Suppression of photovoltaic effect by magnetic field in $\text{Pr}_{0.65}(\text{Ca}_{0.75}\text{Sr}_{0.25})_{0.35}\text{MnO}_3/\text{Nb:SrTiO}_3$ heterostructure

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Suppression of photovoltaic effect by magnetic field in $\text{Pr}_{0.65}(\text{Ca}_{0.75}\text{Sr}_{0.25})_{0.35}\text{MnO}_3/\text{Nb:SrTiO}_3$ heterostructure

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The heterostructure composed of $\text{Pr}_{0.65}(\text{Ca}_{0.75}\text{Sr}_{0.25})_{0.35}\text{MnO}_3$ and 0.7 wt. % Nb-doped SrTiO_3 was fabricated. The heterostructure exhibits an asymmetric current-voltage relation similar to that of p - n junctions and an obvious photovoltaic effect with its maximum value of about 25.1 mV at $T = 140$ K. It is interesting that the magnetic field has a strong suppression effect on photovoltaic effect, and the maximum relative change of photovoltage under the magnetic field of 1 T is about 63% with the illumination of 15 mW/mm² light (532 nm) at $T \sim 140$ K. The physical mechanism is explained by the electronic phase separation mechanism. © 2013 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4832331>]

The study of manganese oxides widely known as manganites, exhibiting colossal magnetoresistance (CMR) effect, has attracted much attention within the area of strongly correlated electron systems.^{1–4} The strong spin-charge-lattice interaction leads to a striking phenomenon called the electronic phase separation (EPS) with the coexistence of exotic electronic and magnetic phases in single crystallines.^{5,6} The coexistence of charge-ordered insulating (COI) and ferromagnetic metallic (FMM) state was found in (La, Pr, and Sr) MnO_3 system through the electron microscopy by Uehara *et al.*⁷ Additionally, a wide variety of experimental and theoretical investigations have convincingly demonstrated the EPS effect in some manganites.⁸ These show that the microscale EPS can be caused by different factors, such as quenched disorders⁹ and homogeneous strain distribution.¹⁰ Meanwhile, the external perturbations,^{11,12} such as temperature, light, substrate strain, and magnetic field, can readily modify the near energetic degeneracy of neighboring phases, magnetic, and structural phase boundaries, leading to the extraordinary physics. For an example, our previous investigations have shown that the EPS may occur in unpatterned $\text{Pr}_{0.65}(\text{Ca}_{0.75}\text{Sr}_{0.25})_{0.35}\text{MnO}_3$ (PCSMO) films with a macroscopic (millimeter) size.¹³ Furthermore, the CMR effect is a specific effect. Both theoretical and experimental results demonstrate that the CMR effect occurs as a percolative process under external magnetic fields in some manganites.¹⁴ Currently, it has attracted more attention that combining manganites with other perovskite oxides could be a promising way for the exploration of uncovered aspects and the design of artificial practical materials. So it is meaningful to be engaged in studying the physical mechanism of systems through the heterostructure platform. In addition, external fields simultaneously affect the properties of manganites-based heterostructures, and the coupling effect between the fields on heterostructures will be explored. In the present paper, the heterostructures composed of PCSMO and

0.7 wt. % Nb-doped SrTiO_3 (NSTO) substrate are prepared, and the effects of magnetic field on photovoltages are investigated. The heterostructure exhibits a typical rectifying behavior and a potential suppression of photovoltage effect under external magnetic fields. Interestingly, the obvious suppression effect shows up within the “prime” EPS instead of the whole EPS region, indicating that a marked percolative process plays a significant role in the effect of magnetic fields on photovoltages.

The PCSMO/NSTO heterostructure was fabricated by growing a PCSMO film on the n -type NSTO single crystal with the area of 5×5 mm² using a pulsed laser deposition method. The frequency of a KrF excimer laser with a wavelength of 248 nm was maintained at 10 Hz. The substrate was kept at 750 °C, and an oxygen pressure of 10 Pa was maintained throughout the deposition. The film thickness of about 150 nm estimated by a SPECEI-2000-VIS ellipsometer was controlled through adjusting the deposition time. The X-ray diffraction (XRD) was performed on a RigakuD X-ray diffractometer (RigakuD/max-2400, Cu K α radiation). According to the θ - 2θ scan of X-ray diffraction pattern shown in Fig. 1(a), the film shows good crystallinity and c -axis orientation. Indium electrodes were pressed on the surfaces of PCSMO film and NSTO substrate to obtain Ohmic contact, respectively. In measurement, the heterostructure was placed in a Janis C300 closed circuit cryostat with quartz glass windows, and the current versus voltage characteristics were measured using a Keithley 2400 multimeter in the temperature range from 60 to 300 K. During the testing process, 10 min was held to allow enough thermal relaxation at each temperature point to reduce the experimental error.

Let us first focus on the cooling and heating process of resistance-temperature curves in PCSMO film. As shown in Fig. 1(b), the PCSMO film displays a metal-insulator transition at $T_{MI} = 140$ K. Furthermore, it is noted that the resistance exhibits a thermal hysteresis behavior. The thermal hysteresis in resistance-temperature curves is a characteristic

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FIG. 1. (a) The XRD θ - 2θ scan curve of a PCSMO/NSTO heterostructure. (b) Cooling and warming curves of resistance for PCSMO film and phase diagram: Insulator region, EPS region (divided into “prime” EPS and “deep” EPS regions). The inset is the $\ln R$ vs $T^{-1/4}$ curve for the PCSMO film. The solid line is fitting to the VRH model above $T_p \sim 200$ K.

of EPS in the vicinity of first-order phase transition.^{15,16} The peak resistance likely results from the percolative transition due to the intrinsic inhomogeneity. For the transport character of manganites in the insulating state, the conduction may operate in term of mechanism: the variable-range hopping (VRH) model,¹⁷ which is expressed as

$$R = R_{i0} \exp(T_0/T)^{1/4}, \quad (1)$$

where R_{i0} is the prefactor and T_0 is the characteristic temperature. As shown in the inset of Fig. 1(b), a plot of $\ln R$ against $T^{-1/4}$ shows a good linearity, and the VRH mechanism works quite well at $T > 200$ K, indicating that the transition temperature is about 200 K. From the fitting, we can get T_0 is about 56.5 MK. So the PCSMO film has a transition from the insulating phase to the EPS phase at $T_p = 200$ K. Based on these results, the temperature regions are divided into three ranges as shown in Fig. 1(b): the insulating state temperature region (above 200 K), the “prime” EPS region (from 100 to 200 K), and the “deep” EPS region (below 100 K).

The current-voltage characteristics of PCSMO/NSTO heterostructure at different temperatures are presented in Fig. 2(a). The positive bias applied on the heterostructure is defined as the current flowing from PCSMO film to NSTO substrate. The heterostructure exhibits an asymmetric current-voltage relation in the measuring temperature range of 60–300 K. The Pr^{3+} is taken place by the divalent ion (Ca^{2+} and Sr^{2+}) in PCSMO, and the PCSMO can be considered as a p -type semiconductor. An energy barrier is formed at the interface of the heterostructure. Under a forward bias condition, the applied voltage reduces the energy barrier, and electrons in the PCSMO may inject into the NSTO. Therefore, the heterostructure shows rectifying behaviors. The diffusion voltage (V_d) as a function of temperature is presented in the inset of Fig. 2(a). It is interesting that the V_d increases from 0.11 to 0.45 V with decreasing temperature from 300 to 140 K and reaches its maximum value of ~ 0.45 V at $T_{MI} = 140$ K, followed by a drop. Overall, the variation of V_d reflects the change of energy barrier at the interface of heterostructure. The junction resistance (R_j) is

FIG. 2. (a) Current-voltage curves of a PCSMO/NSTO heterostructure at different temperatures. Inset: diffusion voltage as function of temperature. (b) A relation between V_d and $\ln R_j$.

defined by dV/dI of the current-voltage curves in the limit $I \rightarrow 0$. As shown in Fig. 2(b), the V_d is proportional to $\ln R_j$ in two different temperature ranges from 60 to 140 K and from 140 to 300 K, respectively. The monotonic increase of V_d with R_j results from a thicker depletion layer and a higher built field. The different slope coefficients of the $\ln R_j$ - V_d curves indicate a change of electronic transport mechanism, which may be associated with the different transport process in different temperature regions.

The photovoltaic effect of heterostructures irradiated by a laser (wavelength: 532 nm) with the light power densities from 5 to 45 mW/mm² at the step of 5 mW/mm² was studied over the temperature range of 60–300 K. As shown in Fig. 3, the light illumination produces the significant photovoltage (V_p) effect, and the values of the photovoltage monotonically increase with the power density. In the insulating temperature range, the V_p of heterostructure shows a slow downward trend and almost disappears above 250 K as the temperature increases. Compared with the insulating region, the V_p exhibits a slow rise tendency with increasing the temperature in the “deep” EPS region. It is interesting that the V_p increases as the temperature decreases and undergoes a sharp drop at $T_{MI} = 140$ K in the “prime” EPS region. The peak of V_p corresponds to the transition temperature (140 K). The maximum value of V_p is about 25.1 mV under the irradiation light density of 45 mW/mm². It is believed that the V_p values are related to the accumulation of photogenerated carriers and depletion layer width at the interface of heterostructure. The energy band diagram of the heterostructure is shown in the inset of Fig. 3(a). For a 532 nm laser, its photon energy is 2.3 eV, which is lower than the band gap of NSTO (3.2 eV) and larger than band gap of PCSMO (1.0 eV).¹⁸ When the heterostructure is irradiated by the laser, photons generate electron-hole pairs. The electrons in PCSMO film flow to NSTO with lower potential, and holes in NSTO layer are drifted to PCSMO film due to the built-in electric field. Finally, the photovoltage occurs. Moreover, the photogenerated carriers from the PCSMO layer play a crucial role in the process of photovoltaic effect. As mentioned above, the

different mechanisms affect the electric properties of PCSMO which is closely related to three factors: the thermal fluctuation, the capture carriers effect at the interface,¹⁹ and the EPS in PCSMO film. First, the depletion layer at the interface of heterostructure becomes thinner with increasing temperature due to a strong thermal diffusion, and therefore the V_p is very small in the insulating region. Compared with the insulating region, the thermal effect is remarkably weak in the “deep” EPS region. The photogenerated carriers are trapped around the defects caused by oxygen vacancy and lattice mismatch at the interface of heterostructure. Thereby the carrier concentration around the depletion layer in PCSMO film is reduced. So the V_p is nearly independent on temperature in “deep” EPS region. Second, a further analysis shows that a large R_j favors a higher V_p .²⁰ So the experimental results show the strongest V_p of PCSMO/NSTO heterostructure at ~ 140 K. Based on the traditional band theory, the change of bandgap at the transition temperature can affect the V_p of the heterostructure. Meanwhile, the FMM and COI phases with distinctly electronic properties coexist in the “prime” EPS region, and the subtle balance between these two phases may be the primary cause, inducing the change of V_p . To confirm these conclusions, further experiments about the V_p of the heterostructure under magnetic fields are conducted.

We measured the V_p of the heterostructure applied by the parallel magnetic fields with the values from 0.2 to 1 T at the step of 0.2 T under the irradiation of laser (532 nm, 15 mW/mm²). The temperature dependence of V_p and PV (PV is defined as $PV = \frac{V(0) - V(H)}{V(0)} \times 100\%$, where $V(H)$ is the V_p of the heterostructure under an applied magnetic field and $V(0)$ is the V_p without any field) of the heterostructure under magnetic fields are shown in Fig. 4. The inset of Fig. 4 depicts the schematic diagram of heterostructure under magnetic fields and light. We found that the magnetic field has a weak influence on V_p in the “deep” EPS and the insulating region, respectively. Especially, a strong suppression of V_p in PCSMO/NSTO heterostructure applied by magnetic fields in the “prime” EPS range is observed, and the maximum PV

FIG. 3. (a) Photovoltage of the heterostructure under the laser (532 nm) with different light densities as a function of temperature. The inset is the energy band diagram of the heterostructure. (b) The photovoltage as a function of power density at different temperatures.

FIG. 4. Temperature dependence of (a) photovoltage of heterostructure irradiated by a laser (15 mW/mm^2) and (b) PV for PCSMO/NSTO under different magnetic fields, respectively. Inset: the schematic diagram of heterostructure under magnetic fields and light.

value is about 63% under the magnetic field of 1 T at $T_{MI} = 140 \text{ K}$. It is noteworthy that the suppression of V_p effect mainly appear in the “prime” EPS region. These behaviors can be explained in the following way. The FMM phase is spin-ordered, and the spin in the insulating phase is disordered. The FMM and the insulating phases are dominant, respectively, in the “deep” EPS and the insulating region. Therefore the external magnetic field has a barely effect on the system in the two phases. The “prime” EPS region is the transition from the insulator state to the FMM state, and there coexists a quantity of FMM and COI phases at the interface of PCSMO/NSTO heterostructure. Under external magnetic fields, the spin orders of domains tend to align along the external field direction, resulting in the electrons transferring more easily across the domain-wall boundaries. Simultaneously, some fractions of COI phases will be converted to FMM phases under magnetic fields, leading to the formation of a complete conduction path.¹² As a result, the fraction of FMM phases is enhanced, and the photogenerated carriers accumulated in both sides of depletion layer are suppressed, leading to the greatly relative changes of V_p in the heterostructure. Besides, the current-voltage characteristics of heterostructure under different magnetic fields at different temperatures are measured. Similarly, the changes mainly happen in the “prime” EPS region. It is observed that the V_d decreases with an increase of magnetic fields. This further reveals that the suppression of V_p effect is related to

the marked percolative process and the EPS. A further study into the intrinsic theoretical mechanism of the unusual phenomena found in our work is ongoing.

In summary, The PCSMO/NSTO heterostructure shows a rectifying current-voltage relation and an obvious suppression of the photovoltaic effect under magnetic fields. All of these evidences clarify a fact that the suppression effects of photovoltages by external magnetic fields result directly from the marked percolative process and the EPS at the interface of manganites based heterostructures. These provide us some insights into the physical mechanisms of the coupling effect in manganites p - n heterostructures under many external fields.

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