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Reversible modulation of electric transport properties by oxygen absorption and releasing on Nb:$SrTiO_3$ surface

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Pt Schottky contacts on (001)-orientated Nb-doped $SrTiO_3$ (NSTO) in both ambient air and vacuum were investigated by the conductive atomic force microscope. The co-existed TiO_2 and SrO termination layers were identified on the terrace-structured NSTO surface, where the former possessed a higher forward current than the latter. In ambient air, the barrier height of Pt/NSTO Schottky junction exhibited periodical variation with cyclic terrace plane and step sites, whereas it became homogeneous in ambient vacuum. We suggested that the oxygen absorption and releasing of surface dangling bonds were the origin for reversible changes in transport properties, which indicates a feasible approach for the surface modulation and band structure tailoring of NSTO based heterojunctions. © *2014 AIP Publishing LLC*. [http://dx.doi.org/10.1063/1.4901346]

INTRODUCTION

Perovskite strontium titanate ($SrTiO_3$) has been intensely studied over the past few decades for its interesting physical properties and potential applications, such as the high dielectric constant (high-κ) dielectric in high-value capacitors,[1,2] the pseudo-ferroelectric in FeRAMs[3] and the superconductivity.[4,5] Pure $SrTiO_3$ is an insulator with a wide band gap of 3.3 eV, whereas it will transit to an n-type semiconductor in the case of oxygen vacancy or Nb doping.[6,7] Nb-doped $SrTiO_3$ (Nb:$SrTiO_3$, NSTO) demonstrated attractive application prospect in ferroelectric material and was extensively investigated recently. Issues concerned include the chemical balance of dopants and defects as well as the properties of surface barrier.[8–12] With the variation of Nb content, the conductivity of NSTO can be semiconductive, metallic, or even superconductive. However, the metal/NSTO contact is usually non-ohmic, exhibiting a rectifying behavior.[7,10–16] Some interesting physical phenomena were already revealed in such heterojunctions. For example, reversible hysteresis loops have been observed in repeated electric cycling, which were known as resistive switching (RS) effect.[7,12,17–21] The physical origin of the RS effect was ascribed to the field-induced changes of Schottky barrier, due to the electron trapping/detrapping in interface states. Therefore, the interface/surface characteristics are particularly important for the design of the NSTO-based devices. In previous researches, the experiments on NSTO surface were mainly carried out in an atmosphere environment and the vacuum condition was seldom concerned.[8,9] Particularly, the influence of the step structure on the surface properties of NSTO was scarcely studied before. As well-known, there are two types of terminated layers for the $SrTiO_3$ single crystal, i.e., the TiO_2 plane and the SrO plane.[22–25] Two natural question are what is the difference of these two layers, and what is the properties of the transition region in between these two layers.

In this paper, using the conducting atomic force microscope technique (C-AFM), we performed systematic characterization of the transport property of the NSTO surface with step structure. We found that the interface barrier between Pt tip and NSTO could be reversibly modulated by exposing sample to dry air or shielding it in a high vacuum atmosphere, indicating an important role of oxygen exchange for the electronic transport process. Moreover, the conductivity of the terrace-structured surface is spatial inhomogeneous in dry air and homogeneous in vacuum atmosphere.

EXPERIMENTAL

Commercial 0.8 wt. % Nb-doped $SrTiO_3$ single crystal with the (001) orientation was first etched by aqua fortis ($HCl:HNO_3 = 3:1$, ph ~ 1) and then annealed in flowing oxygen at 1050 °C for 30 min to obtain a terrace-structured surface with co-existed TiO_2 and SrO terminated layers. The as-prepared sample was attached to a conductive sample holder by silver (Ag) paste. Appropriate electric pulses were first applied to the Ag-NSTO contact to form ohmic behavior. Then, the surface morphology and local conductivity of the surface were simultaneously measured by the C-AFM (SII SPI3800N), adopting a Pt-coated tip with a curvature radius of $\sim$20 nm. Fig. 1(a) is a schematic view of the experiment setup. During the measurements, voltage biases were applied to the sample holder and the Pt probe was grounded. The limit current of our C-AFM system is 100 pA.

RESULTS AND DISCUSSIONS

The surface morphology of as-prepared NSTO sample is shown in Fig. 1(b). Although Pt-coating of the tip reduces the spatial resolution of atomic force micrograph (AFM) image, the terrace-structured surface can still be clearly seen. Fig. 1(c) shows the line profile of the sample surface. We find that the height of the surface steps is always an integral

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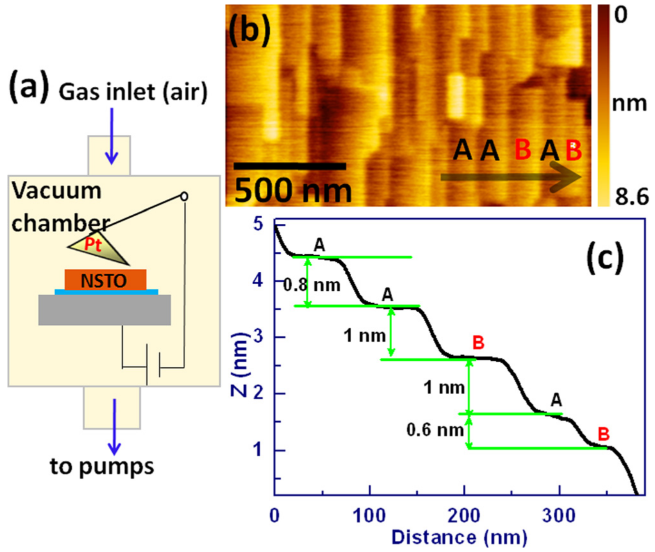

FIG. 1. (a) Experiment setup of the C-AFM measurement with Pt-coated probe. (b) The topographic image of as-prepared NSTO demonstrates terrace-structured surface. (c) A height line profile along the black arrow marked in (b). The height difference between terrace planes is an integral or half-integral multiple of 0.4 nm.

or half-integral multiple of 0.4 nm, which is just the lattice constant of NSTO.[22,23] This result indicates that there are two types of terrace planes (A and B) on sample surface;[11,26,27] the step height between the A-A or B-B planes is an integral multiple of one unit cell, whereas it is half-integral multiple of one unit cell between the A and B planes. These are general features in the AFM images collected from different locations of the sample, confirming that the as-prepared NSTO sample indeed possesses two types of terminated layers. This distinct surface of the sample gives us an opportunity to further investigate the different transport properties of TiO_2 and SrO terminated layers.

The *IV* characteristics of Pt probe-NSTO surface were first measured in the ambient air. As shown in Figs. 2(a) and 2(b), rectified *IV* characteristics are observed for both the A and B planes. For convenience, we define the turning on direction, i.e., the direction from the Pt tip to Ag electrode, as forward direction. Since the Ag-NSTO contact is an ohmic contact, such rectifying behavior should be mainly originated from the Schottky-like junction of the Pt/NSTO contact. Therefore, the distinct *IV* curves reflect different surface conductivities. According to the thermionic emission

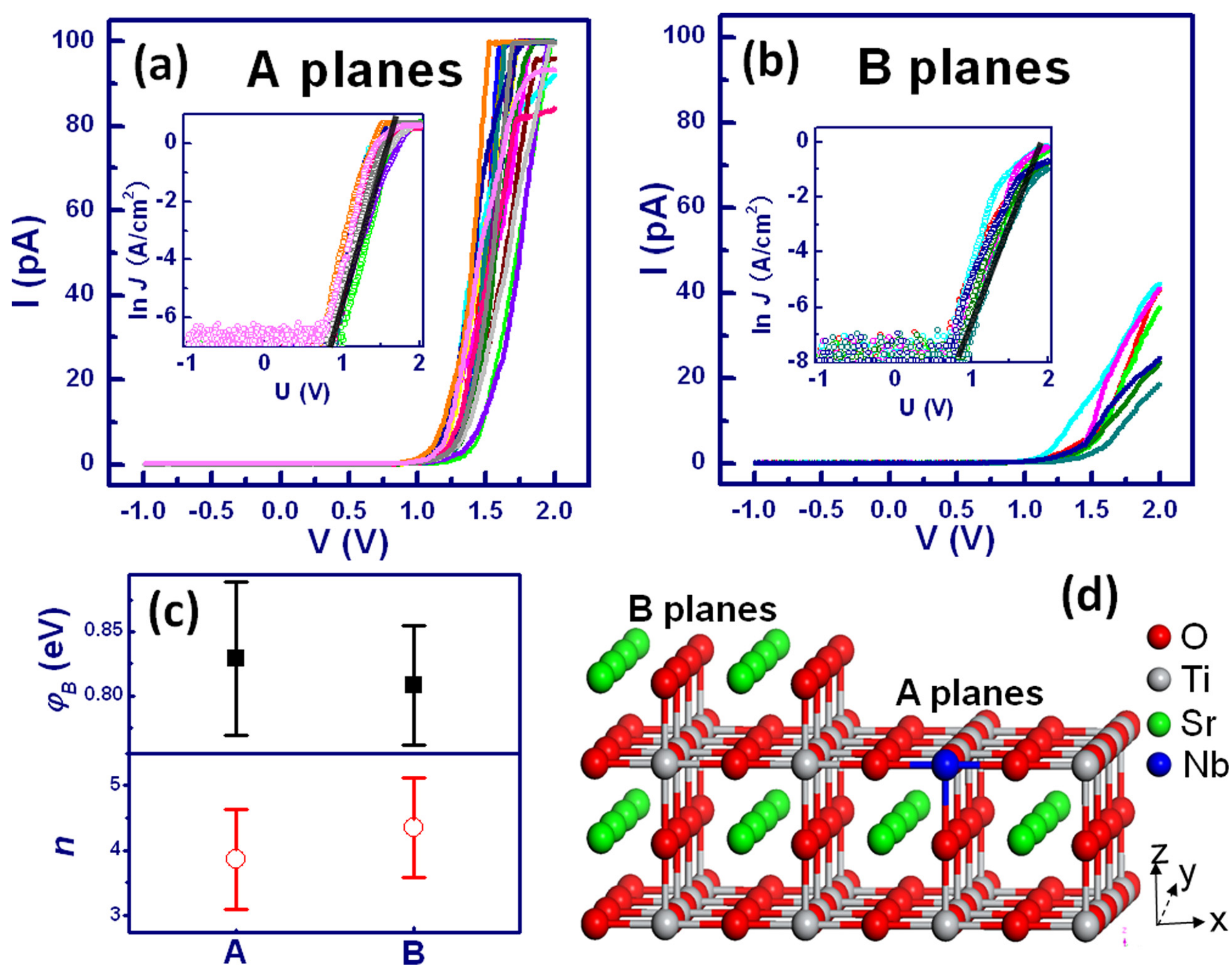

FIG. 2. Rectified *IV* curves of the Pt/NSTO junctions for (a) A planes and (b) B planes measured in ambient air. Insets are the corresponding *InJ-V* curves. (c) Statistical values of φ_b and n extracted from *IV* fitting. The error bar represents the standard deviation. (d) Three-dimensional image of the near-surface atom arrangement of NSTO crystal. The Nb dopants are localized at TiO_2 termination layer.

(TE) theory, the IV relation of Schottky junction obeys the following Shockley equations:[28]

$$J = J_0 e^{\frac{qv}{nk_BT}}\left(1 - e^{-\frac{qv}{k_BT}}\right) \tag{1}$$

and

$$J_0 = A^* T^2 e^{\frac{-q\varphi_b}{k_BT}}, \tag{2}$$

where n is the ideality factor, φ_b is the effective barrier height, k_B is the Boltzmann constant, T is ambient temperature, and A^* is the Richardson constant. If voltage bias V is larger than $3\,k_BT/q$, Eq. (1) can be simplified as $lnJ = lnJ_0 + (q/nk_BT)V$. We found that the IV curves can be well described by the Shockley equation, as demonstrated by the linear InJ-V curves in the insets of Figs. 2(a) and 2(b). The ideality factor and barrier height are then extracted from the slope and intercept of the InJ-V curve, respectively. We have measured 200 IV curves for either the A or B planes, and the deduced φ_b and n are averaged. As shown in Fig. 2(c), the average φ_b of the two terminated layers is very close, ~0.81 eV for A planes and ~0.80 eV for B planes, whereas the ideality factor is different, ~3.97 for the A planes and ~4.43 for the B planes. A large ideality factor means a thick interfacial layer with abundant interface states on the NSTO surface. Remarkably, the currents under forward biases are much larger for the A planes than for the B planes, i.e., the A planes are much more conductive than the B planes. In general, the increased doping concentration of Nb will significantly enhance the conductance of n-type semiconductor NSTO, where the doped Nb^{5+} ions preferentially go to the Ti^{4+} sites in the perovskite lattice.[6] We thus propose that, in the surface region, the Nb dopants are mainly localized in TiO_2 layer as shown in Fig. 2(d). Hence, the contrast in conductivity possibly indicates the A planes should be the TiO_2 termination layer and the B planes should be the SrO termination layer. This inference is consistent with the observation that the ideality factor of A is smaller than that of the B planes. It has been proven that the SrO terminated layer is more chemically reactive than the TiO_2 layer.[29] This actually means a low density of interface states for the TiO_2 layer than for the SrO layer.

Next, we investigated the spatial distribution of surface conduction. Figure 3(a) is a topographic image of the NSTO surface and the arrow denotes the position for a line profile crossing three A planes. The IV curves of ten selected locations along the arrow are shown in Fig. 3(b). These curves are also fitted to the TE theory and the dependence of extracted φ_b and n on surface location is given in Fig. 3(c). An remarkable observation is the periodical variation of φ_b and n with lateral position, which occurs when terrace steps are encountered. From the terrace plane to the step corner, the interfacial barrier φ_b decreases by ~0.12 eV and the n increases by ~2. Figure 3(d) is the simultaneously recorded current mapping under a tip bias of 1.5 V. Again, we find that the step corner regions exhibit a higher current than elsewhere, tallying with the IV measurements. It is possible that there might be many dangling bonds at the terrace surface of NSTO sample. These dangling bonds are saturated by absorbing oxygen from the ambient air. As a result, the density of surface trapping states is reduced.[30,31] Due to Coulomb repulsion, however, oxygen absorption more easily occurs on terrace plane than at step corner. Therefore, the

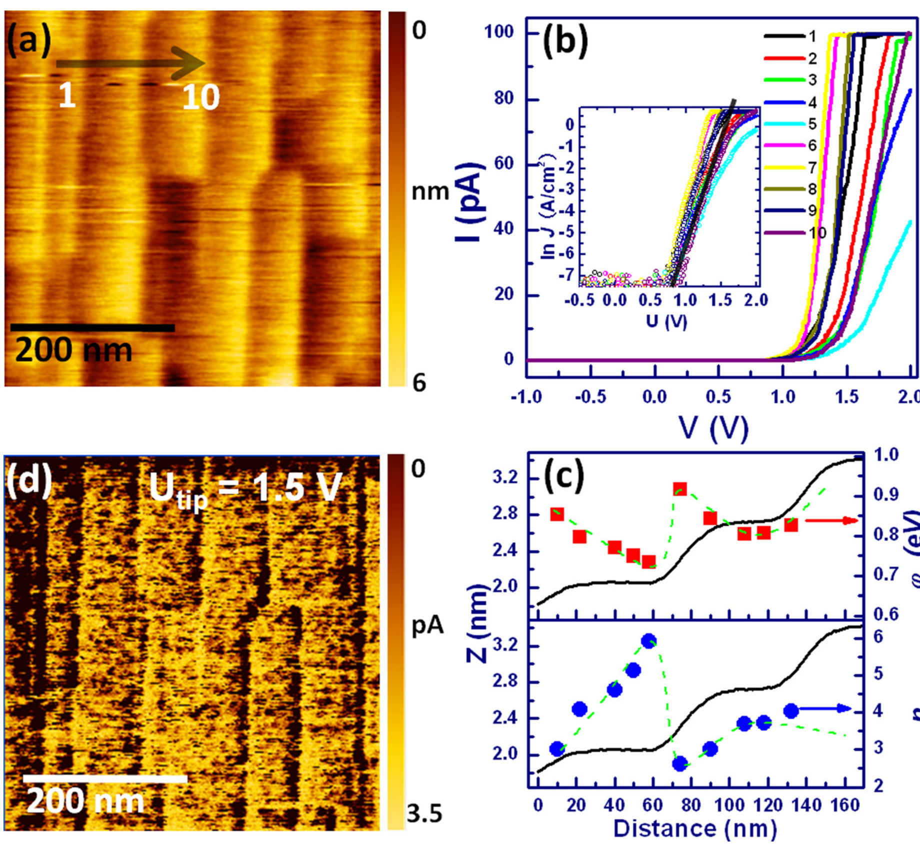

FIG. 3. (a) Topographic image of the NSTO surface and (b) ten IV curves measured in ambient air that horizontally cross three terrace steps. Inset is the corresponding InJ-V curves. (c) The dependence of φ_b and n on surface location demonstrate periodical variations. (d) A current mapping of the same area under +1.5 V bias.

barrier height is higher at the terrace plane than at step corner.

To confirm the effect of oxygen absorption on the local conductivity of NSTO surface, we further performed the experiments in a vacuum of 5×10^{-6} Torr. Figures 4(a) and 4(b) show the *IV* curves of the A and B planes, respectively. Compared with the results obtained in the atmospheric environment, the striking feature of the *IV* curves recorded in vacuum is the deviation from the typical rectifying behavior, and the reversal of the rectifying direction. Figure 4(c) gives the statistics of extracted φ_b and n. The average values of n are obviously increased ($\sim$8.48 for A plane and $\sim$9.34 for B plane), indicating a much higher density of interface states in vacuum. Particularly, the φ_b is $\sim$0.685 eV for A planes and $\sim$0.689 eV for B planes, both of which reduce by $\sim$0.12 eV compared with those in the case of ambient air. Moreover, when we put the sample back to the atmospheric environment, the rectifying behavior and the barrier height of Pt/NSTO junction recover. These results clearly indicate that the exchange of oxygen atoms between surface defect states and the environment can reversibly modulate the surface conductivity of NSTO. As mentioned above, the absorbed oxygen atoms will capture electrons from NSTO bulk and form localized oxygen species such as O^- and O_2^-.[6,10,17] These oxygen species will significantly reduce the vacancy density in the surface region as well as the donor concentration in NSTO. According to the semiconductor theory, the depletion layer width in the NSTO side is proportional to $(\varphi_b/N_d)^{1/2}$.[28] As shown in Fig. 4(d), the release of absorbed oxygen species to vacuum will lead to a reduction in depletion width W_d. As a result, the thermionic-field emission (TFE) caused tunneling current becomes prominent, causing the large leakage current under reverse biases. Meanwhile, in the forward direction, the electron tunneling effect also influences the fitting parameters of Shockley equation, resulting in a lower φ_b and a large n.

The *IV* characteristics of the terrace plane and the step corner, measured in vacuum, were also compared. Figure 5(a) shows the surface morphology and current mapping of a selected area. Different from the data collected in atmosphere, the current mapping here shows that the terrace plane and step corner have essentially the same local conductivity. The *IV* curves measured along the arrow mark are shown in Fig. 5(b), which demonstrate the irregular transport behavior of Pt/NSTO junction in vacuum. As shown in Fig. 5(c), the fitting parameter φ_b keeps constant along the line marked by the arrow, whereas n randomly distribute in the range between 5 and 20. As mentioned above, the absorbed oxygen atoms in surface states will be released when the sample is put into a vacuum environment, which will lead to a homogeneous donor distribution on sample surface. As a result, the periodical variation of φ_b accompanied across the terrace

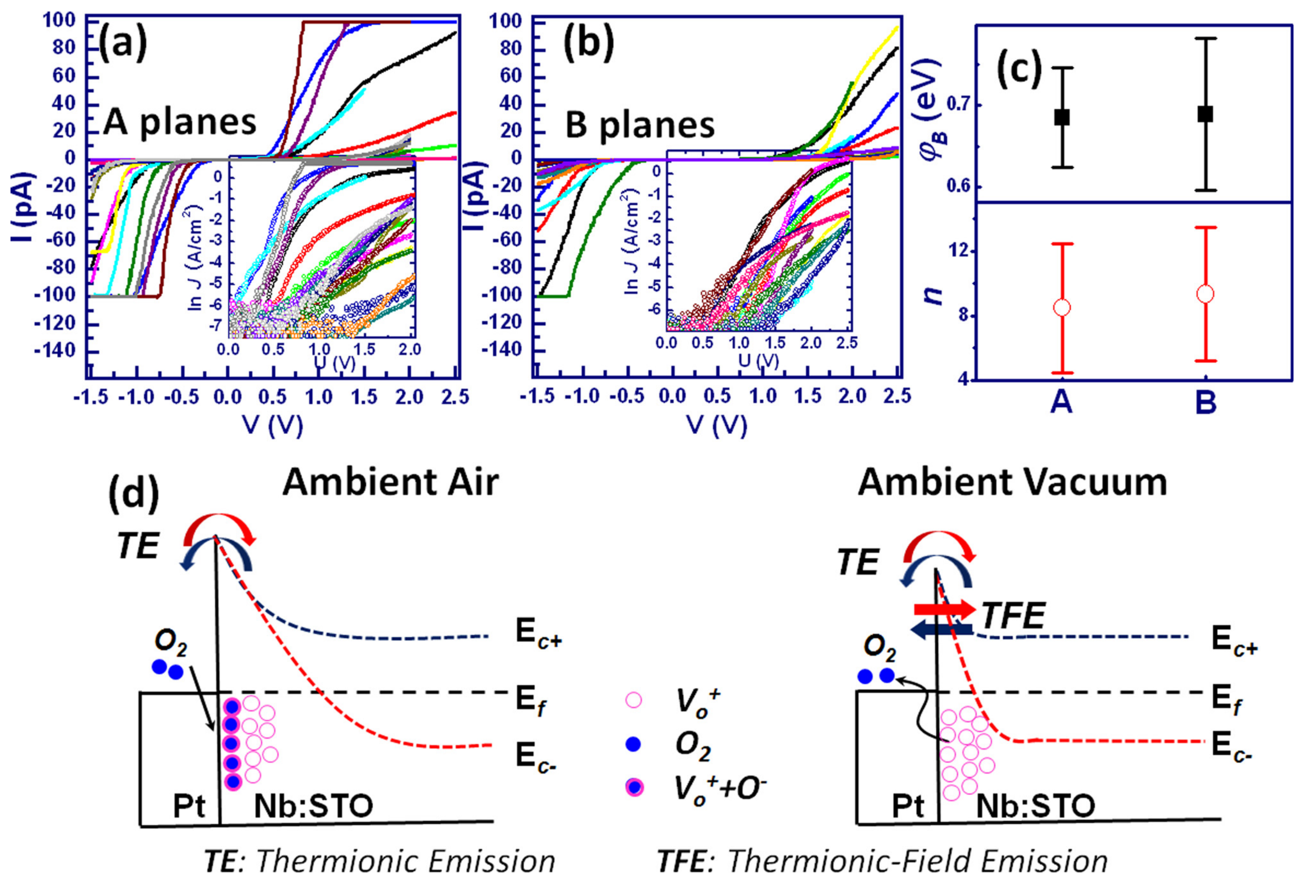

FIG. 4. *IV* curves of Pt/NSTO junctions for (a) A planes and (b) B planes measured in ambient vacuum exhibit unsaturated reverse current. Insets are the corresponding enlarged *InJ-V* curves. (c) Statistical values of φ_b and n for the vacuum condition. The barrier heights of A and B planes are both decreased $\sim$0.12 eV. (d) Schematic view of the band diagram of Pt/NSTO junction. The width of depletion layer is modulated by the absorption and releasing of oxygen atom on NSTO surface. The electrons transport behavior is dominated by TE in ambient air and both TE and TFE in ambient vacuum.

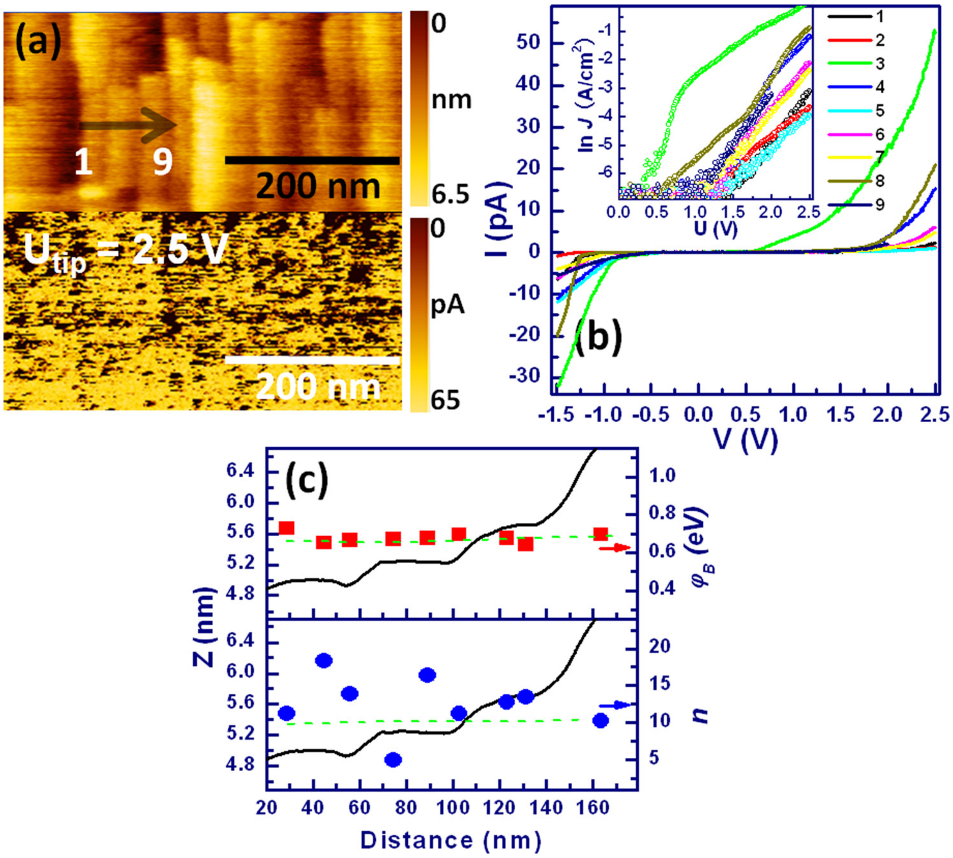

FIG. 5. (a) Surface morphology and current mapping (+2.5 V bias) of a same area measured in ambient vacuum. (b) Nine *IV* curves measured along the black arrow in (a). Inset is the corresponding enlarged *lnJ-V* curves. (c) The extracted of φ_b and n are independent with the surface location in the vacuum condition. Homogeneous distributed surface conductivity is presented.

steps disappears. The reversible oxygen absorption-release cycling demonstrates a non-destructive way to modulate the electric characteristics of the NSTO surface.

CONCLUSION

In summary, the transport property of the terrace-structured surface of NSTO has been studied by the conducting atomic force microscope technique. The coexistence of TiO_2 and SrO terminated layers on sample surface was confirmed by the AFM analysis. We found that the turning on current of the Pt/NSTO junction is considerably higher for the TiO_2 terminated layer than for the SrO layer, which could be ascribed to the accumulation of doped Nb ions in TiO_2 layer. The contact barrier exhibits a periodical variation when scanning Pt tip through the terrace plane and step corner of the NSTO in dry air, whereas it is independent of the position of the tip on sample surface when measurements performed in vacuum. It is believed that the oxygen absorption/ release of surface dangling bonds reversibly modulate the barrier height and depletion width of Pt/NSTO junction, resulting in the notable variations of transport properties. The present work provides a microscopic understanding of the correlation between structural and physical properties for the NSTO surface, demonstrating an application prospect of the perovskite oxide-based devices such as gas sensor.

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