Atomic control and characterization of surface defect states of TiO₂ terminated SrTiO₃ single crystals

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By using an alternative wet-etch procedure, we have obtained high-quality atomically flat TiO₂ terminated surfaces of SrTiO₃ single crystals with the morphology equivalent to that of the conventional wet-etch methods. By applying a combined power of photoluminescence (PL) spectroscopy, reflection high-energy electron diffraction, atomic force microscopy imaging, and soft x-ray absorption (XAS), we were able to identify and monitor the complex evolution of oxygen defect states and Ti valency at the surface and near-surface layers. Our experiments revealed a high level of local defects resulting in the presence of the Ti³⁺ states at the surface. We have developed a method to control the defect states capable of a marked reduction of the defect concentration. We have demonstrated that the PL and XAS are able to distinguish the surface-related Ti³⁺ states from oxygen vacancies trapping charge transfer vibronic excitons that define the PL intensity. The experimental findings will have important implications for the growth of high-quality ultrathin complex oxide heterostructures. © 2008 American Institute of Physics, [DOI: 10.1063/1.2971035]

Recent achievements in high-quality growth of complex oxide heterostructures have paved a way to explore quantum phenomena associated with unusual quantum states at the interfaces.¹⁻³ At present, the nature of surface states, mechanisms of charge compensation and the role of oxygen defects (Vₒ) are among the most actively investigated issues.¹,²,⁴⁻⁸ In connection with the challenge of engineering atomically sharp layers, it has been realized that growth kinetics and the overall quality of the materials are crucially dependent on the initial surface quality. Among several parameters affecting the growth of complex oxides chemical structure, surface and near-surface electronic states and oxygen defects at the termination plane are of prime interest.⁶⁻¹⁰

Despite the significant progress achieved to date, the vast majority of previous work on the defect structure of SrTiO₃ (STO) has been focused on materials with a high concentration of the oxygen vacancies prepared by several methods including ion bombardments and high-temperature annealing in vacuum and reduced gas atmosphere.⁴,¹² In contrast, the presented results elucidate the role of oxygen defects in STO under the typical conditions encountered during the conventional preparation of atomically flat TiO₂ terminated surfaces. In this letter, we present a detailed spectroscopic study and a way to control the surface properties in the important cases of undoped and Nb doped single crystals of STO (001). Below, we describe details of an original chemical wet-etch procedure used to obtain an atomically flat TiO₂ terminated surface. We started with high-quality STO single crystals. As expected, the as-received surfaces were of the mixed SrO/TiO₂ termination with a miscut angle of <0.3° and an average surface roughness of ~70–90 pm. Initially, the crystals were soaked for 20–25 min in de-ionized (DI) water at 70 °C to create soluble hydroxide complexes Sr(OH)ₓ +xH₂O at the surface. Next, 12 min of wet etching in HCl–HNO₃ (3:1) (HCLNO) acidic solution was applied to remove the surface SrO layer. Further, the substrates were thoroughly rinsed out with DI water to remove the acidic contamination and cleaned in acetone and methanol. The entire cleaning procedure took place in an ultrasonic bath. Finally, the etched samples were annealed at 1000 °C for 30 min in the air to facilitate the surface recrystallization. The resulting surface and the surfaces obtained by the conventional buffered HF (BHF) treatment were investigated by a combination of atomic force microscopy (AFM) imaging in a noncontact mode, reflection high-energy electron diffraction (RHEED), photoluminescence (PL), and soft x-ray absorption spectroscopy (XAS). Experimentally, the electronic excitations were produced by the Ti:sapphire short pulses laser (100 fs, and repetition rate of a 83 MHz) with frequency doubling at 370 nm (3.35 eV) and operating at the low power density of 35 nJ cm⁻² per pulse. All the PL spectra have been acquired in the range of 350–700 nm within a fixed time window using a 0.5 m spectrometer and at the room temperature.

Now we turn our attention to morphological properties of the obtained surfaces. A typical surface obtained by our HCLNO method is shown in Fig. 1(a). For comparison, we have also included the images of the reference surfaces created by the standard BHF treatment [see Fig. 1(b)]. As clearly seen, both methods were able to produce large, atomically flat terraces, about 500–700 nm wide and of one unit cell in height with essentially straight edges. For all samples the average area roughness, Rₐ, did not exceed 80–100 pm measured within a terrace. Since an AFM tip delivers information on the local surface morphology only, we have investigated the same samples by RHEED, which provides a statistically accurate view over the large fraction of the sample surface. The resulting RHEED patterns consist of sharp diffraction spots corresponding to the well-defined TiO₂ surface with a long-range crystalline order. These ob-

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As clearly noticeable, the intensity of the developed PL peak is considerably increased and shifted toward the “green” part of the visible spectra. It is also important to note that the TiO₂ surface prepared by the standard BFH route shows the same two-peak behavior but with almost two orders of magnitude increase in the integrated PL intensity compared to the as-received crystals. This clearly indicates that the electronic structure and the number of defect states have been markedly affected during the wet-etching step. The final set of PL spectra, shown in Fig. 2(b), has been taken on the same series of terminated samples after a high pressure reannealing in ultrapure O₂ (750 torr, 650 °C). Once again, the resulting data have revealed the overall remarkable reduction of the PL intensity accompanied by almost complete disappearance of the yellow line.

Next we discuss a possible microscopic origin of the observed phenomena with the aim to encompass for the profound evolution of PL seen during each phase of the measurement. The proposed mechanism can be described as follows. The laser light of 3.35 eV, which is only slightly above the STO band gap of 3.2 eV, excites an electron-hole pair with the hole located mostly in 2p oxygen valence states, and the electron located in the Ti 3d conduction states. The PL process starts only after the relaxation of the created 2p hole toward any of the available 3d Ti electrons creating a charge-transfer vibronic exciton (CTVE). Since the hole can recombine with any of the available Ti 3d electrons, it is natural to expect that the recombination rate scales with a concentration of available carriers from the Ti 3d band and oxygen vacancies at the surface.

To experimentally verify this hypothesis, we have measured a PL spectrum of a 0.5% Nb doped STO crystal. It is well known that Nb doping leads to the appearance of additional electrons in the Ti 3d band by effectively converting Ti⁴⁺ into the Ti³⁺ polaron state. Figure 2(b) shows the result of this measurement. In full anticipation, the doping resulted in the strongly increased intensity of the 530 nm green PL line. Based on this observation, we can associate this distinct PL line with the CTVE trapped by the states of Ti³⁺ ions partially occupying the surface TiO₂ layer. The low intensity of the green line in the as-received crystals [see Fig. 2(a)] lends additional support to this assignment because of the mixed SrO–TiO₂ termination of these samples. The origin of the yellow PL line is more subtle. A possible scenario behind this peak involves CTVE states trapped by oxygen vacancies. This assignment is further supported by the fact that this line has vanished after high-pressure oxidation of the samples followed by the dramatic reduction of the oxygen vacancies.

Another piece of evidence for the presence of a Ti³⁺ state at the TiO₂ surface was obtained by XAS. The data were collected at the Advanced Photon Source (ANL) at the L₃ edge of Ti in the bulk-sensitive fluorescence yield (FY) and the surface sensitive total electron yield (TEY) mode simultaneously in the grazing angle geometry. Figure 3 shows the obtained absorption spectra. By examining the lineshape around L₃ edge (~455–460 eV in Fig. 3) and comparing it to the LaTi³⁺O₃ and SrTi³⁺O₃ bulk reference samples, we can conclude that Ti valency is clearly reduced from the nominal value of 4⁺. If the mixed valency of Ti of the treated surface can be anticipated, the spectra taken in the FY mode revealed a surprisingly similar deviation from bulklike Ti electronic structure taken from Ref. 16. This ob-

![Image](https://example.com/image1.png)

**FIG. 1.** (Color online) AFM images of characteristic TiO₂ terminated substrates. (a) A vicinal surface of the STO samples prepared by the HCLNO method. The average area roughness \( R_a \) is ~80 pm. (b) The surface morphology of the reference STO crystals prepared by the conventional BHF method from Ref. 13–15. In both cases, the elevated 3D view highlights the resulting surface quality along the ledges.

![Image](https://example.com/image2.png)

**FIG. 2.** (Color online) (a) PL spectra of the as-received, treated by HCLNO (SA) and BFH (RA) methods. As seen, upon treatment there is a dramatic change in both the PL intensity and the lineshape of the spectra. (b) The same crystals after reannealing in high-pressure O₂ resulting in the remarkable reduction of the PL intensity. For comparison also shown the PL spectrum of the Nb (0.5%) doped STO.
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The growth of high-quality ultrathin complex oxide heterostructures will have particular significance for the green-yellow PL at the room temperature in STO. These experimental findings will have a remarkable sensitivity to examine the nature of these states and Ti valency at the surface and near-surface layers. From the practical point of view, we have demonstrated the method to control the electronic and defect states at the surface. We have also shown that PL spectroscopy can be used as a remarkably sensitive tool to examine the nature of these states. Toward this end, we have experimentally identified the origin of the most pronounced PL lines appearing in the “green-yellow” spectral range. Specifically, we have attributed the green PL to the recombination of 2p holes by the surface Ti$^{3+}$ polarons, whereas the yellow PL line was assigned to the VCTE states trapped by oxygen vacancies at the subsurface region. This constitutes the observation of the green-yellow PL at the room temperature in STO. These experimental findings will have particular significance for the growth of high-quality ultrathin complex oxide heterostructures.

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