

Surface structures of a Co-doped anatase TiO₂ (001) film investigated by scanning tunneling microscopy

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The surface structure of an anatase Ti_{0.94}Co_{0.06}O₂ (001) film, grown epitaxially on a Nb-doped SrTiO₃ (001) substrate, was investigated using *in situ* scanning tunneling microscopy. For the as-grown film, a (1×*n*) (*n*=3, 4, 5, and 6) reconstructed surface was observed that shows (*n*−2) faint rows between adjacent bright rows. After annealing at 650 °C, nanoparticles appeared, mostly on the step edges. From the *I*−*V* curves measured by scanning tunneling spectroscopy, the tunneling gap of Co:TiO₂ was estimated to be about 3.0 eV, consistent with the band gap (*E_g* = 3.2 eV) of pure anatase TiO₂. However, on nanoparticles, the *I*−*V* curve showed a much smaller gap, suggesting that the particle must be different from TiO₂. © 2003 American Institute of Physics. [DOI: 10.1063/1.1571983]

Recently, Co-doped anatase TiO₂ films have attracted considerable attention due to the possibility of a diluted magnetic semiconductor (DMS). Anatase Co:TiO₂ films were reported to have room temperature ferromagnetism (FM).^{1,2} It was argued that the FM could originate from carrier-induced magnetic interactions,² as in case of the III-V-based DMS.³ On the other hand, Kim *et al.*⁴ performed x-ray magnetic circular dichroism (XMCD) measurements on Co:TiO₂ films annealed at various temperatures and showed that the spectral line shapes of all the samples were nearly identical to that of Co metal. They also showed that particles were formed on the surface during the annealing process. This work suggests that the FM could be induced by the Co clusters.

Surfaces of pure anatase titanium dioxide have been investigated rather intensively, since it has superior photocatalytic properties, which should be strongly related to the atomic arrangement of the surface.⁵ It is well known that (1×4) reconstruction occurs on the anatase TiO₂ (001) surface.^{6,7} Herman *et al.*⁶ suggested the “microfacets” model, based on low-energy electron diffraction, x-ray photoelectron spectroscopy, and angle-resolved mass spectroscopy of recoiled ions. However, this model could not explain the scanning tunneling microscope (STM) images obtained by Liang *et al.*⁷ They proposed the “added-and-missing row” (AMR) model to explain their STM images. More recently, Lazzeri *et al.*⁸ proposed a structural “ad-molecule” (ADM) model using the first principles density functional calculations. However, there remain some controversies on what model can describe the surface structures accurately. In

addition, there has been no report on the surface structure of the anatase Co:TiO₂ films.

In this letter, we report *in situ* STM studies on the (001) surfaces of anatase Co:TiO₂ films that were grown epitaxially on Nb-doped SrTiO₃ (Nb:SrTiO₃) (001) substrates. The as-grown Co:TiO₂ films showed (1×4) surface reconstruction, similar to that observed in pure TiO₂ films. Various STM images were compared with the AMR and the ADM models. After annealing, particles with diameter about 10 nm appeared on the Co:TiO₂ surface. For identification of the particles, scanning tunneling spectroscopy (STS) measurements were performed. It was found that the tunneling spectra of the particles were quite different from that of pure TiO₂. This work suggests that the formation of nanoclusters should be carefully monitored to gain a proper understanding of the mechanism of the ferromagnetism in this potentially important material.

A Ti_{0.94}Co_{0.06}O₂ film was grown on Nb:SrTiO₃ (001) substrate by the laser molecular-beam epitaxy techniques. The detailed deposition condition was described in our previous report.⁹ A clear reflection high-energy electron diffraction pattern, corresponding to (1×4) surface reconstruction, was maintained during the growth, which indicates the film surface was very flat. For STM analysis, the as-grown film was transferred to an UHV chamber (base pressure: ~10^{−12} mbar) without breaking the vacuum, which is connected with the growth chamber. Tungsten STM tips were prepared from a 0.25-mm-diam polycrystalline wire by electrochemical etching in a NaOH solution. It was annealed in the UHV chamber using a tantalum filament to exclude effects induced by an oxidized tip, and then checked by observing the *I*−*V* characteristics of the Au surface on mica.

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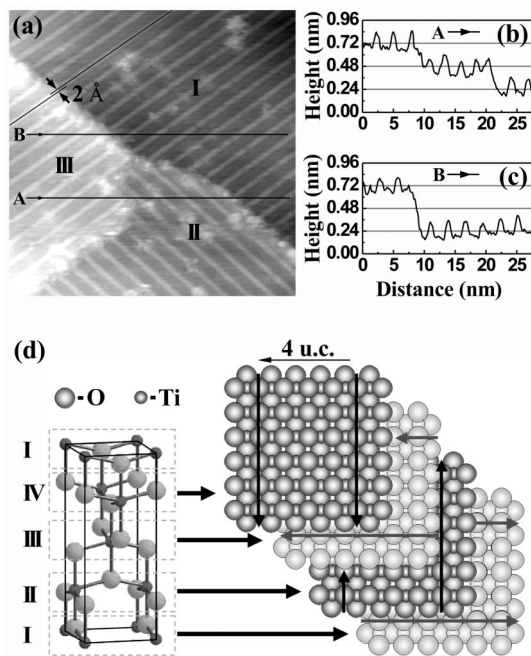


FIG. 1. (a) STM image showing the surface reconstruction of Co:TiO₂. The line profile (b) along the line A and (c) along the line B shows that the minimum step height is 1/4 u.c. The scan size is 30×30 nm². (d) Crystal structure of anatase TiO₂ and schematic diagram of surface reconstruction direction. Black arrows indicate reconstruction directions.

Figure 1(a) shows the STM image of the as-grown film with the surface reconstruction of (1×4), similar to the case of pure anatase TiO₂ films.⁷ The direction of the (1×4) surface reconstruction was found to have an interesting correlation with the step height. The line profile A shown in Fig. 1(b) shows that the minimum step height is 0.24 nm, which corresponds to 1/4 unit cell (u.c.) distance along the *c*-axis. When the step height changes by 1/4 u.c., the reconstruction direction becomes rotated by 90°. In the line profile B, shown in Fig. 1(c), there is a step height change of about 0.48 nm (i.e., 1/2 u.c.), between terraces I and III. It is noteworthy in Fig. 1(a), the bright rows in terrace III are shifted by 0.2 nm (i.e., 1/2 u.c. along the *a* axis), with respect to those in terrace I. This interesting surface structure can be explained by the crystal structure of anatase TiO₂, which has a tetragonal unit cell (*a* = *b* = 0.376 nm, *c* = 0.951 nm) with four atomic TiO₂ layers. As displayed in Fig. 1(d), each TiO₂ layer is composed of the buckled O–Ti–O rows. Layer II can be reproduced from layer I by the 1/4 u.c. vertical translation and the 90° rotation, followed by the 1/2 u.c. horizontal translation. Hence, the bright rows in layer III are parallel to those in layer I and are shifted by 1/2 u.c. along the *a* axis, with respect to those in terrace I, as shown in Fig. 1(a).

Although (1×4) surface reconstruction is dominant, (1×*n*) (*n* = 3, 5, and 6) reconstructions were observed with (*n*–2) additional faint rows. For example, Fig. 2(a) shows (1×4) and (1×5) reconstructions with two and three additional faint rows, respectively. At a biased voltage of 2.2 V, the width and the corrugation of the bright row are about 0.45 and 0.14 nm, respectively. However, as the biased voltage increased, the measured corrugation increased, as observed by Liang *et al.*⁷ This bias dependence should mainly come from the local electronic structure of atomic rows.

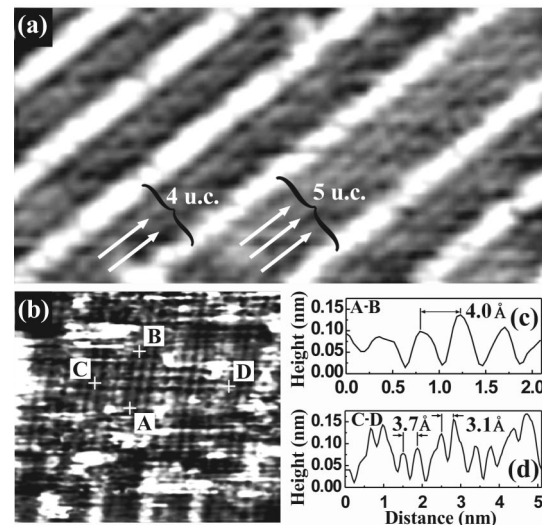


FIG. 2. (a) STM image of the (1×4) and (1×5) reconstructed surface. Two and three additional faint rows were observed in (1×4) and (1×5), respectively (marked by arrows). The scan size is 10×5 nm². (b) Atomic resolved STM image. The scan size is 10.0×8.5 nm². (c) Line profile from A to B. (d) Line profile from C to D.

The two faint rows of the (1×4) reconstruction could be explained by the AMR model and the ADM model. In the AMR model (shown in Fig. 7 of Ref. 7), the two faint rows of the (1×4) surface reconstructed STM images should be derived from the two fourfold coordinated Ti rows, which were generated by missing one oxygen row. In the ADM model (shown in Fig. 1 of Ref. 8), the two faint rows of the (1×4) reconstruction could be derived from fivefold coordinated Ti rows. However, the (1×5) reconstruction could be explained by the ADM model, not by the AMR model. According to the AMR model, the three faint rows could not be generated between 5 u.c. while satisfying the stoichiometry and autocompensation condition. In the case of the ADM model, the three faint rows can be generated by fivefold coordinated Ti rows. In addition, our STM image shows that the corrugation of the (*n*–2) faint rows is identical in each. Hence, the (*n*–2) faint rows come from the fivefold coordinated Ti rows, as in bulk-terminated unreconstructed surfaces.

Figure 2(b) shows the atomically resolved STM image of a (1×4) reconstructed surface. Along the faint row, the individual atoms are resolved with a separation of about 0.4 nm, as shown in Fig. 2(c). Figure 2(d) shows that the distance between two adjacent faint rows is 0.37 nm, which is less than 1 u.c. This small value could be related to the compressive stress, mentioned in the ADM model.⁸ However, as shown in Fig. 2(d), the bright row is composed of two sub-rows separated by 0.31 nm, different from the simulated STM image based on the ADM model.⁸

After annealing at 650 °C for 30 min under an oxygen partial pressure of 5.0×10^{–5} mbar, particles become aggregated mostly at the step edge. As shown in Fig. 3(a), the typical size of the particles is slightly smaller than 10 nm in diameter. Note that pure anatase TiO₂ film did not show such particles even after postannealing in the same condition. The STS curves in Fig. 3(b) show the *I*–*V* curves obtained at a particle with a diameter of about 6 nm and at particle-free region of the Co:TiO₂ film, measured at room temperature.

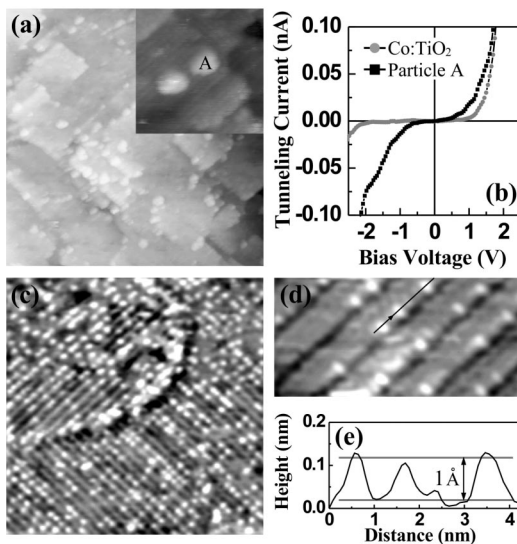


FIG. 3. (a) STM image and (b) I - V curve after annealing at 650 °C for 30 min under an oxygen partial pressure of 5.0×10^{-5} mbar. The scan size is 200×200 nm². (c) STM image after annealing at 1000 °C for 15 min under an oxygen partial pressure of 5.0×10^{-5} mbar. The scan size is 50×50 nm². (d) Close-up view of (c). (e) Line profile along the line in (d).

From the I - V curve, the tunneling gap of Co:TiO₂ was estimated to be about 3.0 eV, which is consistent with the band gap ($E_g = 3.2$ eV) of pure anatase TiO₂. However, for the particle region, the I - V curve looks asymmetric with an apparent gap of 0.8 eV accompanied by an additional feature around -1.2 eV. It is clear that this is not a TiO₂ particle with small amount of Co doping.

Chambers *et al.* reported an observation of highly Co-enriched TiO₂ anatase clusters using a transmission electron microscope.¹⁰ On the other hand, Kim *et al.*⁴ reported a formation of clusters on the surface during the annealing process and, identified that they were mainly composed of Co metal using the XMCD. In addition, we independently performed scanning Auger electron spectroscopy microscope studies, and found that the particles on a films prepared in a similar way have a large amount of Co. At first sight, the gap-like feature on the particle seems to rule out the possibility that the particle is a pure Co cluster. However, a very similar room temperature I - V curve was reported for Co nanoparticles on a thin Al₂O₃ film deposited on a smooth Au(111) surface,¹¹ and the behavior was interpreted as a single-electron tunneling in the double-barrier system STM-tip/Co/Al₂O₃/Au. If the particle in our film is mainly composed of Co, such a double barrier system could be formed with a very thin Co-oxide barrier. Hence, both possibilities, i.e., highly Co-enriched TiO₂ anatase clusters or purely Co particles with Co-oxide coating, are feasible at this moment.

Another interesting observation was made for the film when it was annealed one more time at 1000 °C for 15 min. The Co clusters on the surface seemed to disappear. However, as shown in Fig. 3(c), the bright spots appeared on the top rows of the (1×4) reconstruction. The bright spots were elongated in the perpendicular direction of the bright row [Fig. 3(d)]. As shown in Fig. 3(e), the corrugation was about 0.1 nm from the line profile along the top row, which indicates that the corrugation is not from the adatom. The bright spots could be regarded as Co atoms located in the TiO₂ surface. The high temperature incorporation of Co into the TiO₂ matrix was also reported for laser deposited Ti_{1-x}Co_xO_{2-δ} films.¹² Further investigations are required to clarify the Co matrix incorporation and the possibility of FM in such high-temperature annealed films.

In summary, we investigated the surface of a Co:TiO₂ (001) film grown on Nb:SrTiO₃ (001) using *in situ* STM. As-grown Co:TiO₂ film was very clean without any Co clusters on the surface, and its surface reconstruction was similar to that of a pure anatase TiO₂ surface. After annealing at 650 °C for 30 min under an oxygen partial pressure of 5.0×10^{-5} mbar, nanoparticles were formed mostly at the step edge.

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- ¹Y. Matsumoto, M. Murakami, T. Shono, T. Hasagawa, T. Fukumura, M. Kawasaki, P. Ahmet, T. Chikyow, S. Koshihara, and H. Koinuma, *Science* **291**, 854 (2001).
- ²S. A. Chambers, S. Thevuthasan, R. F. C. Farrow, R. F. Marks, J. U. Thiele, L. Folks, M. G. Samant, A. J. Kellock, N. Ruzycski, D. L. Ederer, and U. Diebold, *Appl. Phys. Lett.* **79**, 3467 (2001).
- ³H. Ohno, *Science* **281**, 951 (1998).
- ⁴J. Y. Kim, J.-H. Park, B.-G. Park, H.-J. Noh, S.-J. Oh, J. S. Yang, D. H. Kim, S. D. Bu, T. W. Noh, H.-J. Lin, H.-H. Hsieh, and C. T. Chen, *Phys. Rev. Lett.* **90**, 017401 (2003).
- ⁵L. Kavan, M. Gratzel, S. E. Gilbert, C. Klemenz, and H. J. Scheel, *J. Am. Chem. Soc.* **118**, 6716 (1996).
- ⁶G. S. Herman, M. R. Sievers, and Y. Gao, *Phys. Rev. Lett.* **84**, 3354 (2000).
- ⁷Y. Liang, S. Gan, and S. A. Chambers, *Phys. Rev. B* **63**, 235402 (2001).
- ⁸M. Lazzeri and A. Selloni, *Phys. Rev. Lett.* **87**, 266105 (2001).
- ⁹D. H. Kim, J. S. Yang, K. W. Lee, S. D. Bu, T. W. Noh, S.-J. Oh, Y.-W. Kim, J.-S. Chung, H. Tanaka, H. Y. Lee, and T. Kawai, *Appl. Phys. Lett.* **81**, 2421 (2002).
- ¹⁰S. A. Chambers, T. Droubay, C. M. Wang, A. S. Lea, R. F. C. Farrow, L. Folks, V. Deline, and S. Anders (unpublished).
- ¹¹H. Graf, J. Vancea, and H. Hoffmann, *Appl. Phys. Lett.* **80**, 1264 (2002).
- ¹²S. R. Shinde, S. B. Ogale, S. Das Sarma, S. E. Lofland, C. Lanci, J. P. Buban, N. D. Browning, V. N. Kulkarni, J. Higgins, R. P. Sharma, R. L. Greene, and T. Venkatesan (unpublished).