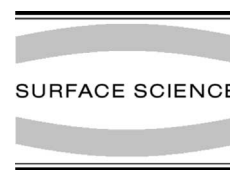




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X-ray surface diffraction analysis of structural transformations on the (001) surface of oxidized SrTiO₃

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Abstract

Surface X-ray scattering was used to study structural modifications on the (001) surface of oxidized SrTiO₃. Grazing incidence in-plane X-ray diffraction revealed a sequence of quasi-powder diffraction peaks originating from crystallites with nearly random in-plane orientation. This diffraction pattern is associated with micro-crystallites of irregular shape observed by atomic force microscopy on the surface after annealing in oxygen. Analysis based on available powder diffraction data identified these crystallites as monoclinic TiO. Different oxygen annealing treatments led to dramatic changes in the specular (00L) crystal truncation rods indicating significant structural modifications in the underlying single crystal SrTiO₃ surface layer. © 2001 Elsevier Science B.V. All rights reserved.

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Perovskite ABO₃ oxides represent an important class of materials exhibiting a wide spectrum of interesting properties. In particular, due to the availability of high quality single crystals, SrTiO₃ has attracted special attention as a prototype perovskite. SrTiO₃ also has important technological applications as a substrate for epitaxial growth of high quality oxide thin films [1,2]. These applications have strongly stimulated the study of

SrTiO₃ surface structural properties and the search for a recipe to prepare smooth and atomically clean surfaces. It was found that a combination of oxygen and UHV annealing yields extremely flat, very stable, Ti-terminated surfaces [3]. The remarkable stability of the surface structures produced by annealing in oxygen [4] suggests that structural rearrangements involve several atomic layers. It was also found that the surface structure strongly depends on the thermal history [4,5]. Changes in stoichiometry leading to the formation of Ruddlesden–Popper phases [6] in the topmost layers of reduced SrTiO₃(001) surfaces have been proposed based on scanning tunneling microscopy and Auger electron spectroscopy results [5,7]. Atomic force microscopy (AFM) analysis after

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oxygen annealing revealed various types of micro-crystallites [8–10] that had formed on the (001) surface as a result of decomposition and segregation processes. Based on secondary ion mass spectroscopy and X-ray photoemission data it was proposed that crystallites observed in Refs. [9,10] were SrO. An X-ray powder diffraction structural characterization performed on pulverized samples showed both Sr- and Ti-rich phases [8]. The obvious drawback of this approach is the inability to distinguish between powder particles originating from surface and bulk structures. A more surface sensitive nondestructive structural probe is required to address this problem. In this letter, we report experimental results obtained by surface X-ray scattering techniques (see reviews of Refs. [11, 12] and references therein). We use grazing incidence X-ray diffraction (GIXD) and crystal truncation rod (CTR) scattering to study oxidized surfaces of SrTiO₃(001) single crystals.

In our experiments we used commercially available undoped (001) oriented single crystals of SrTiO₃ grown by the Vernuil (flame fusion) technique. After a standard chemical cleaning in organic solvents, the crystals were etched in a pH-controlled NH₄F–HF solution to produce a Ti-terminated surface [13], rinsed in de-ionized water and loaded into an ultra-pure quartz tube. The annealing was performed in a constant oxygen flow at 900–1100°C for 3 h with heating and cooling rates of 5°C/min. The crystals were then examined by AFM (Digital Instruments) in contact mode. For almost all of the samples the AFM analysis showed platelet-like micro-crystallites of irregular shapes similar to those observed in Refs. [8–10] for samples prepared in similar conditions. As an example, Fig. 1 shows the AFM image taken from the sample annealed at 1000°C. ¹ Crystallites with an average size of 54 ± 7 nm and height of 4.4 ± 4.1 nm are observed on a very flat step-like surface with an average terrace width of 125 nm.

¹ To exclude possible effect of the chemical etching, several samples have been prepared without this treatment. The AFM analysis showed the same micro-crystallites as observed on the etched samples.

The roughness of the terraces is less than 0.1 nm, i.e. the surface is atomically flat.

The X-ray scattering experiments were performed on beamline X14A at the National Synchrotron Light Source, Brookhaven National Laboratory. The synchrotron radiation beam was monochromized at the energy of 8.00 keV by using a double-crystal monochromator. The incident beam was focussed vertically by a cylindrical mirror and horizontally by a sagittally bent Si(111) crystal. A four-circle X-ray diffractometer with a vertical scattering plane was used for the GIXD and the CTR measurements. In a search for possible surface reconstructions, in-plane scans at grazing incident condition along the major crystallographic directions were performed. However, no fractional-order reflections were found. Surprisingly, however, all in-plane scans from the oxidized samples revealed diffraction peaks incommensurate with the SrTiO₃ lattice. The ω -scans through these peaks showed a very weak angular dependence, i.e. the X-ray intensity was concentrated in the form of diffraction rings. Such a pattern is characteristic of quasi-powder diffraction originating from crystalline particles with (nearly) random in-plane orientation. A typical radial in-plane Q-scan along an arbitrary radial direction that avoids strong bulk reflections is shown in Fig. 2(a) for the sample annealed at 1100°C. The 360° ω -scan for the most intense peak in Fig. 2(a) at $q = 0.94$ rlu is shown in Fig. 2(b). All samples annealed in oxygen showed these same diffraction features. As a control, as-grown and etched crystals that were not oxygen annealed were examined and found to show none of these diffraction or AFM features. This implies that this diffraction pattern is associated with the micro-crystallites observed by the AFM. The average size of the crystallites derived from the width of the diffraction peaks is approximately 50 nm in good agreement with the AFM data for this sample.

The HKL coordinates in SrTiO₃ reciprocal space of 12 of the diffraction peaks clearly observed from radial Q-scans were converted into interplanar d -spacings. These experimental values were then used for structural identification based on the available powder diffraction data for crystalline materials containing any combination of Sr,

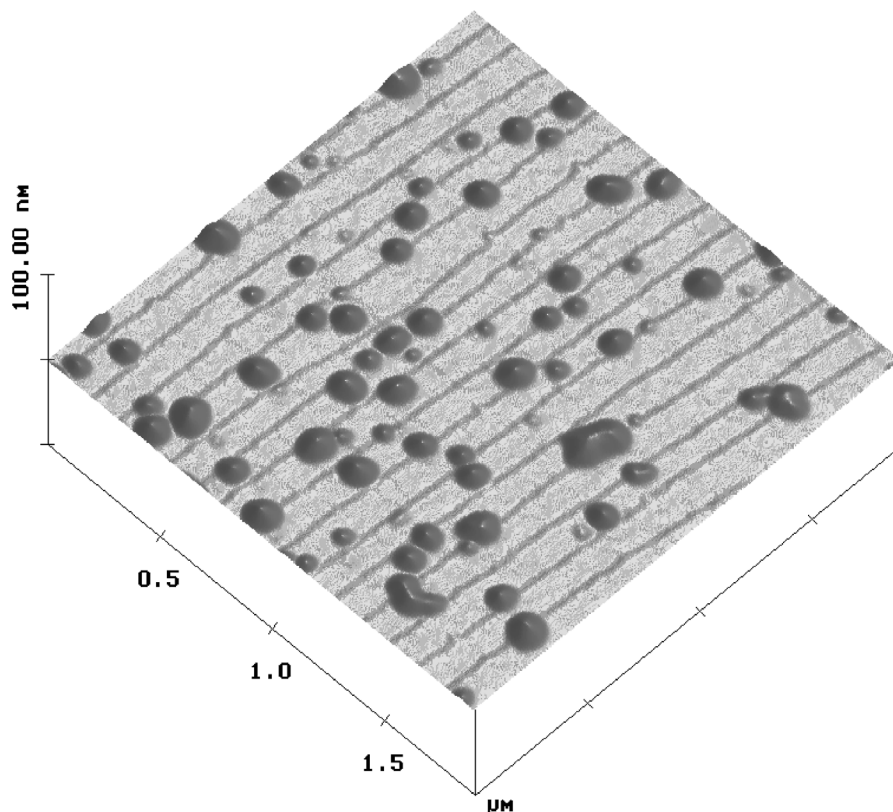


Fig. 1. An AFM image revealing micro-crystalites on a SrTiO₃(001) surface after annealing in oxygen flow at 1000°C for 3 h.

Ti, and O [14]. For each of 48 pdf-files the closest d -spacing corresponding to each of the experimental d -values was found and the value $\chi^2 = \Sigma(d_{\text{exp}} - d_{\text{pdf}})^2/d_{\text{exp}}^2$ was calculated as a figure-of-merit for structure identification. The best three results are shown in Table 1.² The minimum χ^2 -value corresponds to the monoclinic TiO crystal structure [15]. The next two best fit structures include: SrTi₁₂O₁₉ (a ternary compound of unknown structure found in the high temperature isotherm of the Sr–Ti–O system [16]), and a modification of TiO of unknown structure, which is believed to be

² Pdf-file #22-1121 with diffraction data for crichtonite has been excluded from the best fit results: this black mineral contains large amounts of Fe, Mn, Pb and other metals in its lattice and was found only in nature (Bourg d'Oisans, France, see Ref. [23]).

related also to NaCl-type TiO [17]. Also listed in Table 1 are the χ^2 -values for available SrO pdf data. These are more than two orders of magnitude higher. Thus, our analysis unambiguously revealed TiO micro-crystalites on the oxidized SrTiO₃ surface.

Monoclinic TiO is a low temperature phase, which is stable below 990°C in the composition range TiO_{0.9}–TiO_{1.1} and in an even wider range at higher temperatures [15]. The basic structure is of the NaCl type with ordered arrays of O- and Ti vacancies. As a result of this ordering the parent cubic cell with $a_0 = 4.185 \text{ \AA}$ is distorted and the structure shows lower symmetry. All of the experimental d -values have been identified with the maximum deviation of $\delta = |d_{\text{exp}} - d_{\text{pdf}}|/d_{\text{exp}} \approx 2\%$. However, some of the TiO reflections have not been observed in our scans. There are several possible reasons. The powder diffraction data

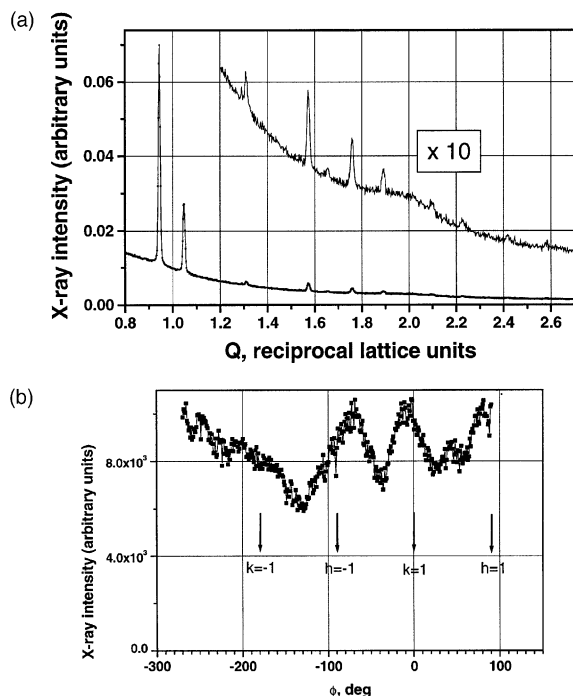


Fig. 2. (a) Typical radial in-plane Q -scan along an arbitrary crystallographic direction measured from the sample annealed for 3 h in an oxygen flow at 1100°C. The measurements were performed at grazing incident and exit angles of $\alpha = \beta = 0.6^\circ$ which corresponds to $L = 0.06$. The q -axis is in bulk SrTiO₃ reciprocal lattice units. (b) The 360° circular ω -scan at the $q = 0.94$ rlu diffraction peak. Major substrate crystallographic directions are shown by arrows. Very weak intensity variations indicate nearly random in-plane orientation of the micro-crystallites.

assumes completely random particle orientation. In our case we can only postulate a nearly random orientation in-plane. Some reflections may not be observed due to the limitations imposed by the

GIXD geometry. The lattice of micro-crystallites is most likely highly strained. Most importantly, it is known [15] that some reflections can vanish depending on the amount of vacancies, their type (Ti or O-type) and degree of ordering. Instead, diffuse scattering is often observed due to the short range order in the arrangement of vacancies.

A structural change as dramatic as the formation of a new phase on the surface should also inevitably modify the structure of the subsurface layer of the underlying crystalline matrix. To address these changes we measured specular CTR profiles from the samples annealed at different temperatures. In Fig. 3(a) the 00L CTR data measured from the sample oxidized at 900°C is shown. A weak and broad peak centered at $L = 1.24$ is clearly observed. This peak originates from a very thin surface layer with a c -lattice parameter that differs from that of the bulk. The Gaussian fit to this peak is shown as a solid line. From the width of this peak we estimate the thickness of this nonbulk-like surface layer to be 16.7 Å. (i.e., about four SrTiO₃ unit cells thick.) Annealing at higher temperatures (1100°C, Fig. 3(b)) results in a dramatic increase in the scattered intensity by more than an order-of-magnitude in a wider L -range from 1.2 to 1.5. If we assume that with increased annealing temperature the c -lattice parameter of the modified surface layer remains constant and only the thickness of the layer increases, we should expect a sharper and more intense peak at the same position as in Fig. 3(a). The fact that the region of the enhanced X-ray intensity is spreading toward higher L indicates that new layers with slightly different c -lattice constants have been formed in the surface region as the annealing proceeds at higher temperatures [18]. This

Table 1
Powder diffraction structural identification of the micro-crystallites

Crystal	Structure	Pdf-file #	χ^2
TiO	Monoclinic	23-1078	1.14×10^{-3}
SrTi ₁₂ O ₁₉	Unknown	22-1443	3.36×10^{-3}
TiO	Unknown	09-0240	6.53×10^{-3}
SrO	Cubic	06-0520	0.196
SrO	Cubic/unknown	48-1477	0.197
SrO	Tetragonal	27-1304	0.250

Three structures yielding the lowest χ^2 -values are shown at the top of the table. The χ^2 -values for available SrO data are also shown for comparison.

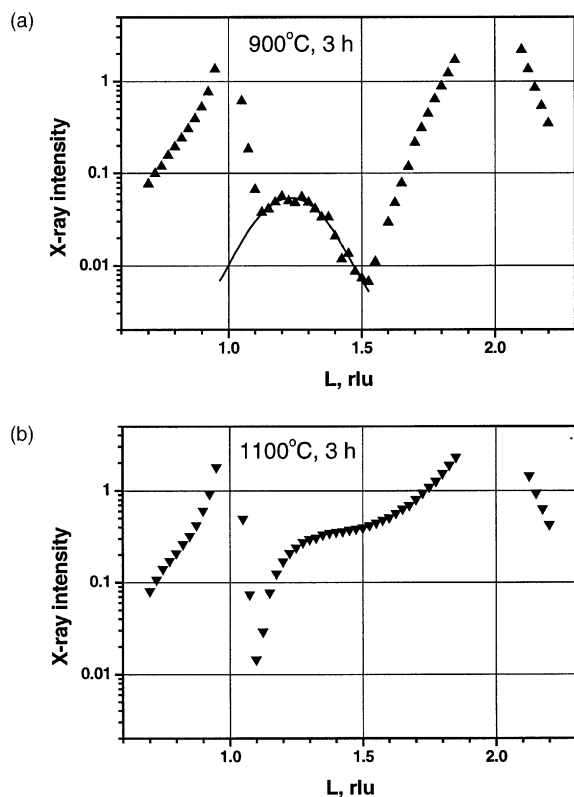


Fig. 3. Specular (00L) CTR profiles for the samples annealed for 3 h at 900°C (a) and at 1100°C (b). A weak diffraction peak in (a) centered at $L = 1.24$ originates from a thin surface layer with a c -lattice constant different from the bulk; the solid line is a Gaussian fit. The thickness of the layer derived from the width of the peak is 16.7 Å, which corresponds to approximately four SrTiO₃ unit cells. Annealing in oxygen at a higher temperature (b) results in an increase of X-ray intensity by more than an order-of-magnitude in the region of $L = 1.1$ to $L = 1.5$. This indicates the formation of new layers with different c -lattice constants.

qualitative interpretation of our experimental CTR data fits remarkably well the model of lamellae formation proposed for reduced surfaces [5].

A plausible scenario of the dramatic events leading to the formation of new phases on the surface involves as a starting point stoichiometric changes in the surface layer. The interfacial segregation processes in oxide crystals under applied gradients of different nature have been studied theoretically and experimentally by many researchers (see e.g., Refs. [19–22] and references therein). These processes governed by kinetic effects result

in alkaline-earth ion enrichment in the interface region. For perovskites, a significant increase towards the surface in Sr and Ba concentrations under annealing has been observed in SrTiO₃ and BaTiO₃ crystals within the surface region of 4–6 nm [19,20]. The next step is the removal of the excess of Sr from the surface. Fluorescence analysis revealed that the species evaporated during SrTiO₃ oxygen annealing consist of mostly Sr [9]. The evaporation of Sr, most likely in the form of Sr oxides, from the surface forces the remainder of the surface Ti ions to form chemically more stable phases. It is yet to be determined what kind of gradient (chemical, thermal, electrical, or mechanical, or the combination thereof) serves as a driving force for these particular experimental conditions. Our preliminary studies point toward a strain gradient in the surface region of as-grown crystals.

In conclusion, surface X-ray diffraction and CTR scattering techniques have been used to study structural transformations at the (001) SrTiO₃ surface under annealing in oxygen. Formation of a new phase on the surface and structural changes in the near surface region have been revealed as a final stage in the chain of events following surface stoichiometry changes. Micro-crystallites observed on the surface by the AFM have been identified as a monoclinic TiO.

Acknowledgements

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References

- [1] V. Agrawal, N. Chandrasekhar, Y.J. Zhang, V.S. Achutharaman, M.L. Mecartney, A.M. Coldman, J. Vac. Sci. Technol. A 10 (1992) 1531.

- [2] C.A. Paz de Araujo, J.F. Scott, G.W. Taylor (Eds.), *Ferroelectric Thin Films: Synthesis and Basic Properties*, Gordon and Breach, New York, 1996.
- [3] Q.D. Jiang, J. Zegenhagen, *Surf. Sci.* 367 (1996) L42.
- [4] Q.D. Jiang, J. Zegenhagen, *Surf. Sci.* 425 (1999) 343.
- [5] Y. Liang, D.A. Bonnell, *Surf. Sci.* 285 (1993) L510.
- [6] S.N. Ruddlesden, P. Popper, *Acta Crystallogr.* 11 (1958) 54.
- [7] Y. Liang, D.A. Bonnell, *Surf. Sci.* 310 (1994) 1.
- [8] K. Szot, W. Speier, J. Herion, Ch. Freiburg, *Appl. Phys. A* 64 (1997) 55.
- [9] K. Szot, W. Speier, *Phys. Rev. B* 60 (1999) 5909.
- [10] K. Szot, W. Speier, U. Breuer, R. Meyer, J. Szade, R. Waser, *Surf. Sci.* 460 (2000) 112.
- [11] R. Feidenhans'l, *Surf. Sci. Rep.* 10 (1989) 105.
- [12] I.K. Robinson, D.T. Tweet, *Rep. Prog. Phys.* 55 (1992) 599.
- [13] M. Kawasaki, K. Takahashi, T. Maeda, R. Tsuchiya, M. Shinohara, O. Ishiyama, T. Yonezawa, M. Yoshimoto, H. Koinuma, *Science* 266 (1994) 1540.
- [14] Powder Diffraction File, International Center for Diffraction Data, Release 1999.
- [15] D. Watanabe, J.R. Castles, A. Jostsons, A.S. Malin, *Acta Crystallogr.* 23 (1967) 307.
- [16] G.J. McCarthy, W.B. White, R. Roy, *J. Am. Ceram. Soc.* 52 (1969) 463.
- [17] U. Kylenstierna, A. Magneli, *Acta Chem. Scand.* 10 (1956) 1195.
- [18] A detailed analysis of the CTR data is in progress.
- [19] S.B. Desu, D.A. Payne, *J. Am. Ceram. Soc.* 73 (1990) 3391.
- [20] S.B. Desu, D.A. Payne, *J. Am. Ceram. Soc.* 73 (1990) 3398.
- [21] D. Monceau, C. Petot, G. Petot-Ervas, *Solid State Ionics* 45 (1991) 231.
- [22] D. Monceau, C. Petot, G. Petot-Ervas, *J. Eur. Ceram. Soc.* 9 (1992) 193.
- [23] I.E. Grey, D.J. Lloid, J.S. White Jr., *Am. Mineral.* 61 (1976) 1203.