APPLIED PHYSICS LETTERS VOLUME 73, NUMBER 20 16 NOVEMBER 1998

Quasi-ideal strontium titanate crystal surfaces through formation of strontium hydroxide

Gertjan Koster, Boike L. Kropman, Guus J. H. M. Rijnders, Dave H. A. Blank,[a)]
and Horst Rogalla
Low Temperature Division, Department of Applied Physics and Center for Materials Research CMO,
University of Twente, 7500 AE Enschede, the Netherlands

(Received 21 April 1998; accepted for publication 16 September 1998)

In recent years, well-defined and nearly perfect single crystal surfaces of oxide perovskites have become increasingly important. A single terminated surface is a prerequisite for reproducible thin film growth and fundamental growth studies. In this work, atomic and lateral force microscopy have been used to display different terminations of $SrTiO_3$. We observe hydroxylation of the topmost SrO layer after immersion of $SrTiO_3$ in water, which is used to enhance the etch-selectivity of SrO relative to TiO_2 in a buffered HF solution. We reproducibly obtain perfect and single terminated surfaces, irrespective of the initial state of polished surfaces and the pH value of the HF solution. This approach to the problem might be used for a variety of multi-component oxide single crystals. True two-dimensional reflection high-energy electron diffraction intensity oscillations are observed during homo epitaxial growth using pulsed laser deposition on these surfaces. © *1998 American Institute of Physics.* [S0003-6951(98)03546-3]

Fundamental understanding of the growth mechanisms involved in thin film growth of metals and semiconductors on well-defined substrate surfaces has led to revolutionary applications. In the future, thin films of oxidic materials will also become more important. Materials with a perovskite structure are an interesting class of oxides, of which $SrTiO_3$ (001) is often used as a substrate material. Although well-defined surfaces of these more complex oxide materials are essential for thin film growth, the mechanisms necessary for obtaining these surfaces are not yet well understood.

The crystal structure of ABO_3 perovskites consists of alternating AO and BO_2 planes. Calculations predict a different surface energy for the two possible terminations, which also varies for different compounds.[1,2] The surface energy of alkaline-II titanates, $BaTiO_3$, $SrTiO_3$ and $CaTiO_3$ is predicted to be dependent on the size of the A-site cation, i.e., in the former two materials the TiO_2 plane is more stable, whereas the CaO plane has a lower energy in the latter case. Accordingly, one expects a preferential termination. However, a surface obtained by cleaving or cutting results in an equal amount of AO- and BO_2-terminated domains separated by half unit cell steps.[1] Furthermore, subsequent polishing and etching lead to several kinds of defects on the surface and, therefore, to not well-defined surfaces on an atomic scale. Various techniques, like annealing in an oxygen atmosphere, bismuth adsorption/desorption and ion beam cleaning, are commonly used to improve the surface quality and thus the growth reproducibility. However, these methods do not guarantee a single terminated surface. We demonstrate that one can take advantage of the difference in physical and chemical properties, e.g., solubility of the A- and B-site cations in acids, in order to achieve a nearly perfect and single terminated surface.

The first step in this direction was made by Kawasaki *et al.*,[3] who treated the $SrTiO_3$ substrates with an NH_4F buffered HF solution (BHF) with different pH values and obtained a uniform TiO_2-terminated surface, as confirmed by ion scattering spectroscopy. Their procedure is based on the selective etching of the more basic oxide SrO and thus the pH value of the solution is claimed to be crucial. The reproducibility and, hence, its success depend severely on the different polishing and annealing procedures prior to the BHF treatment. This often leads to uncontrolled etching and introduces unit cell deep holes in the terraces and deep etch pits, which hamper thin film growth.[4] Here, we report on using the formation of an intermediate Sr-hydroxide complex and subsequent BHF etching to obtain very reproducibly practically perfect TiO_2-terminated surfaces. The dramatic improved surface quality is demonstrated by the first report of true two-dimensional (2D) intensity oscillations by reflection high-energy electron diffraction (RHEED).

The surface morphology of a typical as-received single crystal substrate[5] is imaged by atomic force microscopy (AFM).[6] As shown in Fig. 1(a), the surface consists of terraces, with disordered step ledges and islands on the terraces with typical height differences of half (~2 Å) and single (~4 Å) unit cell steps (the lattice parameter a of $SrTiO_3$ is 3.905 Å). This indicates the coexistence of the two possible surface terminations. RHEED patterns of these surfaces show broad Bragg reflections due to disorder.

Annealing the as-received substrate[7] results in regrowth of the surface,[4,8] as shown in Fig. 1(b). From the friction map shown in Fig. 1(c) and the line scan in Fig. 1(d), we observe that differences in friction contrast are always associated with height differences of $(n+1/2)a$. Hence, we conclude that apart from regrowth of terrace ledges, domains with different surface termination have become clearly visible. The shape of the edges of these domains is different: straight and sharp-edged step ledges exist, but in addition rounded do-

---

[a)] Author to whom correspondence should be addressed. Electronic mail: d.h.a.blank@tn.utwente.nl

Downloaded 24 Oct 2004 to 130.89.218.211. Redistribution subject to AIP license or copyright, see http://apl.aip.org/apl/copyright.jsp

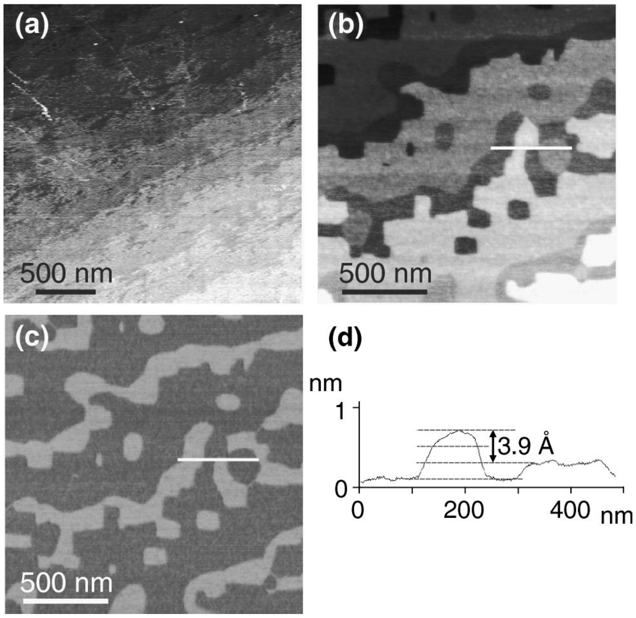

FIG. 1. (a) Atomic force micrograph of an as-received $SrTiO_3$ surface which has been flashed to a temperature of 650 °C, (b) AFM micrograph of an annealed substrate, (c) simultaneously recorded friction map by LFM, (d) the cross section (averaged over ~5 scan lines) along the line shown in (b) is given. Depending on the miscut angle, the duration and temperature of the anneal step can be adjusted to obtain straight terrace ledges. This particular example is chosen to show the different features.

mains can be identified.[9] This observation is common for all substrates that we have studied.

To shed more light on the apparent difference in friction, several imaging modes have been used. Phase contrast measurements in tapping mode reveal that domains having a high friction display higher phase changes, due to mechanical interaction. An adhesion map,[6] see Fig. 2, shows that domains with high friction also display a high adhesion force. From these experiments we conclude that the observed friction contrast originates from distinct properties of the surface depending on the termination.[10–12] In addition, we have observed that the low friction domains become rougher upon aging, probably due to a reaction with the ambient environment. We have used the deposition of TiO_2 on a mixed terminated surface shown in Fig. 1(b) as a chemical probing method[13,14] and observed different wetting on the two terminations. On the low friction domains flat topped islands are formed, whereas smaller and very rough islands are formed on the high friction areas. From these observations we conclude that high friction domains correspond to TiO_2 termination, since it is known that a B-site material will not wet a B-site terminated crystal.[15] Our results seem to contradict the results obtained by Fompeyrine *et al.*,[9] although this can be caused by differences in preparation methods.

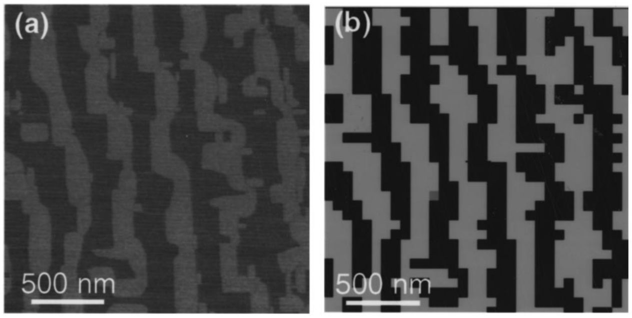

FIG. 2. (a) LFM micrograph of an annealed substrate, (b) adhesion map of the same area as displayed in (a). In this micrograph 64×64 force curves are taken, and the value of the deflection of the cantilever is shown at a fixed distance from the surface. The bright color indicates that the tip has already retracted from the surface, whereas a darker color indicates that the tip is still in contact. Note that the step ledges in (a) are much straighter than the ledges shown in Fig. 1.

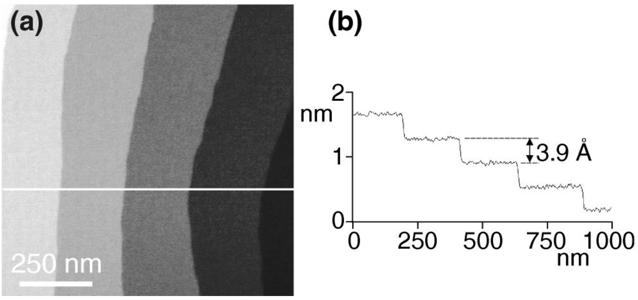

FIG. 3. (a) AFM micrograph of a nearly perfect and atomically flat surface, obtained after soaking in water, followed by etching in a BHF solution and annealing, (b) cross section, averaged over ~3 scan lines along line in (a).

During AFM experiments performed in a liquid cell filled with H_2O, we have observed a subtle change in morphology on the low friction domains under the influence of water. It is known that SrO reacts with CO_2 and H_2O at room temperature to form stable compounds like $SrCO_3$ and $Sr(OH)_2$, respectively. It is unlikely that water will react with the chemically very stable TiO_2-terminated layers.[16] Hence, we expect that, in the presence of water, the topmost layer of SrO-terminated domains forms a Sr-hydroxide complex, which is known to dissolve in acidic solutions. To utilize this behavior in water, an as-received substrate was ultrasonically soaked in analytical grade and demineralized water for 10 min, followed by a short (~30 s.) dip in a standard, commercially available BHF solution.[17] To remove the remnants of the previous treatments and facilitate recrystallization, a final annealing step is performed at 950 °C for 1 h.

After annealing, the surface has been studied by AFM. The analysis shows a nearly perfect single terminated surface with very straight terrace ledges, as shown in Fig. 3(a). The line scan in Fig. 3(b) only shows single unit cell steps of $SrTiO_3$. No friction contrast is observed. This result has been reproduced on many equally treated substrates.

X-ray photoelectron spectroscopy (XPS) measurements have been performed on $SrTiO_3$ substrates at different stages during the preparation. The O 1*s* envelope consists of two contributions: a peak located at ~530.0 eV from the titanate oxygen, and a peak located at ~531.6 eV due to surface hydroxyl groups. The highest concentration of surface hydroxyls is present on the water-soaked and as-received substrate as indicated by angular measurements. These hydroxyls are associated with the Sr, since the surface Sr 3*p* peaks are shifted slightly towards lower binding energies.[18] The C 1*s* peak (located at 284.8 eV, used as reference peak) is present on all samples and is also located on the surface. No evidence of carbonates is found. On the etched and subsequently annealed substrate,[17] the C 1*s* intensity is very low compared to the Sr 3*p*, Sr 3*d* and Ti 2*p* peaks, which is a further indication of the quality of this surface.

Furthermore, sharp 0th-order Bragg reflections in the

Downloaded 24 Oct 2004 to 130.89.218.211. Redistribution subject to AIP license or copyright, see http://apl.aip.org/apl/copyright.jsp

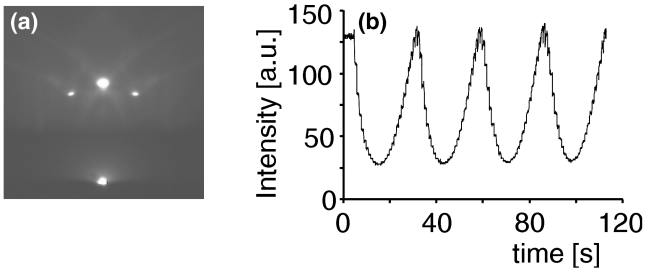

FIG. 4. (a) RHEED pattern of the quasi-ideal $SrTiO_3$ surface shown in Fig. 3(a), (b) intensity of the specular reflection recorded during deposition of 4 ML of $SrTiO_3$ by PLD (see Ref. 14). The perfect 2D oscillations (with a period of 26 s) are modulated by the laser pulse with a frequency of 1 Hz.

RHEED pattern and very low diffuse background intensity confirm the perfect crystalline surface [see Fig. 4(a)]. During homo epitaxial growth on these surfaces using pulsed laser deposition (PLD),[14] true 2D RHEED oscillations of Bragg intensity without a diffuse component are measured [see Fig. 4(b)]. The intensity as a function of the coverage during one period can be perfectly fitted to a two-level model,[19] indicating that the $SrTiO_3$ surface can be considered to be an ideal 2D surface.

In conclusion, we have reproducibly obtained quasi-ideal $SrTiO_3$ surfaces for thin film deposition and fundamental growth studies. Due to the enhancement of the selectivity in solubility by the formation of a Sr-hydroxide complex, confined to the topmost SrO layer, the *p*H value of the BHF solution and etch time become much less critical. Because of the possibility of reducing the etch time, formation of etch pits and holes due to prolonged etching is prevented. The key point in our approach is the separation of the main reaction steps, i.e., hydroxylation of the SrO, followed by its dissolving in BHF. A similar approach to the problem of obtaining single terminated surfaces might be used on a variety of multi-component oxide single crystals. Homo epitaxial growth on these quasi-ideal $SrTiO_3$ surfaces results for the first time in true 2D RHEED intensity oscillations.

The authors thank Holger Schönherr for performing the phase contrast tapping mode and AFM measurements in water, Cas Damen and Arnout Hamster for fruitful discussions and the Dutch foundation for fundamental research on matter FOM for financial support.

[1] V. E. Henrich and P. A. Cox, *The Surface Science of Metal Oxides* (Cambridge University Press, Cambridge, 1994).

[2] S. P. Chen, J. Mater. Res. **13**, 1848 (1998).

[3] M. Kawasaki, K. Takahashi, T. Maeda, R. Tsuchiya, M. Shinohara, O. Ishiyama, T. Yonezawa, M. Yoshimoto, and H. Koinuma, Science **226**, 1540 (1994); M. Kawasaki, A. Ohtomo, T. Arakane, K. Takahashi, M. Yoshimoto, and H. Koinuma, Appl. Surf. Sci. **107**, 102 (1996).

[4] G. Koster, B. L. Kropman, G. J. H. M. Rijnders, D. H. A. Blank, and H. Rogalla, Mater. Sci. Eng. B (accepted for publication).

[5] The $SrTiO_3$ single crystals used in this study are obtained from ESCETE, Single Crystal Technology B.V., Enschede, the Netherlands.

[6] Scanning probe microscopy experiments were performed on a Nanoscope III (DI, Santa Barbara, CA), capable of contact and tapping mode imaging. For the contact mode, standard DI Si_3N_4 cantilevers were used with nominal force constants of $k=0.18$, 0.38, and 0.58 Nm^{-1}, whereas for tapping mode Si cantilevers with resonance frequency ranging from 310 to 400 kHz were utilized. Contact forces were kept as low as possible and are estimated to be <10 nN. Lateral or frictional forces are measured simultaneously by the four-quadrant detector. No attempts have been made to quantify the friction force, since the exact lateral force constants of the cantilevers are unknown, the alignment of the laser on the cantilever changes and the humidity in the laboratory is not constant. In all friction force micrographs high frictional forces are displayed as bright white colors and lower forces as dark colors (range of 0.1 V). The observed friction contrast is comparable to that found by Fompeyrine *et al.* (see Ref. 9). The topographical features in the contact mode micrographs are confirmed by tapping mode imaging.

[7] All thermal treatments have been performed in a modified tube oven, using flowing O_2 (at a rate of $150\,\ell\,h^{-1}$). The substrates were placed on an aluminum oxide boat inside a quartz tube. The substrates are flashed to 650 °C for several (1–10) minutes prior to imaging. This temperature is well below the observed threshold of 800 °C for regrowth or recrystallization of the step ledges (see Refs. 4 and 8). Annealing is performed above this threshold at 950 °C for 1 h. The temperature is raised at a rate of about 0.5 $°C\,s^{-1}$, and allowed to cool down to room temperature in 3 h.

[8] R. Sum, H. P. Lang, and H.-J. Güntherodt, Physica C **242**, 174 (1995).

[9] J. Fompeyrine, R. Berger, H. P. Lang, J. Perret, E. Mächler, Ch. Gerber, and J.-P. Locquet, Appl. Phys. Lett. **72**, 1697 (1998). Their substrates are reduced in vacuum ($p=10^{-7}$ Torr) at temperatures above 600 °C, before any friction contrast is observed. They conclude high friction domains to be SrO terminated.

[10] J. Tamayo, R. García, T. Utzmeier, and F. Briones, Phys. Rev. B **55**, R13436 (1997).

[11] The observed friction contrast can be attributed to two different properties of the surface. The first has a chemical nature: different chemical functionalities exert different friction forces on the Si_3N_4 tip (for more details, see Refs. 10 and 12). A second origin of friction is more mechanical in nature, and deals with the stiffness of the cantilever and the tip-sample combination, as expressed in the respective Poisson coefficient, Young's and shear modulus (Ref. 12). Since the friction force depends linearly on the applied load, higher adhesion forces between tip and sample result in higher friction forces. In air, the difference in adhesion is usually caused by differences in water adsorption on the surface.

[12] C. D. Frisbie, L. F. Rozsnyai, A. Noy, M. S. Wrighton, and C. M. Lieber, Science **265**, 2071 (1994); R. M. Overney, E. Meyer, J. Frommer, H.-J. Güntherodt, M. Fujihira, H. Takano, and Y. Gotoh, Langmuir **10**, 1281 (1994).

[13] G. Koster, B. L. Kropman, G. J. H. M. Rÿnders, D. H. A. Blank, and H. Rogalla (unpublished).

[14] All depositions are carried out at 850 °C using single crystals as targets. The O_2 pressure was kept at 0.15 mbar for the deposition of TiO_2, whereas 0.05 mbar is used for $SrTiO_3$. The energy of the electrons used for RHEED is 20 kV, using an angle of incidence of about 1°. The PLD system with high pressure RHEED is described by G. J. H. M. Rijnders, G. Koster, D. H. A. Blank, and H. Rogalla, Appl. Phys. Lett. **70**, 1888 (1997).

[15] R. Tsuchiya, M. Kawasaki, H. Kubota, J. Nishino, H. Sato, H. Akoh, and H. Koinuma, Appl. Phys. Lett. **71**, 1570 (1997).

[16] M. Komiyama and M. Gu, Appl. Surf. Sci. **120**, 125 (1997).

[17] The demineralized water is produced by Millipore Elix equipment ($R=10-15\ M\Omega$ cm and $pH=6-7$), whereas the BHF solution is obtained from Merck ($NH_4F{:}HF=87.5{:}12.5$ with $pH=5.5$).

[18] R. P. Vasquez, J. Electron Spectrosc. Relat. Phenom. **56**, 217 (1991).

[19] The results on homo epitaxial growth will be published in a separate paper. The theoretical intensity oscillations are described in M. G. Lagally, D. E. Savage, and M. C. Tringides, in *Reflection High Energy Electron Diffraction and Reflection Electron Imaging of Surfaces*, edited by P. K. Larsen and P. J. Dobson (Plenum, London, 1989), pp. 139–174.

Downloaded 24 Oct 2004 to 130.89.218.211. Redistribution subject to AIP license or copyright, see http://apl.aip.org/apl/copyright.jsp