Direct visualization and control of SrO$_x$ segregation on semiconducting Nb doped SrTiO$_3$ (100) surface

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Abstract
We investigated how SrO$_x$ segregates on a Nb doped SrTiO$_3$ (100) surface by in air annealing. Using atomic force and photoemission electron microscopes, we can directly visualize the morphology and the electronic phase changes with SrO$_x$ segregation. SrO$_x$ islands less than 2 μm in size and 1–5 unit cells thick nucleate first and grow in a labyrinth domain pattern. After prolonged annealing, SrO$_x$ forms a ~ 10 nm thick film. We show that the domain pattern can be controlled by introducing a surface miscut angle of SrTiO$_3$. Additionally, the segregated SrO$_x$ has a lower work function, compared to that of SrTiO$_3$. These results suggest that the control and tunability of SrO$_x$ segregation is applicable to the design of a new functional electronic devices in the semiconducting SrTiO$_3$ based heterostructure.

Keywords SrTiO$_3$ · SrO$_x$ · Surface segregation · Photoemission electron microscope

1 Introduction
SrTiO$_3$ (STO) is one of the most popular substrate materials for transition metal oxide heterostructures [1–9]. This is not only due to the commercial supply of very high quality crystals, but also many interesting phenomena in STO based heterostructures [4–10]. For example, high-$T_c$ superconductivity has recently been discovered in a monolayer FeSe film on electron doped STO substrate [4]. Two-dimensional conducting electrons are formed at the interface between two band insulators, LaAlO$_3$ film and STO substrate [5, 9]. These interesting phenomena are strongly dependent on the surface treatment method of the STO substrate [4, 5]. An improved understanding and methods of manipulating the STO surface are of central importance. The recipes, which commonly consist in a combination of chemical acid etching and thermal annealing, to achieve the atomical A-site (SrO) [11–14] and B-site (TiO$_2$) [15–19] terminated surfaces have been intensively developed over 20 years. As a result, a TiO$_2$-termination induced by etching is relatively well-understood and routinely used nowadays, but the recipe to control a SrO-termination still remains elusive.

There are two well-known methods to achieve a SrO-covered STO surface: one is the deposition of a SrO monolayer on a TiO$_2$-terminated STO substrate [11, 12] and the other is annealing of electron doped STO in air or with molecular oxygen gas [13, 14, 20]. In this letter, we elucidate how SrO$_x$ segregates on the surface of Nb doped STO (Nb:STO) crystals during air annealing. The morphology and the electronic phase changes with the segregation are directly visualized using photoemission electron microscopy (PEEM) and atomic force microscopy (AFM). We demonstrate the total process, from the atomical SrO$_x$ segregation to the ~ 10 nm thick film formation, on the surface by annealing, as well as the controllability of the segregation by varying the surface miscut angle and electron doping concentration. We expect that our results will provide novel insights, not only to
develop the recipe for the SrO-terminated STO surface, but also to design a new STO based heterointerface with SrO\textsubscript{x} segregation control.

## 2 Experiment

We prepared several different Nb:STO substrates by varying the surface treatment recipes. Before annealing, atomically flat substrates were prepared by buffered-hydrofluoric acid (BHF) etching to create TiO\textsubscript{2}-terminated Nb:STO surfaces [15–17]. Then, we annealed the substrates from 1000 to 1300 °C for 2 to 72 h. Additionally, we compared the surface of Nb:STO with different surface miscut angles and Nb doping concentration using the same preparation. Note that the BHF etching was applied to all samples and the annealing was performed in air, except when in vacuum annealing is explicitly mentioned.

The PEEM, work function ($W_F$) and x-ray photoemission spectroscopy (XPS) measurements were performed at the MAESTRO facility at Beamline 7.0.1 of the Advanced Light Source [21]. The PEEM images were obtained by exciting photoelectrons using the ultraviolet (UV) light of a Hg arc discharge lamp (~ 4.5 eV). The brightness in the PEEM images is dominantly determined by the intensity of the secondary electrons. The $W_F$ of Nb:STO is around 3.9 eV [22]. This implies that a different brightness in images stems from a local difference in $W_F$ of the sample. The quantitative local $W_F$ value was measured in the PEEM instrument using the secondary electron cut-off with a He-I (21.2 eV) source. The XPS was measured in the micro-ARPES endstation in total-energy resolution (photons + electrons) of around 50 meV, corresponding to photon energy of 240 eV at around 90 K. The measurement power density of the photon source was kept at 0.5 W cm\textsuperscript{-2}, relatively week intensity. We found that the electronic structure of sample surface was kept stable under the UV irradiation. Note that the Nb:STO shows a significant UV irradiation effect, such that much intense UV power density of ~ 4 W cm\textsuperscript{-2} could generate oxygen vacancies on the STO surface [8, 23–26], but the cation stoichiometry is not considerably affected. The non-contact mode AFM was performed in air and at room temperature.

## 3 Results and discussion

We found that the island structures having a different $W_F$ value compared to that of Nb:STO appear on surface after annealing. Figure 1a and b show PEEM images of 0.5 wt% Nb:STO substrates after etching and 72 h of annealing at 1000 °C (0.5Nb-1000C-72 h), respectively. While the just etched sample is homogeneous, we observe dark spots with a different $W_F$ appear after annealing (cf. Fig. 1b). To get structural information in the dark spots, we examined both samples with AFM. The just etched sample has a very flat surface in Fig. 1c, while the 0.5Nb-1000C-72 h sample shows a clear step structure in Fig. 1d. We obtained the line profile in Fig. 1e along the red dashed line shown in Fig. 1d. The line includes a step induced by annealing. The step heights are around 200 and 600 pm which are not matched with the 400 pm unit cell of Nb:STO [15, 16] or its multiples.

The dark spots can be attributed to several unit cells of SrO\textsubscript{x} segregated by annealing. The A-site segregation easily occurs in the perovskite structure due to the favored Schottky-type disorder [20, 26]. Additionally, the A-site segregation shows steps of half a unit cell or one and a half unit cells of the original perovskite structure on the surface [27, 28]. The unit cell of SrO\textsubscript{x} is around 200 pm and its electronic structure is different from that of STO [27, 28]. Thus, we can explain the two electronic phases observed in PEEM and the different step heights in the AFM images with the SrO\textsubscript{x} segregation on the surface. Additionally, the XPS results also support our picture of SrO\textsubscript{x} segregation on the Nb:STO surface after annealing. The Sr 3d spectra of just etched and 0.5Nb-1000C-72 h samples in Fig. 1f and g are fitted by two components: the bulk (blue) and the surface (green) components at around 133.8 and 134.5 eV binding energy, respectively. The surface component can be attributed to segregated Sr atoms on the surface [14, 29, 30], and it is stronger for the annealed sample.

In more annealing step, the segregated SrO\textsubscript{x} islands form a labyrinth domain pattern, and grow in a ~ 10 nm thick film by filling the gaps between domains. The PEEM image of 0.5Nb-1300C-2 h in Fig. 2a shows the SrO\textsubscript{x} labyrinth pattern clearly. Then, as shown in 0.5Nb-1300C-12 h in Fig. 2b, the gaps between domains are filled and form a closed SrO\textsubscript{x} film with new islands nucleated on it. The AFM images in Fig. 2c–e also show a consistent SrO\textsubscript{x} segregation process. Additionally, in the line profiles along the red dashed lines in the bottom panels, we measure the heights of SrO\textsubscript{x} domains and films to be ~ 10 nm. The schematic diagrams of the segregation process, based on our experimental results, are illustrated in Fig. 3. This mesoscopic length scale pattern can be understood by elastic theory in the presence of interactions between domain boundaries [31–33]. A commonly accepted explanation of 2D islands on solid surfaces is based on the delicate balance between attractive forces between neighboring atoms and the long-range repulsive interactions due to surface stress. If two phases of different surface stress coexist, then the surface lower the surface free energy by forming striped domains. Therefore, the stripe width and periodicity are decided by the balance between the energy of forming linear domain boundaries between the two phases and the energy of the long-range substrate and surface stress.
The low concentration of Nb doping induces less SrO\textsubscript{x} segregation due to low electron concentration in the STO [20]. The results of 0.05Nb-1300C-2 h in Fig. 4 show less segregation, compared with that of 0.5Nb-1300-2 h in Fig. 2. There is the surface miscut angle difference between both samples, but we also confirmed that 0.05Nb-1300C-12 h, having a surface miscut angle smaller than 0.05°, did not exhibit the big SrO\textsubscript{x} islands shown in Fig. 2b (not shown). These results suggest the Nb doping concentration proportional to the electron concentration is more important to determine the amount of the SrO\textsubscript{x} segregation.

We investigated in vacuum annealing effect for the segregated SrO\textsubscript{x}. The segregated islands in the pristine 0.5Nb-1100C-2 h sample show darker color than the surrounding
Fig. 2 PEEM images of a 0.5Nb-1300C-2 h and b 0.5Nb-1300C-12 h samples. AFM images of c 0.5Nb-1300C-2 h, d 0.5Nb-1300C-6 h and e 0.5Nb-1300C-12 h. The line profiles along the red dashed lines in c–e are shown in the bottom panels. Note that the AFM in 0.5Nb-1300C-12 h sample is measured in the area far from the island shown in b

Fig. 3 Schematic diagrams of SrO$_x$ segregation on Nb:STO. a TiO$_2$ terminated Nb:STO after BHF etching. b SrO$_x$ islands nucleation and c labyrinth pattern of its domain in annealing. d SrO$_x$ film formation, and appearance of new big islands on the film after more annealing steps

Nb:STO areas in PEEM (Fig. 5a). However, after in vacuum (10^{-9} Torr) annealing at 150 °C for 10 min, the contrast between the segregated SrO$_x$ islands and the other Nb:STO areas reverses (Fig. 5b). The SrO$_x$ areas becomes brighter than that of Nb:STO. The SrO$_x$ is not a stable phase in air, so many adsorbrates can be attached to it [34, 35] and detach by in vacuum annealing. To confirm our hypothesis, we measured the core levels before and after

Fig. 4 PEEM and AFM images of a, b 0.05Nb-1300C-12 h and c, d 0.05Nb-1300C-72 h samples. The SrO$_x$ domain has a stripe pattern. This sample has a surface miscut angle ~0.1°, while the samples in Figs. 1, 2 have it <0.05°
in vacuum annealing. The O 1 s core level in Fig. 5c shows a clear change. The spectra in the higher binding energy range are attributed to the surface adsorbates [36]. The in vacuum annealing reduces the spectral weight in the higher binding energy range, which indicates the removal of the surface adsorbates. This can explain the change of contrast in Fig. 5a and b. Note that we confirmed that more adsorbates are attached to the segregated SrOx in air than that of Nb:STO by comparing with the O 1 s core level of Nb:STO. A clear implication of our work is that the electronic properties at the semiconducting STO based heterointerfaces can be tuned by control of the SrOx segregation.

4 Conclusion

In summary, we investigated how SrOx segregates on the surface of Nb:STO with annealing using PEEM, XPS and AFM techniques. Our results provide the total process of SrOx segregation from atomic level to ~10 nm thick film formation. We also demonstrated the controllability of the segregation by tuning the surface miscut angle and the electron doping level of STO. The $W_F$ of SrOx are also different from that of Nb:STO. A clear implication of our work is that the electronic properties at the semiconducting STO based heterointerfaces can be tuned by control of the SrOx segregation.

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