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in perovskite oxide heterostructures with the
critical thickness**

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GUO-ZHEN YANG

EPL, **102** (2013) 37007

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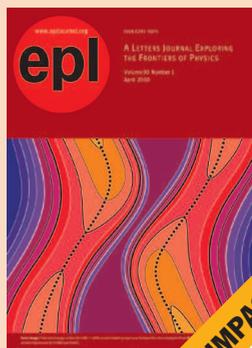
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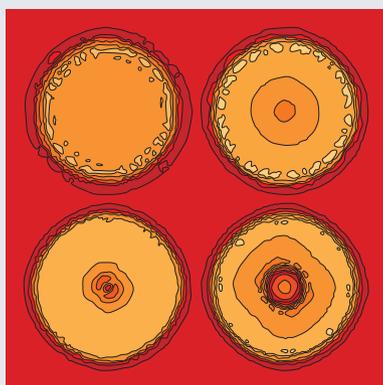
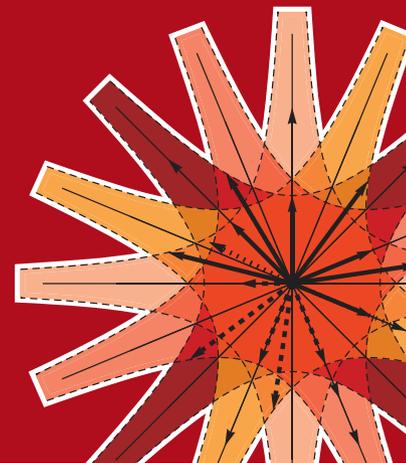
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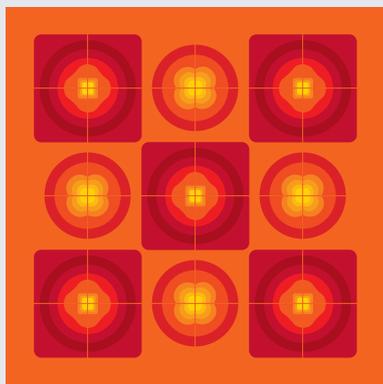
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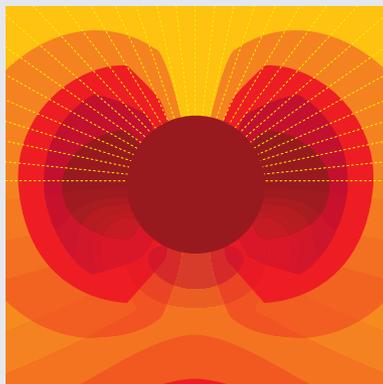
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The mechanism of the maximum photovoltage in perovskite oxide heterostructures with the critical thickness

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received 23 January 2013; accepted in final form 23 April 2013

published online 16 May 2013

PACS 73.50.Pz – Photoconduction and photovoltaic effects

PACS 73.40.Lq – Other semiconductor-to-semiconductor contacts, *p-n* junctions,
and heterojunctions

Abstract – A calculation based on the one-dimensional time-dependent drift diffusion model was carried out in order to study the mechanism of the maximum photovoltage obtained in perovskite oxide heterostructures. We found that the critical thickness of the thin films with which the maximum photovoltage was obtained depends on the width of the depletion region, the diffusion length of the minority carriers, and the light absorption coefficient in the films. The results reveal some physical insights in the maximum photovoltage and should be useful in designing the perovskite oxide heterostructures to improve the photovoltaic effect.

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Photoinduced effects in perovskite oxides have been of great interest in the past few decades, such as photoinduced phase transition [1], lateral photovoltaic effect [2,3], switchable ferroelectric photovoltaic effect [4–6]. High photoelectric conversion efficiency may bring about enhancements to these photoinduced effects. The thickness of perovskite oxide films can have influence on the many properties of the film, such as transport properties [7], optical properties [8] and the electron structures [9]. Recently, it has been reported that maximum values of photovoltage are obtained in the oxide heterostructures of $\text{La}_{0.9}\text{Sr}_{0.1}\text{MnO}_3/\text{SrNb}_{0.01}\text{Ti}_{0.99}\text{O}_3$ (LSMO1/SNTO) and the $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3/\text{Si}$ (LSMO3/Si) with the critical thicknesses of LSMO films, which are roughly equal to the widths of the depletion region in the films of the heterostructures [10]. To see the physics inside this phenomenon, we introduced the one-dimensional time-dependent drift diffusion (1DTDDD) [11,12] model to carry on the theoretical investigation of this phenomenon. Our calculation shows that the critical thickness of the films in the heterostructures is also associated with the diffusion length of the minority carriers and the light absorption coefficients besides the length of the depletion layer in the LSMO films.

According to the experiment described in ref. [10], LSMO films with various thicknesses and doping

concentrations were deposited on SNTO and Si substrates, respectively. A XeCl laser pulse with the width of 20 ns was vertically irradiated on the surfaces of the films, and the instantaneous photovoltages were measured. It was found that the photovoltage can reach the maximum if the thickness of the film is roughly equal to the width of the depletion region in the film of the heterostructure. In order to study the photoelectric process, we carried out 1DTDDD-based calculations on the LSMO1/SNTO system. The 1DTDDD model consists of the Poisson equation and the current continuity equations, given as [11,12]

$$\frac{\partial}{\partial x} \left[\varepsilon \frac{\partial \varphi(x,t)}{\partial x} \right] = -e[p(x,t) - n(x,t) + N], \quad (1)$$

$$\frac{\partial n(x,t)}{\partial t} = \frac{1}{e} \frac{\partial j_n(x,t)}{\partial x} + G(x,t) - R(x,t), \quad (2)$$

$$\frac{\partial p(x,t)}{\partial t} = -\frac{1}{e} \frac{\partial j_p(x,t)}{\partial x} + G(x,t) - R(x,t), \quad (3)$$

where φ , n , p , j_n , and j_p represent the electrostatic potential, the electron concentration, the hole concentration, the electron current density, and the hole current density, respectively; e , ε , and N are the elementary charge, the dielectric permittivity, and the net ionized impurity density, respectively; G and R are the generation and the recombination rates of the electron-hole pairs,

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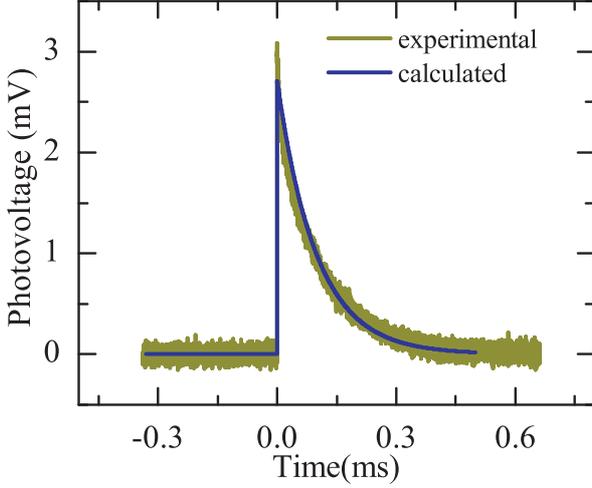


Fig. 1: (Colour on-line) Experimental and calculated photovoltage dynamic process in the LSMO/SNTO heterostructure. The experimental data is from ref. [11].

respectively. G can be written as

$$G = I_0 \alpha \beta e^{-\alpha x}, \quad (4)$$

where I_0 , α , and β are the density of photon flux, the light absorption coefficient, and the quantum efficiency. Using the Shockley-Read-Hall model [13], the generation rate of the carriers can be expressed as

$$R = \frac{pn - n_i^2}{\tau_n(p + n_i) + \tau_p(n + n_i)}, \quad (5)$$

where n_i , τ_n , and τ_p are the intrinsic carrier density, the lifetime of electrons, and the lifetime of holes, respectively.

The currents in the bulk region, as presented in terms of drift and diffusion, are [14]

$$j_n(x, t) = -e\mu_n n(x, t) \frac{\partial \varphi(x, t)}{\partial x} + k_B T \mu_n \frac{\partial n(x, t)}{\partial x}, \quad (6)$$

$$j_p(x, t) = -e\mu_p p(x, t) \frac{\partial \varphi(x, t)}{\partial x} - k_B T \mu_p \frac{\partial p(x, t)}{\partial x}, \quad (7)$$

where μ_n , μ_p , k_B , and T are the mobility of electrons, the mobility of holes, the Boltzmann constant, and the temperature, respectively.

Here, the thermionic emission mechanism [15] is introduced to describe the current across the interface. With the position of the interface denoted as x_I , the electron current density can be written as [12]

$$j_n(x_I, t) = -\eta_n \left\{ n(x_{I-}, t) \frac{A_{n1}^*(x_{I-}) T^2}{N_c(x_{I-})} \times \exp\left(\frac{H(\Delta E_c) \Delta E_c}{k_B T}\right) - \theta_n n(x_{I+}, t) \times \frac{A_{n2}^*(x_{I+}) T^2}{N_c(x_{I+})} \exp\left(-\frac{H(-\Delta E_c) \Delta E_c}{k_B T}\right) \right\}, \quad (8)$$

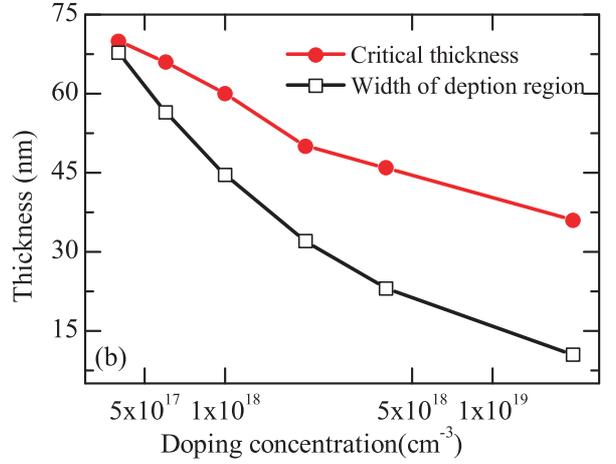
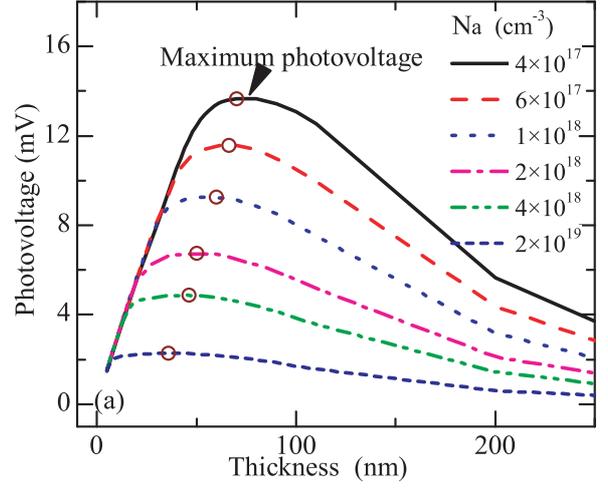


Fig. 2: (Colour on-line) (a) Thickness dependence of photovoltage with various doping concentration. Na means acceptor concentration. (b) Doping concentration dependence of the critical thickness and the width of the depletion region.

where θ_n is the ratio of the effective masses of electrons on the two sides of the interface; H is the unit step function; A_n^* is the effective Richardson constant for electrons; N_c is the effective density of states in the conduction bands; ΔE_c is the difference of the bottoms of conduction bands. η_n is a coefficient related to the different effective masses of the materials between the two sides. The expression for η was discussed in ref. [16]. The hole current density can be written in a similar form as [12]

$$j_p(x_I, t) = \eta_p \left\{ p(x_{I-}, t) \frac{A_{p1}^*(x_{I-}) T^2}{N_v(x_{I-})} \times \exp\left(-\frac{H(-\Delta E_v) \Delta E_v}{k_B T}\right) - \theta_p p(x_{I+}, t) \frac{A_{p2}^*(x_{I+}) T^2}{N_v(x_{I+})} \times \exp\left(\frac{H(\Delta E_v) \Delta E_v}{k_B T}\right) \right\}, \quad (9)$$

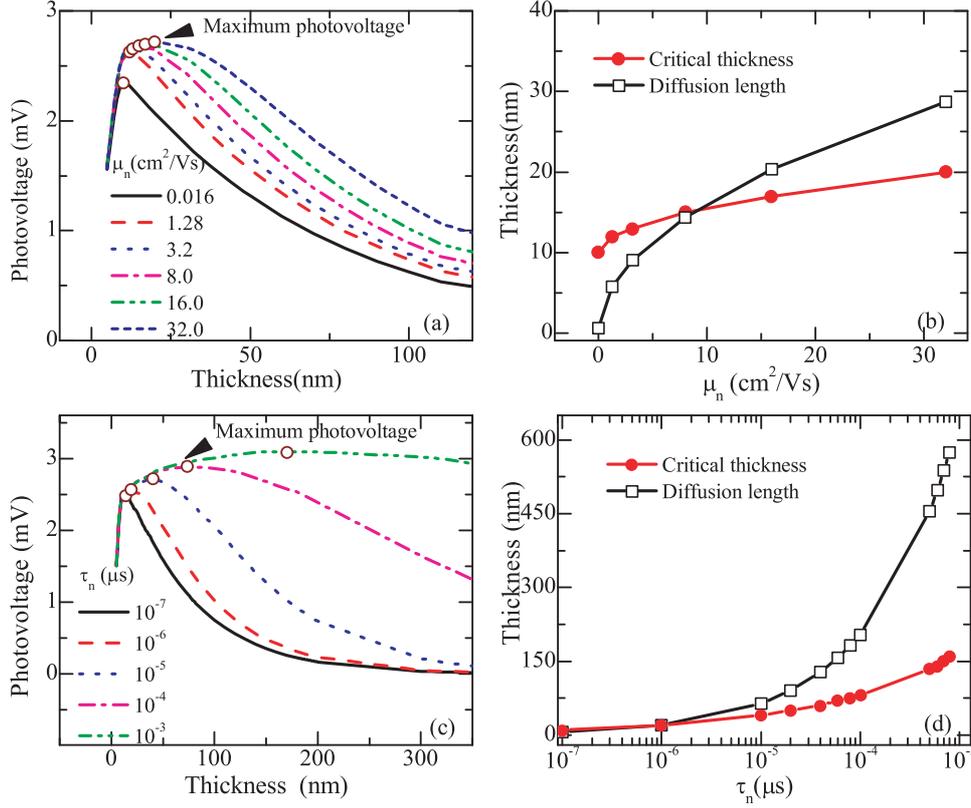


Fig. 3: (Colour on-line) (a) Film thickness dependence of photovoltage with various minority carrier mobility in the film. (b) Electron mobility dependence of critical thickness and diffusion length. (c) Film thickness dependence of photovoltage with various minority carrier lifetimes. (d) Electron lifetime dependence of critical thickness and diffusion length.

Table 1: Material parameters [10,18–23].

	LSMO1	SNT0
Dielectric constant (ϵ_0)	10	150
Electron mobility (cm ² /V s)	10	33
Hole mobility (cm ² /V s)	1.8	6
Affinity energy (eV)	3.98	4.05
Band gap (eV)	1	2.8
Electron effective mass (m_0)	4	7
Hole effective mass (m_0)	6	10
Doping concentration (cm ⁻³)	2.3×10^{19}	2.12×10^{20}
Light absorption coefficient (m ⁻¹)	1.5×10^7	1.2×10^7
Quantum efficiency	0.05	0.088

The boundary conditions for eqs. (1)–(3) are written as

$$\varphi(L, t) = 0, \quad E(0, t) = 0, \quad (10)$$

$$j_n(0, t) = j_n(L, t) = 0, \quad (11)$$

$$j_p(0, t) = j_p(L, t) = 0, \quad (12)$$

where L is the total length of the heterostructure.

The differential equations (1)–(3) were discretized with a finite-difference method and then solved with the damped Newton's method.

The lifetime of minority carriers in the film is one of the key parameters which may decide the critical thickness. Because the decay time of the photovoltage depends on the lifetime [17], we obtained the value of the lifetime by calculating the decaying process and matching the calculated results with the experimental data. The LSMO1/SNT0 heterostructure with the thickness of LSMO1 being 30 nm in ref. [10] was chosen to be studied, as the maximum photovoltage was obtained in this structures. Figure 1 shows that the decaying process fits well with the experimental data if the lifetime of the electrons in the LSMO1 thin film is taken as 10^{-5} μs. The other parameters are listed in table 1 [10,18–23].

Based on the calculations, we found that the width of the depletion region in the film is one of the factors on which the critical film thickness depends. The calculated results with various doping concentrations of the LSMO1 films in the heterostructures are shown in fig. 2. With the increase of the doping concentration, the depletion region narrows down. This leads to the decrease of the critical thickness of the film for the maximum photovoltage as well. Photo-generated carriers diffuse to the interface, and get separated by the built-in electric field in the depletion region. The calculation results show that most of the photo-generated carriers locate at the edges of the depletion region. The further the positively charged

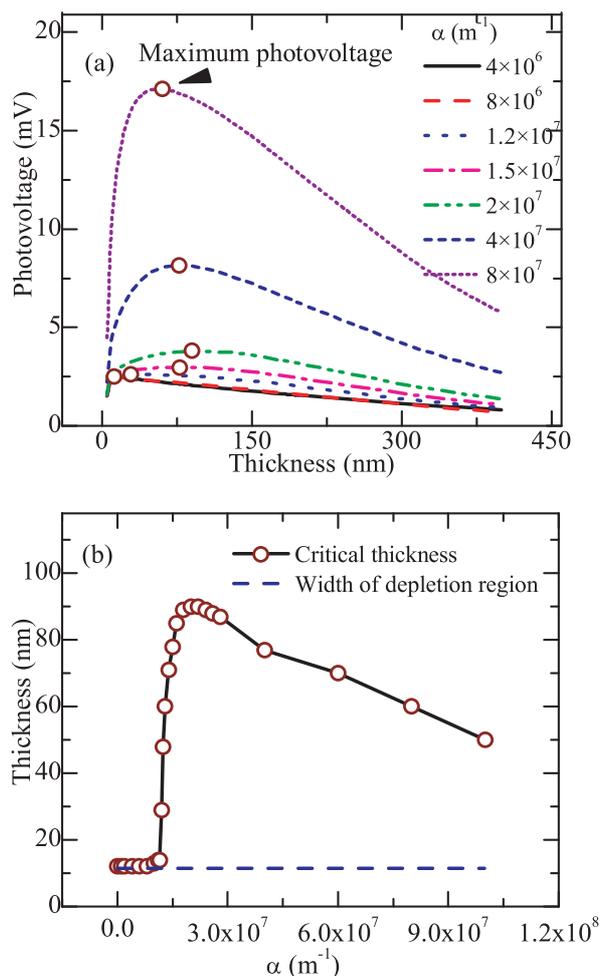


Fig. 4: (Colour on-line) (a) Thickness dependence of photovoltage with various light absorption coefficient. (b) Dependence of critical thickness on the light absorption coefficient. The dashed line denotes the width of the depletion region in the film.

holes and the negatively charged electrons are parted, the larger the electric potential difference there is. Therefore, photovoltage becomes larger as the width of the depletion region increases, as shown fig. 2(b). As the thickness of the film is reduced below the width of the depletion region in the film, the distance between the light-generated electrons and holes decreases, and so does the photovoltage. The collection efficiency for carriers generated in the depletion region is close to unity, while the efficiency for those generated outside the depletion region is negatively correlated to the distance from the depletion region to the point where the carriers are generated [24,25]. Thus, photovoltage becomes smaller with the increase of the film thickness, if the thickness of the thin film is larger than the width of the depletion region plus a part of the diffusion length of the minority carriers in the film. Due to the very small collection efficiency of the carriers generated at the positions further than the diffusion length away from the interface region, the critical thickness is just about the

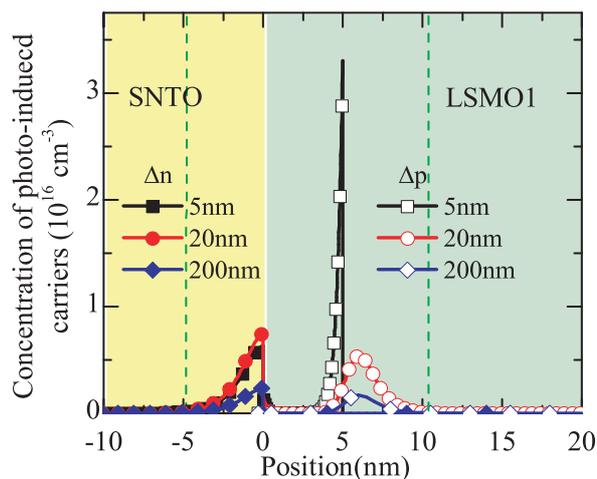


Fig. 5: (Colour on-line) The distribution of the photoinduced carriers in the LSMO1/SNTO heterostructures with films of various thicknesses. The lines with filled symbols denote the concentration of the electrons, and the lines with unfilled symbols denote the concentration of the holes. The interface locates at 0 point in the x -axis, and the dashed lines roughly denote the borders of the depletion region.

width of depletion region in the film where the diffusion length is small.

The second factor affecting the critical film thickness for obtaining the maximum photovoltage is the diffusion length of the minority carriers of the films in the heterostructures. In the film with diffusion length comparable to or larger than the width of the depletion region in the thin film of the heterostructures, photo-generated carriers outside the depletion region contribute to the photovoltage as well. The diffusion length of the minority carriers in the film, which can be expressed as $\sqrt{k_B T \mu \tau} / e$, is positively correlated to the mobility and the lifetime of those carriers. Figures 3(a) and (c) show that the photovoltage increases with the increasing of the diffusion length if the thickness is greater than the width of the depletion region in the films of the heterostructures. The increase of the diffusion length enlarges the amount of the light-generated carriers diffusing to the depletion region without being recombined outside the depletion region, *i.e.*, the collection efficiency increases. Thus, the critical thickness increases with the increasing of the diffusion length, as shown in figs. 3(b) and (d). The mobility of the carriers inside and outside the depletion region can be different because the mobility is relevant to the concentrations. However it should be noted that the dependence of the photovoltage is mainly on the mobility of the carriers outside the depletion region. In our case, the concentrations of the light-generated carriers are much smaller than the doping density. Hence, the concentrations of the carriers outside the depletion region are about equal to the doping densities. Since the dependence of the photovoltage on the mobility of the carriers inside the depletion region is weak, the concentration dependence of the mobility does not strongly affect the photovoltage.

Finally, we investigated the effect of the light absorption coefficient of the film by changing its value and comparing the corresponding critical thickness. Figure 4(a) shows that for a film with the thickness larger than the width of the depletion region in the film, further increasing of the thickness does not increase the photovoltage if the light absorption coefficient is less than about $1 \times 10^7 \text{ m}^{-1}$. Figure 4(b) shows that the critical thickness of the film is about the width of the depletion layer with the light absorption coefficient less than $1 \times 10^7 \text{ m}^{-1}$ for the heterostructures of LSMO1/SNTO. With further increasing the light absorption coefficient above $1 \times 10^7 \text{ m}^{-1}$, the critical thickness of LSMO1 films increases to about 90 nm and then decreases. In this case, light is absorbed not only in the film of LSMO1, but also in the substrate of SNTO. In the LSMO1 film, the quantum efficiency is slightly lower and the diffusion length of minority carriers is much smaller than in the substrate of SNTO. With a small light absorption coefficient of the film, increasing the film thickness make little change to the distribution of the light. Thus the critical thickness is just about the width of the depletion region. If the light absorption coefficient is larger, and the thickness of the film is larger than the width of the depletion layer in it, there will be additional light-generated carriers in the heterostructure, which leads to an increase of the critical thickness of the film. However, if the light absorption coefficient keeps going higher, the most of the light would be absorbed by the edge of the film, thus the light intensity in the regions with high carrier collection efficiency decays exponentially with the light absorption coefficient, which results in a decrease of the critical thickness of the LSMO1 film.

From these results the mechanism of the maximum photovoltage in the LSMO1/SNTO perovskite heterostructure is revealed. As shown in fig. 5, photoinduced carriers are separated to the edges of the depletion region. Reducing the thickness of the film below the width of the depletion region decreases the distance between the photoinduced holes and electrons which are apart. It also decreases the absorption of light by the film. Thus the photovoltage decreases. Increasing the thickness of the film above the width of the depletion region may enhance the absorption of light, and leads to an increase of the photovoltage. However, further increasing the thickness of the film causes that the reduction of the light arriving in the depletion region due to the absorption before the light reaching that region. And most of photoinduced carriers far from the interface region can be recombined before they could diffuse to the depletion region. Thus less photo-induced carriers are separated by the built-in field while the distance between the locations where the photoinduced electrons and holes mainly distributes keeps unchanged, which lowers the photovoltage. In this case, the maximum photovoltage is determined by the competition between the increasing of the absorption of light in the film and the decreasing of the collection efficiency of the light-generated carriers outside the depletion region. The absorption of

light is related to the absorption coefficient of the film. The collection efficiency is related to the diffusion length of the carriers in the film. Therefore, the critical thickness of the film is between the width of the depletion region and sum of the width of the depletion region and the diffusion length of the minority carriers in the film.

In conclusion, according to our results based on self-consistent calculations, the dependence of the critical thickness of the film in the LSMO1/SNTO heterostructure for the maximum photovoltage on the width of the depletion layer in the film, the diffusion length of minority carriers, and the light absorption coefficient of the film is as follows. If the diffusion length of the minority carriers is much shorter than the width of the depletion region width or the light absorption coefficient is very low, the critical thickness is roughly equal to the depletion region width in the film. Otherwise, it increases as the diffusion length gets longer. With the increase of the light absorption coefficient, it increases to a maximum value and then decreases. These results unraveled the mechanism of the maximum photovoltage obtained in the LSMO1/SNTO heterostructure, and would be useful for improving the photovoltaic effect in perovskite oxide heterostructures.

* * *

This work was supported by the National Basic Research Program of China (Nos. 2012CB921403 and 2013CB328706) and the National Natural Science Foundation of China (Nos. 10825418 and 11134012).

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