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Spontaneous polarization behaviors in hybrid halide perovskite film

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Spontaneous polarization behaviors of hybrid perovskite $CH_3NH_3PbI_3$ film were confirmed by *in situ* PFM and spectroscopic ellipsometry. The film exhibits uniform spontaneous polarization and ferroelectric domain inversion performance. The fitted dielectric constants spectra agree well with the calculated ones. We attribute the spontaneous polarization behaviors of hybrid perovskite to lone pair electrons, and its outstanding photovoltaic performance partially originates from spontaneous polarization and plasma resonance. This report will facilitate understanding of the instinct physical essence of hybrid perovskite solar cells.

Keywords: Spontaneous polarization; Hybrid halide perovskite; Plasma resonance; Ellipsometry; Ferroelectric domain

The application of organic–inorganic hybrid halide perovskite compounds in solar cells has been rapidly developed. The photoelectric conversion efficiency (PCE) of organometallic perovskite solar cells has surpassed that of both conventional dye-sensitized and organic photovoltaic devices. Revolutionary PCE of over 15% has been reported on hybrid perovskite light-absorber based solar cells [1–3]. Currently, the most widely used hybrid perovskite material in solar cells is methyl ammonium lead iodide ($CH_3NH_3PbI_3$, or $MAPbI_3$), where MA is a positively charged organic cation at the center of a lead iodide cage structure (PbI_6) [4]. Except for the narrow band gap of 1.53 eV, two superior properties of $MAPbI_3$ based solar cells are responsible for their excellent photovoltaic performance. The first one is the effective charge separation and concomitant ultra-long carrier lifetimes. Electron–hole diffusion lengths exceeding 1 μm have been observed in an organometallic trihalide perovskite film [5]. The second one is the large open circuit voltages [6]. However, the intrinsic mechanism behind-the-scenes is still unclear.

For traditional inorganic perovskite materials, their photoelectric properties are closely related to the spontaneous electric polarization behavior of the crystal lattice, which is a key factor for macroscopic performance of perovskites. Open-circuit voltages significantly higher than the bandgap can be generated from ferroelectric photovoltaic devices with periodically ordered polarization domain walls. On the other side, the direction of photocurrent is usually parallel to the net in-plane polarization [7]. Most inorganic perovskites (ABX_3) display spontaneous electric polarization because B cation moves away from the center of BX_6 octahedron and correspondingly breaks the centrosymmetry of the crystal lattice. This phenomenon is particularly pronounced in hybrid halide perovskites, where the asymmetry of organic cation ensures the absence of an inversion center in the crystal lattice [6].

For further design of high-efficient and stable perovskite solar cell materials, it is crucial to understand the ferroelectric domain and dielectric performance of hybrid halide perovskite. It has been realized that ferroelectric and dielectric behaviors of organometallic trihalide perovskite caused by spontaneous electric polarization might give rise to the above excellent photovoltaic performance. A photon-induced giant dielectric constant phenomenon has been observed in lead halide perovskite film [8]. Geometric dielectric permittivity of $MAPbI_3$ was recently calculated [9] and the possibility of the presence of ferroelectric domains in $MAPbI_3$ theoretically predicted [6]. Our previous work has also obtained an open voltage of 1.62 V based on the $BiFeO_3$–$MAPbI_3$ composite film, which is larger than the band gap of $MAPbI_3$. This large open voltage is also ascribed to the spontaneous polarization of composite perovskites [10].

In this letter, we experimentally reported the spontaneous electronic polarization behaviors of $MAPbI_3$ film, confirmed by *in situ* PFM and spectroscopic ellipsometry (SE) methods. The electric domains, switch behavior,

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optical constants and complex dielectric constants spectra of $MAPbI_3$ film were investigated.

The preparation procedure of $MAPbI_3$ films was carried out according to Ref. [11]. Briefly, CH_3NH_3I and PbI_2 were dissolved into dimethylformamide (DMF) with the molar ratio of 1.1–1.3:1 at 60 °C. DMF solution of $MAPbI_3$ was coated on the FTO glass substrate by spin coater at 70 °C and then crystallized at 100 °C for 15 min. PFM measurements were performed on an atomic force microscope (Asylum Research MFP-3D). The complex dielectric constant spectrum was fitted from the obtained data (within a wavelength rang of 400–800 nm) by SENTECH SE850 spectroscopic ellipsometer.

Figure 1 displays morphology and phase images of the as-deposited $MAPbI_3$ film within a $2 \times 2\ \mu m^2$ area. The averaged roughness (R_a) of the measured surface is ca. 31 nm. The film surface is relatively rough, suggesting the island growth mode during film growth. In Figure 1b, the film exhibits spontaneous ferroelectric domains. The averaged phase angle of inner dipole is 33.3°, and at a few grain boundary edges, bright areas shows that the phase angle is near 180° due to electric charge effect. Most of the domains match corresponding topographic features, because spontaneous domain wall structure is limited by the strain between neighbor grains. Phase degree measured by PFM reflected angles between the probe tip and dipoles in the film. The amplitude and phase of the response could be measured by using a lock-in amplifier (Fig. 1c). The most important characteristic for ferroelectrics is the electric hysteresis loop. We also obtained the ferroelectric hysteresis loop of $MAPbI_3$ film by applying a periodic reverse voltage (-15 to $+15$ V) on the PFM probe tip. From Figure 1d, the maximum polarization could be verified under ca. ±9 V.

By implementing a DC voltage to the tip during PFM scan, it is able to reversibly switch the polarization of $MAPbI_3$ film. After two consecutive scans with opposite 10 V voltages, the ferroelectric domain could be redrawn easily. There are two different colors in each PFM image, suggesting at least two types of domains (Fig. 2a and b). After drawing phase degree distribution curves of labeled lines, it can be seen that positive bias voltage leads to a phase degree of 0°, and inversely, negative bias voltage leads to a phase degree of 180°.

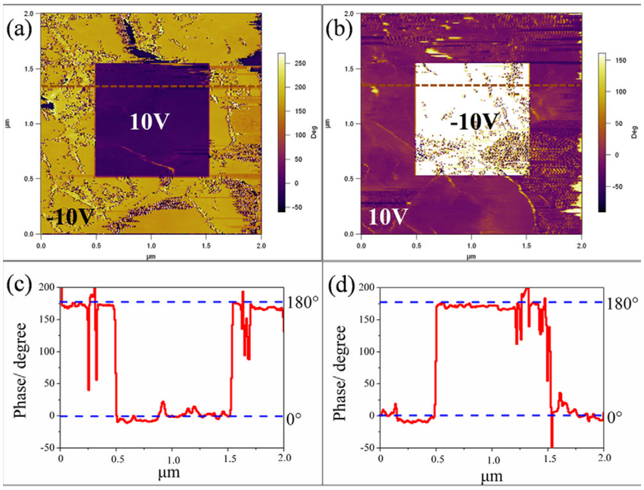

Figure 2. (a and b) Polarization reversal phase degree images of $CH_3NH_3PbI_3$ film under opposite bias voltages. Directions of the deflection voltages are marked and the labeled brown lines cross the two regions under opposite bias; (c and d) the corresponded phase degree curves of $CH_3NH_3PbI_3$ film labeled in images (a) and (b), respectively.

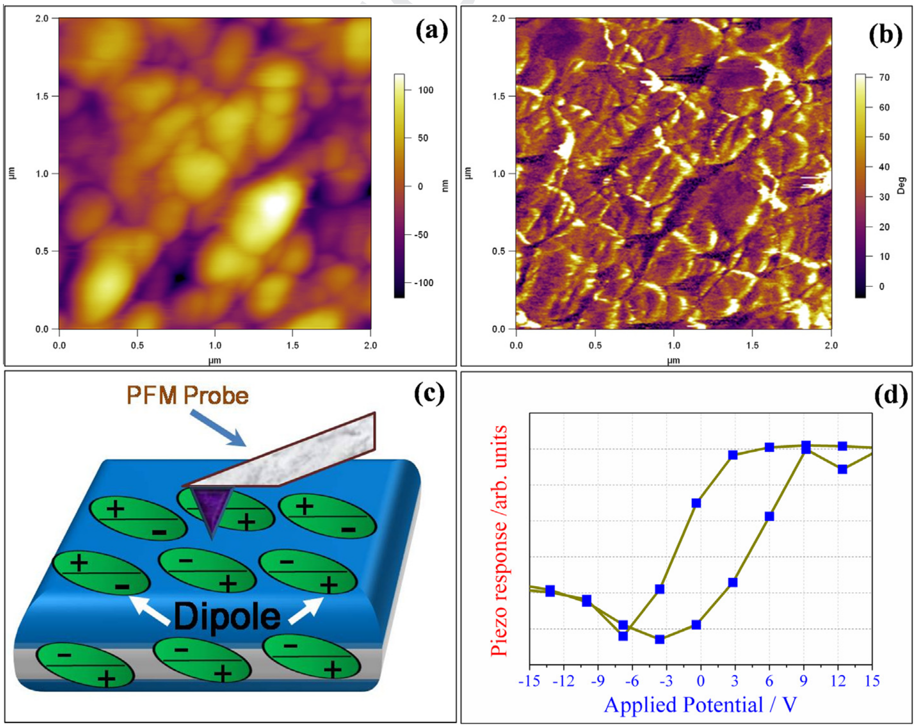

Figure 1. (a) Morphology, (b) phase image of $CH_3NH_3PbI_3$ film measured by PFM, (c) geometry of the phase degree measurement and (d) ferroelectric hysteresis loop measured by PFM.

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