Effect of surface orientation on intrinsic island formation on SrTiO$_3$ surfaces

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Abstract. Intrinsic islands were formed on Nb-doped SrTiO$_3$ (100) and (111) surfaces by high-temperature annealing (1200 °C) under oxygen atmosphere. The influence of surface orientation on the chemical composition and structure of islands was investigated by using Auger electron spectroscopy, energy-dispersive X-ray spectroscopy as well as electron diffraction in a transmission electron microscope. For a given island size, the same compositional profiles were observed for both surface orientations. While the bigger islands (with a height of several 100 nm) contain almost only Sr as cations, the smaller islands (with a height of few 10 nm) also contain Ti. Identical lattice-plane distances in all islands point to a distinct crystal structure for islands growing on (001) and (111) surfaces.

1. Introduction

High-temperature annealing of the surface of strontium titanate (SrTiO$_3$) leads to surface reconstruction [1,2,3]. After extended annealing, secondary phases form as islands on the surface [4,5]. The driving force of such surface modifications is the defect thermodynamics of SrTiO$_3$, which is sensitively affected by temperature, oxygen partial pressure ($p$(O$_2$)) and dopant concentration [6,7]. Donor-doped SrTiO$_3$, for example, acts as a semiconductor at room temperature with electrons as the major mobile defects. After high-temperature annealing (1000–1400 °C) under oxygen-rich atmosphere, the material becomes insulating due to the consumption of electrons by incorporation of oxygen into the SrTiO$_3$ lattice. Charge neutrality enforces the formation of doubly negative Sr vacancies for counterbalancing existing donors. The formation of Ti vacancies, on the other hand, can be assumed to be negligible due to their higher formation energy [7,8]. Upon generation of Sr vacancies the excess of Sr ions is expected to form a Sr-rich secondary phase, e.g. Sr-rich islands at the surface of SrTiO$_3$ [9,10] and/or the Sr-rich Ruddlesden–Popper phase (Sr$_{n+1}$Ti$_n$O$_{3n+1}$) at grain boundaries [10].
Even though the formation of Sr-rich islands is driven by the defect chemistry of bulk SrTiO$_3$, the island properties in terms of shape, lateral ordering, size and areal density strongly depend on the surface normal. In our previous work [9] dealing with polycrystalline SrTiO$_3$ doped with 5 at% Nb, we showed a clear correlation between areal density of the islands and the surface orientation in such a way that the low indexed surfaces, namely (100), (110) and (111), showed low, moderate and high island areal density, respectively. As a first approximation, the areal densities of all other surface orientations can be interpolated from these three low-index orientations [9].

In the present paper, the dependencies of the island structure and chemical composition on the surface orientation are reported. For this purpose, islands on top of 2 at% Nb-doped SrTiO$_3$ (001) and (111) surfaces were prepared and investigated.

2. Experimental details
The procedure of island formation on top of (001) and (111) surfaces of 2 at% Nb-doped single crystalline SrTiO$_3$ (Crystec, Germany) was as follows. Firstly, the single crystals were annealed at 1630 °C under a reducing atmosphere (5% H$_2$ + 95% Ar) for 15 hours. This reduction treatment provides a thermodynamically well-defined starting condition and also maintains the condition used for the polycrystal preparation from the previous work. Subsequently, the samples were oxidized at 1200 °C for 120 hours. The resulting islands on the surfaces were observed by optical microscopy (LEICA, DMRM). For structural studies of islands, selected-area electron diffraction (SAED) was performed on the cross section of the islands. The chemical composition of the islands was investigated by Auger electron spectroscopy (AES) (JEOL, JAMP-7810) scanning Auger Microprobe, 5 keV, electron beam size: 35-50 nm) and energy-dispersive X-ray spectroscopy (EDXS) in a transmission electron microscope (TEM) (Zeiss LIBRA 200FE, 200 kV). TEM cross-section samples of the island/SrTiO$_3$-substrate were prepared by the focused ion beam technique with Ga ions as a source operated at a kinetic energy of 30 keV and beam currents of 0.1 nA and 30 pA for rough and fine milling, respectively.

3. Results and discussion

3.1. Island formation and morphology
The (001) and (111) surfaces of SrTiO$_3$ showed drastic topographical changes upon oxidation at 1200 °C for 120 hours. A large number of islands developed on both surfaces (Figure 1). Significant differences in the size and in the shape of islands are observed with respect to the surface orientation. On top of the (100) surface small droplet-like islands with a height up to few 10 nanometers, and larger pyramid-shaped islands with a maximum height of up to 1500 nm are observed. Islands on the (111) surface exhibit flat and cut-pyramid shapes, respectively, with a maximum height of 500 nm. Presumably, the shapes of the large islands are non-equilibrium shapes determined by kinetic processes like facet growth [11,12] or anisotropic surface diffusion.

The island areal density on the (111) surface is much higher as compared to the (100) surface which was also observed in 5at% Nb-doped samples [9]. In Reference [9] we showed that the island density exhibits the same orientation dependency as the surface free energy, i.e. surfaces with high surface free energy are more densely covered by islands. This can be related with different diffusivities of atoms on (111) and (001) surfaces, respectively, or with different critical island sizes. Our present observations do not allow us yet to distinguish between these processes.
Figure 1. Optical micrographs of islands on top of (a) a (001) and (b) a (111) surface of 2 at% Nb-doped single crystalline SrTiO3. The different island contrast is due to the differential interference contrast mode which was used for imaging. Note that this makes many islands in Figure (b) appear rather faint. Island formation took place by annealing the single crystals at 1200 °C for 120 hours under oxygen atmosphere.

3.2. Chemical composition of islands

AES measurements were carried out on islands with different heights located on both (001) and (111) surfaces (Figure 2). For both surface orientations, a height dependency of the chemical composition was found: big islands (with a height of several 100 nm) contain almost only Sr cations whereas smaller islands (with a height of few 10 nm) also contain Ti cations. Moreover a slight decrease of the oxygen content with increasing island size occurs.

Figure 2. Compositions of islands with different sizes located on top of (a) (001) and (b) (111) surfaces. Accuracy of quantitative analysis is limited to ±5 at%. The height of the islands is denoted merely with numbers. The corresponding islands are presented in the electron back scattered images (insets).

A complementary EDXS analysis performed on a big island (with a height of 1400 nm) on top of the (001) surface confirmed the existence of Sr ions as the almost exclusively detectable cation in the whole area of the big island. In the SrTiO3 substrate, on the other hand, a Sr/Ti ratio close to
unity is observed (Figure 3). Concerning the composition of small islands (a few tens of nanometer in height), complementary EDXS data are not available.

![Figure 3. Cationic composition profile of a big island (1400 nm in height) located on the (001) surface. The EDXS line scan measurements (step size: 50 nm) starting in the island, crossing the interface and continuing in the bulk of SrTiO$_3$, show a sharp chemical transition from SrO$_x$ in the island to SrTiO$_3$ in the substrate.](image)

The gradual increase of the Sr concentration at the cost of Ti by increasing the island height is interpreted as follows. Surfaces of reduced SrTiO$_3$ are reported to be Ti-rich, possibly forming Ti-rich islands [5]. Subsequent oxidation forces the diffusion of Sr ions towards the surface, as expected from defect chemistry of donor-doped SrTiO$_3$. Part of the excess Sr will be incorporated into the Ti-rich islands resulting in a composition close to SrTiO$_3$ (small islands in Figure 2) with slightly enhanced Sr concentration, but also new Sr-rich islands can nucleate and grow (big islands in Figure 2).

### 3.3. Crystal structure of island

SAED investigations were performed on cross sections of islands with heights of 1400 and 250 nm (i.e. Sr-rich islands) located on (001) and (111) surfaces, respectively. In order to determine the orientation relationship between island and substrate, low-index zone axes of the substrate and corresponding SAED patterns of the islands were obtained. As an example, Figures 4 and 5 present SAED patterns of islands and SrTiO$_3$ substrate in [011] projection for (001) and (111) surfaces, respectively. We generally found that the SAED patterns of the islands are the same for both surfaces, and that the relative orientation between island and substrate is the same with a maximal deviation of about 5°. This shows that the island structure and the orientation relationship are greatly independent of surface orientation.
Figure 4. SAED pattern of the island located on the (001) surface. (a) Bright-field TEM image of the island. (b) SrTiO$_3$ [011] zone-axis pattern. (c) SAED pattern of the island.

Figure 5. SAED pattern of the island located on the (111) surface. (a) Bright-field TEM image of the island. (b) SrTiO$_3$ [011] zone-axis pattern. (c) SAED pattern of the island obtained.

4. Conclusion
High-temperature (1200 °C) annealing of 2 at% Nb-doped SrTiO$_3$ (001) and (111) surfaces results in the formation of monocrystalline oxide islands on the surfaces. For both surface orientations, the chemical composition of the islands correlates strongly with the height of the islands: Islands with heights of a few 10 nm reveal chemical compositions which are close to that of SrTiO$_3$, while islands with heights of several 100 nm consist of only Sr and O. The identical lattice-plane distances of the islands point at a distinct crystal structure independent of the surface orientation. The exact crystal structure remains to be resolved.

Although the present results indicate that island structure and chemistry are independent of surface orientation, the variation of island areal density with surface orientation shows that the kinetics of island formation and growth depends on surface orientation. We suppose that this is closely related to the different surface diffusivities of Sr cations depending on the surface orientation, surface reconstruction and the resulting surface defects which might support island formation.
References
[1] Y. Liang, D.A. Bonnell, J. Am. Ceram. Soc. 87 (1995) 2633
[2] M.R. Castel, Surf. Sci. 505 (2002) I
[3] N. Erdman, L.D. Marks, Surf. Sci. 526 (2003) 107
[4] R. Meyer, K. Szot, R. Waser, Ferroelectrics 224 (1999) 323
[5] K. Szot, W. Speier, Phys. Rev. B 60 (1999) 5909
[6] J. Daniels, R. Wernicke, Philips Res. Rep. 31 (1976) 544
[7] R. Moos, T. Bischoff, K.H. Härdtl, J. Mater. Sci. 32 (1997) 4247
[8] N.G. Eror, U. Balachandran, J. Solid State Chem. 40 (1981) 85
[9] B. Rahmati, J. Fleig, W. Sigle, E. Bischoff, J. Maier, M. Rühle, Surf. Sci. 595 (2005) 115
[10] B. Rahmati, J. Fleig, E. Bischoff, W. Sigle, M. Rühle, J. Europ. Ceram. Soc. 25 (2005) 2211
[11] J.A. Venables, G.D.T. Spiller, M. Hanbucken, Rep. Prog. Phys. 47 (1984) 399
[12] T. Michely, M. Hohage, M. Bott, G. Comsa, PRL 70 (1993) 3943