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Theoretical study on the photodoping effects in $La_{1-x}Sr_{x}MnO_{3}/SrNb_{y}Ti_{1-y}O_{3}$ p–n heterojunction

Leng Liao, Kui-juan Jin^{*}, Hui-bin Lu, Jie Qiu, Peng Han, and Li-li Zhang

Beijing National Laboratory for Condensed Matter Physics, Institute of Physics, Chinese Academy of Sciences, Beijing 100190, P.R. China

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^{*} Corresponding author: e-mail kjjin@aphy.iphy.ac.cn

The dynamic process of photodoping effect in the heterojunction of $La_{0.9}Sr_{0.1}MnO_3/SrNb_{0.01}Ti_{0.99}O_3$ is revealed theoretically. By solving Poisson Equation and time-dependent carrier continuity equations, the evolutions of the carrier concentrations and the electrical potential are obtained selfconsistently. The calculated photovoltage evolution agrees well with the experimental data. The present results demonstrate that the large variation of carrier concentration mainly locates in the space-charge region of the oxide heterojunction. It means that the photodoping effect mainly occurs in the space-charge region of heterojunction.

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1 Introduction The perovskite oxides attract much attention owing to their interesting magnetic, electronic, transport properties [1-4], and unusual photo-induced effects [5-15]. The concentration of carriers in the perovskite oxides can be changed by the light without changing the crystal structure or the chemical composition of the material. It is regarded as photodoping effect [16], due to its similarity to the chemical doping. Furthermore, in the peroskite oxides, the concentration of doping has a strong effect on the magnetic and electric properties [17]. Therefore, the photodoping effect can indicates a lightcontrolling over the electric and even magnetic properties of the perovskite oxides [18]. So that it is possible to create some novel functional devices, such as light-tunable magnets [19]. However, because of the complexity of perovskite oxide, the mechanism of photodoping effect in perovskite oxides is still not so clear. Thus, carrying on a theoretical study on the dynamic process of photodoping effects in the perovskite oxides structures should be helpful for the understanding of the photoelectric effect in oxides. In this work, we studied the dynamic process of photodoping effect in La_{0.9}Sr_{0.1}MnO₃/SrNb_{0.01}Ti_{0.99}O₃ (LSMO/ SNTO) heterojunction based on the time-dependent drift-



diffusion model [20] and Richardson thermionic emission current model [21]. Using finite difference method, Crank–Nicholson implicit scheme and Newton iteration, we solved the Poisson equation and the continuity equations self-consistently, and the evolution of photovoltage, the distributions of potential, and carrier concentration are obtained. Based on our calculation, we find that, although the photocarriers are generated all over the region of heterojunction, the variation of carrier concentration mainly locates in the space-charge region. In other words, the photodoping effect in the space-charge region is much stronger than that in the other regions. We expect it should have strong effect on the magnetic and electric properties in the heterostructure as well.

2 Theoretical model The system studied in this work is a heterojunction with a uniform and vertical irradiation on the surface of p-type region (LSMO) as shown in Fig. 1. For simplicity, the movement of carriers is assumed just along the growth direction of the heterojunction. Therefore, the dynamic photoelectric process in this system is treated as a one-dimensional process. Here, we introduce a one-dimensional *time-dependent* drift-diffusion

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model to describe the dynamic photodoping process in the dit perovskite oxide heterojunctions.

In this model, the Poisson equation and *time-dependent* continuity equations are given as follows,

$$\frac{\partial^2 \varphi(x,t)}{\partial x^2} = -\frac{e}{\varepsilon} [p(x,t) - n(x,t) + N], \qquad (1)$$

$$\frac{\partial n(x,t)}{\partial t} = -\mu_{\rm n} n(x,t) \frac{\partial^2 \varphi(x,t)}{\partial x^2} - \mu_{\rm n} \frac{\partial n(x,t)}{\partial x} \frac{\partial \varphi(x,t)}{\partial x}$$
$$+ \frac{kT\mu_{\rm n}}{\partial^2} \frac{\partial^2 n(x,t)}{\partial x} + G(x,t) - R(x,t) \qquad (2)$$

 ∂x^2

е

$$\frac{\partial p(x,t)}{\partial t} = \mu_{\rm p} p(x,t) \frac{\partial^2 \varphi(x,t)}{\partial x^2} + \mu_{\rm p} \frac{\partial p(x,t)}{\partial x} \frac{\partial \varphi(x,t)}{\partial x} + \frac{kT\mu_{\rm p}}{e} \frac{\partial^2 p(x,t)}{\partial x^2} + G(x,t) - R(x,t), \quad (3)$$

where $\varphi(x, t)$, p(x, t) and n(x, t) represent the electrostatic potential, the concentrations of hole and electron, respectively; e, ε and N denote the electron charge, the dielectric permittivity, and the net ionized impurity concentrations, respectively. μ_p and μ_n denote the mobility of hole and electron, respectively. k and T denote Boltzmann constant and temperature, respectively. In our calculation, T is taken as 300 K. G(x, t) is the photo-created electron-hole pair generation rate, which can be written as

$$G(x,t) = I_0(t)\alpha\beta \exp(-\alpha x), \qquad (4)$$

where $I_0(t)$ denotes the intensity of incident photon flux and is taken as 2.6×10^{23} /cm² s in our calculation. α denotes the photon absorption coefficient, and β denotes the quantum efficiency, respectively. In our calculation, α are taken as 1.5×10^5 cm⁻¹ and 1.2×10^5 cm⁻¹ for LSMO [22] and SNTO [23], β are set as 0.05 and 0.088 for LSMO and SNTO, respectively. The laser pulse duration in the calculation was taken as 25 ns, being identical with the experiment. R(x, t) denotes the recombination rate represented by Shockley–Read–Hall (SRH) model [24].

$$R(x,t) = \frac{p(x,t) n(x,t) - n_{\rm i}^2}{\tau_{\rm n0}(p(x,t) + n_{\rm i}) + \tau_{\rm p0}(n(x,t) + n_{\rm i})},$$
(5)

where n_i is the intrinsic carrier density, τ_{n0} and τ_{p0} are the lifetimes of electron and hole, respectively. The values of net ionized impurity concentration are obtained from the Hall measurement with $N = 1.0 \times 10^{19}$ /cm³ in LSMO and $N = 1.0 \times 10^{20}$ /cm³ in SNTO, respectively.

At the interface of heterojunction, the Richardson thermionic emission current is employed as interface con-

dition [21]:

$$j_{\text{Rich-p}} = \frac{A_{\text{pl}}^* T^2}{N_{\text{vl}}} \cdot \exp\left(-\frac{|\Delta E_{\text{v}}|}{kT} \cdot \theta(-\Delta E_{\text{v}})\right) \cdot p(x_{\text{interf}} - 0)$$
$$-\frac{A_{\text{p2}}^* T^2}{N_{\text{v2}}} \cdot \exp\left(-\frac{|\Delta E_{\text{v}}|}{kT} \cdot \theta(\Delta E_{\text{v}})\right) \cdot p(x_{\text{interf}} + 0),$$
(6)

$$j_{\text{Rich-n}} = -\frac{A_{\text{n1}}^*T^2}{N_{\text{cl}}} \cdot \exp\left(-\frac{|\Delta E_{\text{c}}|}{kT} \cdot \theta(\Delta E_{\text{c}})\right) \cdot n(x_{\text{interf}} - 0) + \frac{A_{\text{n2}}^*T^2}{N_{\text{c2}}} \exp\left(-\frac{|\Delta E_{\text{c}}|}{kT} \cdot \theta(-\Delta E_{\text{c}})\right) \cdot n(x_{\text{interf}} + 0),$$
(7)

where, $j_{\text{Rich-p}}$ and $j_{\text{Rich-n}}$ are the Richardson thermionic emission hole and electron current, respectively. x_{interf} denotes the position of interface; The effective Richardson constants of hole and electron in p- and n-type regions of heterojunction are expressed as $A_{pl}^* = 4\pi e m_{pl}^* k^2 / h^3$, $A_{p1}^* = 4\pi e m_{p1}^* k^2 / h^3$ $A_{p2}^* = 4\pi em_{p2}^* k^2/h^3$, and $A_{p2}^{\mu} = 4\pi e m_{p2}^{\mu} k^2 / h^3$, with the corresponding effective hole (or electron) masses m_{p1}^* and m_{p2}^* (or m_{n1}^* and m_{n2}^*) in p- and n-type regions, respectively. The N_{v1} and N_{v2} (or N_{c1} and N_{c2}) are called the effective density of states function in valence band (or in the conductive band) in the p- and n-type regions, with the definition that $N_{v1} = 2(2\pi m_{pL}^*kT/h^2)^{3/2}$ and $N_{v2} = 2(2\pi m_{pR}^*kT/h^2)^{3/2}$ (or $N_{c1} = 2(2\pi m_{nL}^*kT/h^2)^{3/2}$ and $N_{c2} = 2(2\pi m_{nR}^*kT/h^2)^{3/2}$). $\Delta E_v = E_{v2} - E_{v1}$ and $\Delta E_c = E_{c2} - E_{c1}$, where E_{v2} and E_{v1} (or E_{c2}) and E_{cl}) are the energy of top of valence band (or bottom of conductive band) in p- and n-type regions, respectively. $\theta(x)$ is the step function: if x < 0, $\theta(x) = 0$; else if $x \ge 0$, $\theta(x) = 1.$

The boundary conditions for Eqs. (1), (2), and (3) are taken as

$$\varphi_{\rm R}(t) = E_{\rm L}(t) = 0, \qquad (8)$$

$$j_{\rm B-p}(t) = -\frac{V_{\rm ph}(t)}{S \cdot R} \frac{\mu_{\rm p} p_{\rm B}(t)}{(\mu_{\rm p} p_{\rm B}(t) + \mu_{\rm n1} n_{\rm B}(t))},$$
(9)

$$j_{\rm B-n}(t) = -\frac{V_{\rm ph}(t)}{S \cdot R} \frac{\mu_{\rm n} n_{\rm B}(t)}{(\mu_{\rm p} p_{\rm B}(t) + \mu_{\rm n} n_{\rm B}(t))},$$
(10)

where $\Phi_{\rm R}(t)$ is the electrostatic potential on the right boundaries and $E_{\rm L}(t)$ is the left boundary electric field; $j_{\rm B-p}(t)$ and $j_{\rm B-n}(t)$ denote the boundary hole and electron current density, respectively; $V_{\rm ph}(t)$ denotes the photovoltage; $p_{\rm B}(t)$ and $n_{\rm B}(t)$ denote the concentrations of hole and electron on the boundaries, repectively; *R* and *S* denote the parallel resistance and the cross area of junction, respectively. In our calculation, *R* is take as 50 Ω and *S* is taken as

| | La _{0.9} Sr _{0.1} MnO ₃ | SrNb _{0.01} Ti _{0.99} O ₃ |
|---|--|--|
| dielectric constant (ε_0) | 10 | 150 |
| electron mobility $(cm^2/(V s))$ | 10 | 33 |
| hole mobility $(cm^2/(V s))$ | 1.8 | 6 |
| band gap (eV) | 1.0 | 2.8 |
| electron effective mass (m_0) | 4.0 | 7.0 |
| hole effective mass (m_0) | 6.0 | 10.0 |

 Table 1 Material parameters (Ref. [4, 26, 27]).

 $2.5\times10^{-4}~\text{cm}^2.$ The other important parameters are shown in Table 1.

The initial values of $\varphi(x, 0)$, p(x, 0) and n(x, 0) for solving Eqs. (1), (2), and (3) are obtained through solving the conventional static drift-diffusion model [20] as follows.

$$\frac{\partial^2 \phi(x,0)}{\partial x^2} = -\frac{e}{\varepsilon} [p(x,0) - n(x,0) + N], \qquad (11)$$

$$-\mu_{n}n(x,0)\frac{\partial^{2}\varphi(x,0)}{\partial x^{2}} - \mu_{n}\frac{\partial n(x,0)}{\partial x}\frac{\partial \varphi(x,0)}{\partial x}$$
$$+\frac{kT\mu_{n}}{e}\frac{\partial^{2}n(x,0)}{\partial x^{2}} - R(x,0) = 0, \qquad (12)$$

$$\mu_{p}p(x,0)\frac{\partial^{2}\varphi(x,0)}{\partial x^{2}} + \mu_{p}\frac{\partial p(x,0)}{\partial x}\frac{\partial \varphi(x,0)}{\partial x} + \frac{kT\mu_{p}}{e}\frac{\partial^{2}p(x,0)}{\partial x^{2}} - R(x,0) = 0,$$
(13)

3 Results and discussion The LSMO/SNTO heterojunction was fabricated by deposing a 40 nm thick p-type LSMO layer on n-type SNTO (001) substrate by laser molecular-beam epitaxy (Laser-MBE) [25]. A 50 Ω parallel



Figure 1 (online colour at: www.pss-a.com) (a) Experimental evolution of photovoltage in the LSMO/SNTO heterojunction connected with 50 Ω resistance. The insert presents the illustration of heterojunction for voltaic measurement. (b) The calculated evolution of photovoltage.



Figure 2 (online colour at: www.pss-a.com) (a) Calculated energy-band profile in the LSMO/SNTO heterojunction, in which the carrier movement is exhibited. (b) The distribution of electric-field in LSMO/SNTO heterojunction. The region between 25 nm and 45 nm is space-charge region. The insert presents the illustration of charge distribution in space-charge region.

resistance is connected with LSMO/SNTO heterojunction. A XeCl pulsed laser (energy of 1.5 J, wavelength of 308 nm, repetition rate of 1 Hz and duration of 20 ns) was irradiated on the surface of LSMO layer to excite photovoltage, which was measured by a 500 MHz oscilloscope. The incident energy of the laser pulse is 0.1 mJ with the wavelength of 308 nm and the irradiated area of heterojunction of 0.3 cm^2 . The energy of 308 nm photon is about 4.0 eV, which is larger than the band gaps of LSMO (~1.0 eV) and SNTO (~2.8 eV). Therefore, the photocarriers can be produced both in the LSMO and SNTO. Figure 1(a) represents the experimental evolution of photovoltage response in LSMO/SNTO heterojunction and the full width at half maximum (FWHM) is ~120 ns. The calculated evolution of photovoltage is exhibited in Fig. 1(b). The comparision of the calculated results and the measured data is shown in Fig. 1(a).

Through solving Eqs. (11)–(13), the energy band profile and electric field intensity distribution in LSMO/SNTO heterojunction can be obtained self-consistently without light irradiation. These results are given in Fig. 2(a) and (b), respectively. As shown in these figures, the two boundaries of space-charge region locate on x = 25 nm and 45 nm, respectively. When light irradiates on the heterojunction, the electrons and holes are created in the bottom of conduction band and top of valence band, respectively. Subsequently, these photo-induced electron-hole pairs diffuse into the spaces-charge region. In this region, the electron-hole pairs are separated by built-in field, and the electrons and holes drift into p-LSMO and n-SNTO regions, respectively. The movement of carriers induces the redistribution of charge in the space-charge region and the changing of the electric potential difference between n- and p-type regions. The detailed movement of the photocarrers in LSMO/SNTO is discussed in the follows.





Figure 3 (online colour at: www.pss-a.com) (a) Holeconcentration variation at 4, 8, 12, 16 and 20 ns. (b) The electronconcentration variation at 4, 8, 12, 16 and 20 ns. The region between two dash lines is the space-charge region as shown in Fig. 2.

Figures 3 and 4 exhibit the evolution of carrier concentration and potential distribution in the period of 0-20 ns, respectively. In this period, the light irradiates on the heterojunction and the electron-hole pairs are created in both LSMO and SNTO layers. When the carriers diffuse into the space-charge region, the electrons and holes drift into the SNTO and LSMO layers by the built-in field, respectively. In Fig. 3, it is shown that the concentrations of electron and hole increase in SNTO and LSMO regions, respectively. When photo-created holes and electrons drift into the boundaries of space-charge region, the effect of diffusion reaches equilibrium with that of drift. The former pushes the photo-created carriers into the space-charge region while the latter pulls them out of that region. Therefore, the photo-induced holes and electrons can not move



Figure 4 (online colour at: www.pss-a.com) Electric potential distribution at 0, 4, 8, 12, 16 and 20 ns. The insert exhibits the electric potential distribution in LSMO/SNTO heterojunction without irradiation.





Figure 5 (online colour at: www.pss-a.com) (a) Holeconcentration variation at 100, 200, 300, 400 and 500 ns. (b) The electron-concentration variation at 100, 200, 300, 400 and 500 ns. The region between two dash lines is the space-charge region as shown in the Fig. 2.

out of the space-charge region and the carriers accumulate in this region. As shown in Fig. 3, the concentrations of hole and electron increase in the right and left sides of the space-charge region, respectively. In the homogeneous region, the variation of carrier-concentration is much smaller than that in the space-charge region. This result indicates that the photo-induced doping concentration appears only in the space-charge region. Moreover, the movement of photo-carriers reduces the charge polarization in the spacecharge region. This phenomenon is explained that both positive and negative charge in n- and p-type regions is decreased by these carriers. Therefore, the potential difference between p- and n-type regions decreases with time while laser is on. As shown in Fig. 4, the electric potential in p-LSMO region rises with time. This behaviour corresponds to the photovoltage rising.



Figure 6 (online colour at: www.pss-a.com) Electric potential distribution at 100, 200, 300, 400 and 500 ns. The insert exhibits the electric potential distribution in the LSMO/SNTO heterojunction without irradiation.

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Figures 5 and 6 exhibit the evolutions of carrier concentration and potential distribution in the period of 100-500 ns while the laser is off. In this period, the photovoltage is a decaying process as shown in Fig. 1. Because the laser has been off and there are no carriers created any more, the effect of carriers diffusing into the space-charge region is weakened. Therefore, the equilibrium of drift and diffusion near the boundaries of space-charge region is broken and the effect of drift becomes greater than that of diffusion. The photo-created carriers are gradually pulled out of the space-charge region as shown in Fig. 5. Subsequently, these carriers leak out of the heterojunction through the parallel resistance. This induces the resuming of charge distribution in the space-charge region and the potential in LSMO reduces to the initial value with time as shown in Fig. 6. Consequently, the photovoltage decays to 0.

4 Summary In conclusion, on the basis of timedependent drift-diffusion model and Richardson thermionic emission current model, the mechanism of photodoping effect in pervoskite oxide heterojunction LSMO/SNTO is revealed. We obtained the dynamic evolution of photovoltage, which agrees well with the experimental data. The time-dependent evolution for the distribution of carrier concentration and potential is obtained. Our calculated results exhibit that the photo-induced variation of carrier concentration mainly locates mainly in the space-charge region. Namely, the photodoping effect in the space-charge region of LSMO/SNTO heterojunction is the strongest, which should somehow affect the magnetic and electric properties of the heterostructure.

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