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Effect of ferroelectricity on charge conduction in a PCBM/perovskite device structure

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ABSTRACT

The ferroelectricity in hybrid perovskite solar cells has attracted much attention and its effect on the device transport and photovoltaic properties is still under debate. In this paper, we investigate theoretically the effect of ferroelectricity on the redistribution of charge in a PCBM/perovskite device through the Poisson equation. The spontaneous polarization is set to be a hyperbolic tangent function of applied electrical field. The carriers in both the layers are assumed to be in quasi-equilibrium, and the (dark) current stems from the recombination at the PCBM/perovskite interface. The electrostatic potential profiles throughout the device and the current-bias ($I-V$) curves are obtained numerically. It is found that for the bias forward scan, larger potential drop will be on the PCBM layer, and for the bias reverse scan larger potential drop will be on the perovskite layer. The hysteresis of $I-V$ curves is also obtained. These results shed new light on the effect of ferroelectricity in hybrid perovskite materials.

During the past few years the organic-inorganic hybrid halide perovskite solar cells have attracted much attention because of the rapid increase of their power conversion efficiency. Now the cell efficiency has exceeded 20%, which makes the hybrid perovskite solar cells a promising candidate for the next generation commercial solar cells [1–5]. Numerous investigations have been made on the hybrid halide perovskite solar cell and lead-free hybrid perovskite photovoltaics, and the extraordinary performance of the solar cell might be ascribed to the beneficial properties of the material, such as long electron-hole diffusion distance, high photoabsorption rate, small exciton binding energy, etc. [1,5,6]. Although substantial amount of knowledge has been acquired in recent investigations, some of the physical properties for the halide hybrid perovskite solar cell are still ambiguous and under debate. The ferroelectricity property in the perovskite is one of these issues that needs further investigation. Many experiments and first-principle calculations have investigated the spontaneous polarization strength, the polarization domain and the ferroelectric lattice structure of halide hybrid perovskites [7–16].

There is a hypothesis that the spontaneous polarization in the halide hybrid perovskite could form an internal field, helpful in disassembling the excitons to free electrons and holes [1,5], but solid experimental evidence is still needed to prove it. The ferroelectricity is also thought to be one of the causes of the current-voltage hysteresis which diminishes the device performance, although the ion migration is concluded to be the main contribution to the hysteresis [5,9,17–19]. In addition, the ferroelectricity of hybrid perovskites can also relate to the device's semiconductive properties and other photoelectronic attributes [20,21]. To create the high efficiency solar cells and other functional devices such as photodetectors [22] and transistors [23] based on hybrid perovskites, a more detailed understanding of the effect of ferroelectricity is highly desirable. Now, different experiments have shown controversial results on the ferroelectricity of hybrid perovskites. Some experiments found the ferroelectric domains and the domain polarization direction switching, supporting the presence of ferroelectricity [7–13], while there are also experimental results indicating the absence of ferroelectricity or domain relaxation in short time [24,25]. Moreover, the effect of ferroelectricity on the device transport properties under bias as well as the photovoltaic properties are also under debate [17,26], warranting further investigation. In this paper, we will theoretically investigate the electrostatic potential distribution and the current-bias transport property of a hybrid perovskite device in dark, taking into consideration the perovskite's ferroelectricity.

We will consider a planar structure of PCBM/perovskite device, connected by metal contacts on both sides. The thickness of the PCBM layer is l, while the thickness of perovskite layer is $(L-l)$ nm. This device structure is similar to Ref. [27]. The presence of PCBM layer has significant influence on the performance of the device. Different experiments have showed that using the PCBM layer could greatly reduce

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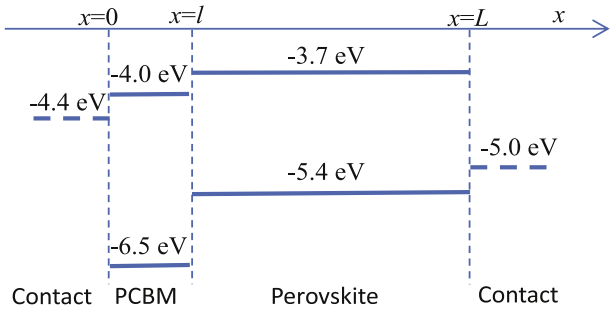

Fig. 1. The band diagram of the device. The device is in layer structure, and x-axis is perpendicular to the layers.

the I-V hysteresis [27,28]. This might be attributed to the mechanism that the PCBM layer can largely reduce the charge trap density in the hybrid perovskite layer, thus the trapping and detrapping processes will be dramatically reduced [28]. There is a conjecture that PCBM can also reduce the ion migration at the interface. Therefore, the presence of the PCBM layer could help us to concentrate on the effect of ferroelectricity in the device. The energy band diagram is shown schematically in Fig. 1. In this structure, the lowest unoccupied molecular orbital (LUMO) and the highest occupied molecular orbital (HOMO) of the PCBM layer are lower than those of perovskite layer's, respectively. Thus, the PCBM layer acts as electron transporting layer. On the PCBM side, the electron injection contact is placed and on the pervoskite side we introduce a hole injection contact. When bias is applied on the device in case of no light (dark), the electrons are assumed to be injected into the PCBM layer from the left contact, and holes into the perovskite layer from the right contact. The energy barrier for both the electron injection and hole injection are chosen to be 0.4 eV. Based on the band diagram, the device built-in potential V_{bi} is 0.6 V, which is the difference between the work functions of the left and right contacts.

We are interested in the current-voltage properties of the device in the presence of ferroelectricity. To achieve this purpose, it is assumed that throughout the whole device the carriers are in (quasi-)equilibrium. Therefore the Poisson equations are introduced to manipulate the electrostatic potential. Moreover, we assume that the carriers present in the PCBM layer are only electrons, and in the perovskite layer the carriers are only holes. The minority carriers, the electrons in perovskite layer and the holes in PCBM layer, are neglected since their densities are very small compared to the majority carrier densities, and they are easily recombined by the majority carriers. We commence the investigation of ferroelectricity's effect by first considering the dark case, when there is no light shining on the device to create additional carriers. In this case the current is generated from the recombination of electrons and holes at the interface between perovskite and PCBM layers. As a consequence, the only non-equilibrium process takes place at the interface.

In our model, the electrostatic potential and the carrier density satisfy Poisson equation in both the PCBM and perovskite layers. For the PCBM layer, the carrier is electron, and the equation is expressed as

$$-\nabla^2\phi_1(x) = \frac{-e}{\varepsilon_0\varepsilon_S}n(x), \tag{1}$$

$$n(x) = n_0 e^{-(E_{LUMO}-e\cdot\delta\phi_1(x)-\varepsilon_L)/k_BT}, \tag{2}$$

$$e\cdot\delta\phi_1(x) = e\phi_1(x) - e\phi_{10}(>0), \tag{3}$$

where ε_S is the dielectric constant of PCBM; E_{LUMO} is the energy of LUMO in PCBM; ε_L is carrier chemical potential of this layer; n_0 is the PCBM molecule density. ϕ_{10} is the electrical potential at the left interface at $x = 0$.

For the perovskite layer, the carrier is hole, and the corresponding Poisson equation is

$$-\nabla^2\phi_2(x) = \frac{e}{\varepsilon_0\varepsilon_F}p(x) - \frac{e}{\varepsilon_0\varepsilon_F}\nabla\cdot\mathbf{P}_b, \tag{4}$$

$$p(x) = p_0 e^{(E_{HOMO}+e\cdot\delta\phi_2(x)-\varepsilon_R)/k_BT}, \tag{5}$$

$$e\cdot\delta\phi_2(x) = e\phi_{20} - e\phi_2(x) \quad (>0), \tag{6}$$

$$\mathbf{P}_b = \mathbf{P}_s\tanh\left(\frac{E \pm E_c}{2\delta}\right), \tag{7}$$

where $\mathbf{P}_b$ is the spontaneous polarization and $\mathbf{P}_s$ is the saturated polarization. We only consider the electrostatic potential profile in x direction (perpendicular to the layer interface), therefore the direction of $\mathbf{P}_s$ is assumed to be parallel to x in Fig. 1. $E = -d\phi_2(x)/dx$ is the electrical field; E_c is coercive field; $\delta = E_c\left[\ln\left(\frac{1+P_r/P_s}{1-P_r/P_s}\right)\right]^{-1}$; P_r is the remnant polarization [29]. The '+' sign is chosen when the electrical field is increasing (bias forward scan), while '−' sign is chosen for decreasing electrical field (bias reverse scan). The spontaneous polarization $\mathbf{P}_b$ as a function of electrical field E can be expressed by several functions, and here we use the hyperbolic tangent function expression, following the discussion in Ref. [29]. In our model, all the layers are assumed to be in-plane isotropic, hence both Poisson equations are reduced to one-dimensional differential equations.

The boundary conditions at $x = 0, l, L$ are needed to obtain the electrostatic potential profiles and the carrier density distributions. When the applied bias is set, the total chemical potential difference is determined. Hence for the interfaces at $x = 0$ and $x = L$, we set the values of potentials as boundary conditions

$$\phi_1(0) = \phi_{10}; \quad \phi_2(L) = \phi_{20}. \tag{8}$$

The boundary conditions at $x = l$ are

$$\begin{aligned}&\phi_1(l) + U_b = \phi_2(l)\\ &\varepsilon_0\varepsilon_S E_1(l) + \sigma_S = \varepsilon_0\varepsilon_F E_2(l) + P_b(E_2(l)),\end{aligned} \tag{9}$$

where U_b is the potential difference at the interface, which might originate from the band mismatch between the two layers, the interface bonding effect, and interfacial polarity. σ_s is the surface charge density, which could originate in the case of the bad screening from the PCBM side [30]. We assume that there is no potential drop at the interface, $U_b = 0$. The polarization in the perovskite layer is separated into two parts, one of which is a linear part and could be included in $\varepsilon_0\varepsilon_S E$. The spontaneous polarization is expressed as P_b. Therefore $\mathbf{D} = \varepsilon_0\mathbf{E} + \mathbf{P} = \varepsilon_0\varepsilon\mathbf{E} + \mathbf{P}_b$. In the calculations, it is assumed that $\sigma_s = 0$ and all the polarized *free* surface charge is zero.

The Poisson equation for the PCBM layer Eq. (1) could be solved analytically in one dimension. Since the right side of the equation is only a function of the electrostatic potential ϕ, the second order differential of ϕ can be changed to $\frac{d^2\phi(x)}{dx^2} = -\frac{dE}{dx} = \frac{EdE}{d\phi(x)}$. Then the differential equation is integrated twice to give $\phi(x)$. By setting two parameters as

$$C_1 = E_{10}^2 - \left(\frac{2e}{\varepsilon_0\varepsilon_S}n_0 e^{-\alpha_L/k_BT}\right)\cdot\left(\frac{k_BT}{e}e^{e\phi_{10}/k_BT}\right), \tag{10}$$

$$C_2 = \left(\frac{2e}{\varepsilon_0\varepsilon_S}n_0 e^{-\alpha_L/k_BT}\right)\cdot\left(\frac{k_BT}{e}\right) \tag{11}$$

the expression of the electrostatic potential is

$$e^{e\phi_1(x)/k_BT} = \frac{C_1}{C_2}\frac{4e^{\frac{e\sqrt{C_1}x}{K_BT}}\left|\frac{\sqrt{C_1+C_2e^{e\phi_{10}/k_BT}}-\sqrt{C_1}}{\sqrt{C_1+C_2e^{e\phi_{10}/k_BT}}+\sqrt{C_1}}\right|}{\left[1-e^{\frac{e\sqrt{C_1}x}{K_BT}}\left|\frac{\sqrt{C_1+C_2e^{e\phi_{10}/k_BT}}-\sqrt{C_1}}{\sqrt{C_1+C_2e^{e\phi_{10}/k_BT}}+\sqrt{C_1}}\right|\right]^2}, \quad (\text{for } C_1 > 0) \tag{12}$$