due to asymmetric charge transfer. This effect is a fascinating mechanism with numerous unique features such as extremely large photovoltage, photocurrent proportional to the polarization magnitude, and charge-carrier separation in homogeneous media.[7–9]

Unfortunately, long after its discovery, BPVE effect remains to be an academic curiosity rather than any realistic applications because it is a complicated job to screen for high-performance piezoelectrics from considerable quantities of inorganic perovskites.[10]

Until recently, BiFeO$_3$ (BFO) has drawn much interest, largely because its band gap of 2.2–2.8 eV, which is suitable for the visible light to generate the electron-hole pairs.

Extremely large open photo voltage (OPV) is obtained in single crystals and epitaxial BFO thin films in a very tiny area, e.g., an open voltage of 15 V has been detected from the BFO single crystal film with 200 μm 109° domain walls under solar simulator.[11]

Compared with single crystal and epitaxial films, polycrystalline films have their unique superiority such as simple procedure, cost effective, ease of fabrication to large area, etc. However, the measured OPV of polycrystalline films was only 0.2–0.5 V.[12–15]

In this letter, we used the polycrystalline BFO thin film, which was modified by the inorganic-organic hybrid halide perovskite CH$_3$NH$_3$PbI$_3$ to fabricate the bilayer perovskite solar device. In addition, a large open-voltage of 1.62 V has been observed in this energy conversion system. Conversion efficiency over 1.5% under 100 mW/cm^2 visible light irradiation was also obtained.

BFO sol processed by dissolving Bi(NO$_3$)$_3$·5H$_2$O and Fe(NO$_3$)$_3$·9H$_2$O as the processor polycrystalline film was deposited on a FTO substrate through spin-coating technology. The as-obtained film was dried at 300 °C and annealed at 600 °C for crystallization. This procedure was repeated 10 times to obtain ca. 200 nm thickness. Then, dimethylformamide (DMF) solution of CH$_3$NH$_3$PbI$_3$ was spined on the BFO polycrystalline film at 70 °C and crystallized at 100 °C for 15 min. After that, electrolyte was packaged between photoelectrode and Au counter electrode. Current-voltage (I-V) curves were measured using a Keithley 2410 sourcemeter. The light source was a Xenon lamp and the illumination energy density was 100 mW/cm^2. Atomic force microscope (AFM), piezo response force microscopy (PFM), and Kelvin probe force microscopy (KPFM) measurements were performed on an atomic force microscope (Asylum Research MFP-3D).

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The measured light-induced voltage/current density curves, schematic diagrams of modified BFO device and simplex BFO polycrystalline thin film measured under AM 1.5 (100 mW/cm^2) are exhibited in Figs. 1(a) and 1(b). The BFO device had a short-circuit photocurrent of 0.001 mA·cm^{-2} and an open-voltage of 0.3 V. It can be noticed that the modified BFO film produced a 1.74 mA·cm^{-2} short-circuit photocurrent and an open-voltage of 1.62 V, yielding an efficiency of 1.48%. It can be seen that the V_{oc} of the composite perovskite device was above five times larger, and the I_{sc} was three orders of magnitude larger than the BFO ones.

Overall, open voltage of the photoelectric device is determined by the differences between its two electrodes, which can be expressed as

$$E = \varphi_a - \varphi_b, \tag{1}$$

φ_i is the work function of the electrode material.

In our device, φ_a is the work function of FTO and φ_b is the work function of BFO.

Open voltage of simplex BFO polycrystalline thin film device was 0.3 V, which is approximately equal to the voltage obtained from literatures.[13,14] It can be understood by the traditional semiconductor heterojunction theory. This value was calculated through the difference between the work function of BiFeO$_3$ (4.3 eV) and FTO (4.6 eV).[17–20] Thus, the BPVE contributes little to the device's open voltage of BFO polycrystalline thin film.

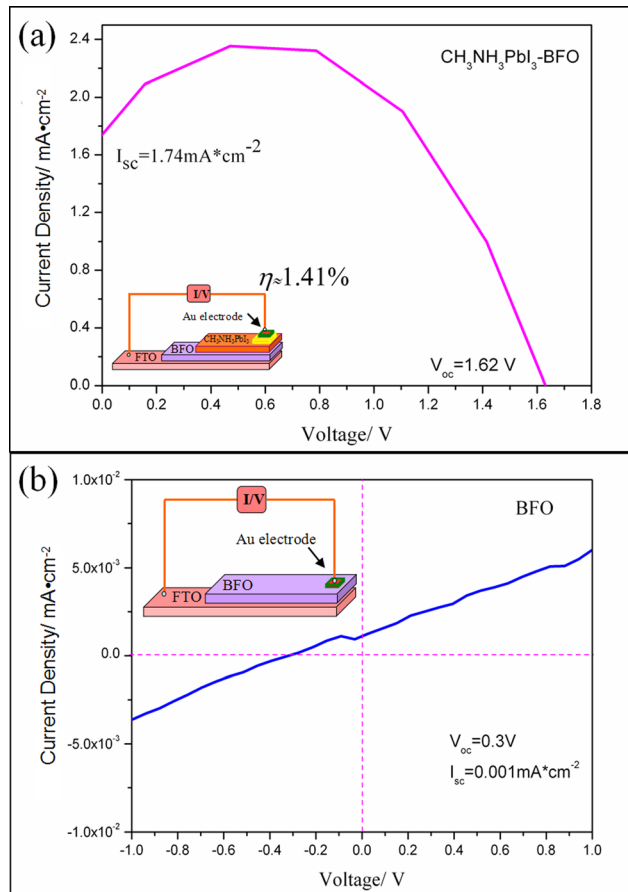FIG. 1. I-V curves and structural schematics of the two kinds of photoelectric devices. (a) BFO-CH$_3$NH$_3$PbI$_3$ and (b) BFO.

The measured work function of the composite films surface is yield by the following expression:

$$\varphi = \varphi_0 + \Delta\varphi_\chi + \Delta\varphi_d. \tag{2}$$

Here, φ is the measured work function of the films surface; φ_0 is the work function of the stoichiometric oxide; $\Delta\varphi_\chi$ is the change in work function caused by an increase in the concentration of low electronegativity cations, and $\Delta\varphi_d$ is the change in work function caused by increasing the density of donor states. Transition metal oxide's work function is closely associated with the oxygen vacancies and oxidation state of cations. Low state of cationic is more electronegative and will lower the work function of the whole system. Electronegativity of ionic compounds can be calculated through the following equation:

Taking the compound A$_a$B$_b$C$_c$, as an example. Its electronegativity can be calculated by the following equation:

$$\chi = (\chi_A^a * \chi_B^b * \chi_C^c)^{1/(a+b+c)}, \tag{3}$$

where χ_i (i = A, B, C) is the absolute electronegativity of ions, a, b, and c is the stoichiometric ratio of each ions.

Thus, computing results of cations' electronegativity are 4.36 eV for Bi^{3+}Fe^{3+} and 6.62 eV for [CH$_3$NH$_3$Pb]$^{3+}$. The electronegativity of [CH$_3$NH$_3$Pb]$^{3+}$ is much stronger than that of Bi^{3+}Fe^{3+}. It is reasonable to believe that the interface modification of BFO by CH$_3$NH$_3$PbI$_3$ plays an important role in the decline of BFO's surface work function.

In CH$_3$NH$_3$PbI$_3$, the dominant donor CH$_3$NH$_3$ serves as the main n-type defects. In bulk materials, the large-size CH$_3$NH$_3$ ion helps to stabilize the perovskite structures and donate one electron to 3D Pb-I framework for charge balance. Moreover, the n-type CH$_3$NH$_3$ increases in density of donor states of the interface by donating one electron to O^{2-} anions.

Therefore, work function of BFO film was lower after its surface was modified by the organic-inorganic hybrid perovskite.

KPFM was utilized to determine the surface potential of the modified BFO film. We found evenly distributed potential on the crystalline surface of CH$_3$NH$_3$PbI$_3$ after comparing the height and potential images (Figs. 2(a) and 2(b)). Moreover, there was an outward barrier at the edge of the grain, which could be identified as the interface between BFO and CH$_3$NH$_3$PbI$_3$. Data curve showed that the barrier height was about 0.07 V. Although the experimental value is small, it is found that there is a large variation in the valence-band top and conduction-band bottom of BFO and CH$_3$NH$_3$PbI$_3$ after calculating their band structure. Band positions of BFO and CH$_3$NH$_3$PbI$_3$ can be given by the equation

$$E_{CB} = \chi - E_c - 0.5E_g, \tag{4}$$

where E_c is usually a constant equal to 4.5 eV, x is the electron affinity of the semiconductor, and E_g is the relevant band gap.[21] The calculated result is shown in Fig. 4(c). Barrier height between the two perovskite was above 1.7 eV, in theory. Photo generated holes transported from CH$_3$NH$_3$PbI$_3$ to BFO, and the electrons were reversed.
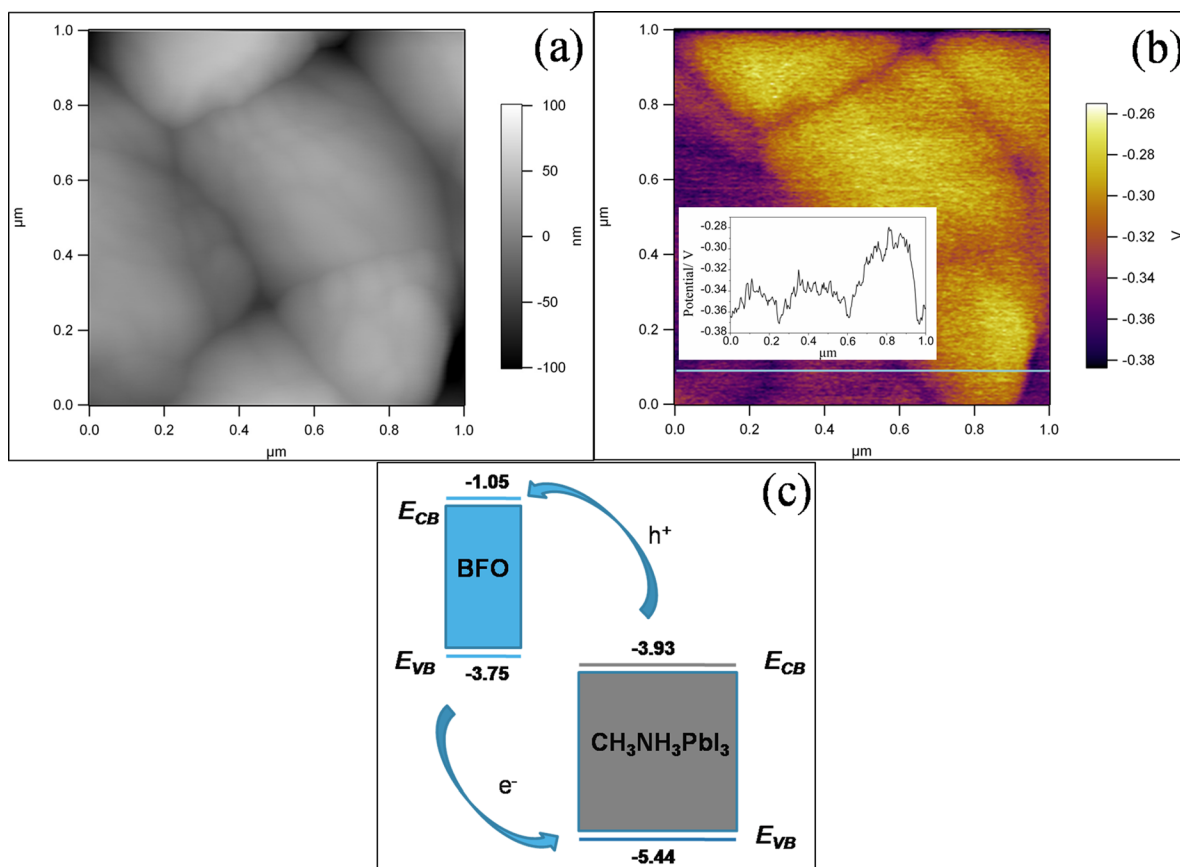
FIG. 2. Height (a), potential image (b) of BFO-$CH_3NH_3PbI_3$ composite film (the inset in (b) is the potential curve of the line), and energy band structures of BFO and $CH_3NH_3PbI_3$ (c).

Figure 3 shows the XRD patterns of the BFO, $CH_3NH_3PbI_3$, and modified BFO films deposited on FTO glass. It can be observed that the BFO polycrystalline film is with free orientation, which is distinct from the epitaxial single crystal film. We assume that the domain wall directions of spontaneous polarization are mutually offset with each other, leading to an external open voltage determined by the potential difference of the two materials aside the interface. However, for the bilayer film, after $CH_3NH_3PbI_3$ modified the BFO polycrystalline film, the $CH_3NH_3PbI_3$ exhibited orientation in some certain directions, as showed in Figure 2(c). Only (202), (404), (220), (330), and (224)
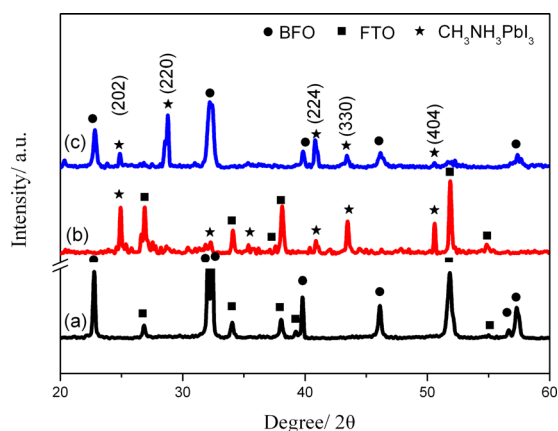

FIG. 3. XRD patterns of the BFO (a), $CH_3NH_3PbI_3$ (b), and BFO-$CH_3NH_3PbI_3$ (c) films deposited on FTO glass.

faces were found in the XRD pattern.[22] For comparison, the XRD pattern of $CH_3NH_3PbI_3$ deposited on FTO was exhibited, and an obvious free orientation film was obtained. Thus, we conclude that because both BFO and $CH_3NH_3PbI_3$ have the similar perovskite structure, BFO is available to induce oriental growth of $CH_3NH_3PbI_3$. The photovoltaic properties of perovskites with orientation are usually superior to that of random films. The BPVE depends on the spontaneous polarization, the polarization plane of the light. Orientation films have high crystalline quality with reduced defects and enhanced depolarization field. Moreover, the consistency of spontaneous polarization further induced the BPVE. Ager developed a PV mechanism driven by the periodic potential structure formed by ferroelectric domains in 2011. They ascribed the PV effect to charge separation at the domain walls, accumulating electrons (holes) on one side and depleting the other carrier. But the directions of domain walls are randomly distributed in the polycrystalline film, BPVE actually cancels each other out in separately domain walls.[16] Thus, open voltage in perovskite solar cells can be strongly bound up with the accumulation of polarization electric fields in the crystalline orientated film.

In order to investigate the influence of oriental growth of $CH_3NH_3PbI_3$ on BFO surface to spontaneous polarization directions, height, and phase images were obtained utilizing by PFM mode executed by an atomic force microscope. For the BFO film (Fig. 4(a)), the film exhibited relatively uniform size distribution around 120 nm.
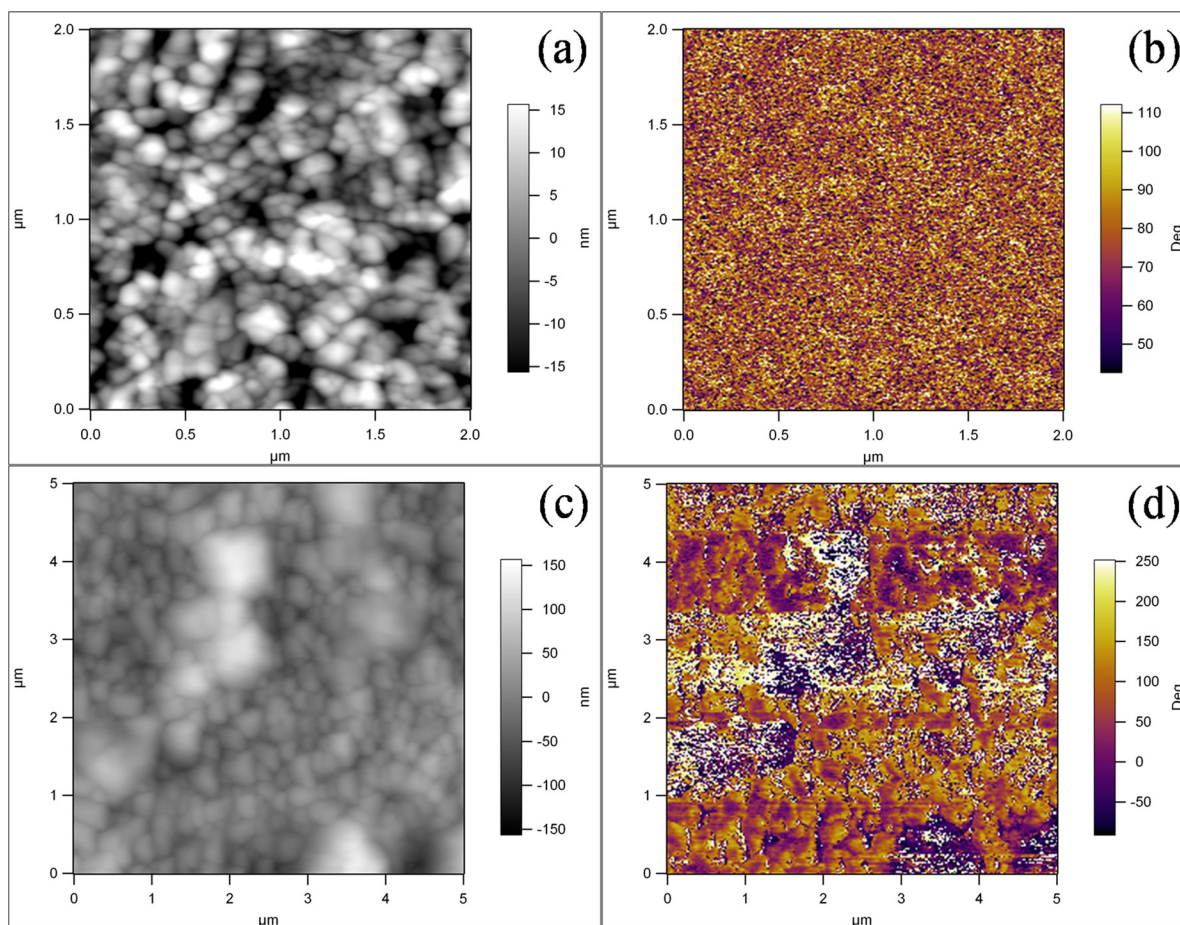
FIG. 4. Height and phase image of the BFO film ((a) and (b)) and BFO-CH$_3$NH$_3$PbI$_3$ composite film ((c) and (d)).

However, there is not any corresponding relation between the distribution of crystalline grain and polarization phase contrasts. The dispersed distribution of phase degrees demonstrates that the detected film had no obvious external polarization. Therefore, no BPVE effect was observed in the single polycrystalline BFO film, the open voltage was mainly determined by the traditional semiconductor heterojunction theory, which has been discussed before. On the other hand, BFO-CH$_3$NH$_3$PbI$_3$ composite film exhibited two sizes of crystal particles (Figure 4(c)), the larger ones with dimensions of 0.5–1.0 μm and smaller ones around 200 nm, which are larger than that of the BFO substrate film. CH$_3$NH$_3$PbI$_3$ layer covered on the surface of the original BFO particle, therefore, the particle size of the modified BFO was a little larger than that of before modification. Fig. 4(d), the PFM image shows mainly two contrasts (orange-brown lumps) with a very small content of white-yellow lumps. Roughly, the larger particles exhibited a dark contrast with the phase degree of ca. $-30°$, whereas the smaller grains showed a bright contrast, with the phase degree of ca. 150°. Even for different planes of the same one crystalline grain, the opposite polarization direction can also be observed. This can be explained by the effect of the oriented crystallization of CH$_3$NH$_3$PbI$_3$ on surface of BFO. CH$_3$NH$_3$PbI$_3$, as a new kind of hybrid material with perovskite structure, is a non-centrosymmetry substance at room temperature.[23] Those domains with opposite polarization directions will generate two opposite polarization electric fields. Moreover, the ultimate direction of the voltage is determined by the predominant 150° domains.

From the above theoretical and experimental analysis, it can be found that the enhanced open voltage of the composite film photovoltaic device is due to the reduced surface potential and predominant direction of spontaneous polarization caused by the CH$_3$NH$_3$PbI$_3$ modified BFO film.

In summary, we obtained a large open voltage of 1.62 V by corporation of BFO polycrystalline films with the modification of organolead halide perovskite CH$_3$NH$_3$PbI$_3$. The extremely large photovoltage is attributed to the predominant direction of spontaneous polarization and reduced work function of BFO film modified by the CH$_3$NH$_3$PbI$_3$. BFO is able to provide the lattice matching substrate for oriented growth of the modified CH$_3$NH$_3$PbI$_3$. This letter will shed light on the photodetectors and optoelectronic applications of BFO polycrystalline films.

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