

Study of SrO segregation on SrTiO₃(100) surfaces

Han Wei^a, L. Beuermann^a, J. Helmbold^b, G. Borchardt^b, V. Kempter^a,
G. Lilienkamp^a, W. Maus-Friedrichs^{a,*}

^aInstitut für Physik und Physikalische Technologien, TU Clausthal, Leibnizstr. 4, D-38678 Clausthal-Zellerfeld, Germany

^bInstitut für Metallurgie, TU Clausthal, Robert-Koch-Str. 42, D-38678 Clausthal-Zellerfeld, Germany

Received 4 September 2000; received in revised form 17 November 2000; accepted 30 November 2000

Abstract

Annealing as-received lanthanum doped (5 at.% La) SrTiO₃(100) single crystals in air at 1300°C for 120 h results in the formation of insulating islands on the surface which have typical dimensions of up to 50 μm. These surfaces are investigated by metastable impact electron spectroscopy (MIES), ultraviolet photoelectron spectroscopy (UPS), X-ray photoelectron spectroscopy (XPS), metastable impact electron emission microscopy (MIEEM) and photoelectron emission microscopy (PEEM). The insulating islands consist of stoichiometric SrO. Between these islands an additional Sr enrichment is found in the top surface layers. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Perovskites; Sensors; Surfaces

1. Introduction

SrTiO₃ single crystal surfaces have been investigated previously because of their relevance in sensor applications, photocatalysis and as substrates for the epitaxial growth of high-*T_c* superconductors.^{1–5} During the heat treatment of SrTiO₃ single crystal surfaces in an ambient⁶ or oxygen atmosphere⁵ the appearance of Sr_xO_y and Ti_xO_y phases on top of or near to the surface have been reported, which strongly reduce the sensitivity of SrTiO₃ sensors.

Up to now the formation mechanism and the chemical composition of the additional phases are not well known. This is also true for the role of donor doping as to this phase formation process. Crystals with a medium to high donor concentration (> 1 at.%) show a stronger tendency to develop strontium-rich microcrystals on the surface compared with crystals of lower dopant content or undoped and acceptor doped crystals, respectively. This may be connected to the strontium vacancy compensation mechanism which is predominant in donor doped SrTiO₃ under oxidizing conditions. Therefore, switching from reducing to oxidizing conditions at ele-

vated temperatures requires the removal of an amount of strontium atoms which is proportional to the donor content. This excess strontium might form the second phase on the surface.

In this work we present our results concerning the influence of high temperature annealing in air on the surface properties of La-doped SrTiO₃(100). Investigations were performed by a combination of several spectroscopic and microscopic techniques. Due to their different information depths these techniques are capable to distinguish between subsurface and top surface layers very clearly.

2. Experimental

We used the spectroscopic and microscopic tools metastable impact electron spectroscopy (MIES), ultraviolet photoelectron spectroscopy (UPS), X-ray photoelectron spectroscopy (XPS), metastable impact electron emission microscopy (MIEEM) and photoelectron emission microscopy (PEEM). Apparatus and set-up are described in detail elsewhere.^{7–10}

Polished SrTiO₃(100) crystals (Crystec GmbH, Berlin, Germany) doped with 5 at.% of lanthanum were used without further preparation.

All measurements shown below were taken from the same crystal. The first investigation was conducted

* Corresponding author. Tel.: +49-5323-722310; fax: +49-5323-723600.

E-mail address: wmf@physik.tu-clausthal.de (W.M. -Friedrichs).

before any heat treatment. Subsequently, the sample was annealed in ambient atmosphere at 1300°C for 120 h and then the spectroscopic measurements (MIES, UPS, XPS) and at last the microscopic measurements (MIEEM, PEEM) in a second apparatus followed.

3. Results and discussion

Fig. 1 shows a set of corresponding PEEM (a) and MIEEM (b) pictures, respectively, which are typical for the surface after heat treatment. The field of view is 100 μm in all cases and the integration times are 0.5 s for the PEEM and 50 s for the MIEEM images. A number of regular microcrystals is observed which appear during the heat treatment. The as-received surface is smooth. On the annealed surface, island sizes

were found between 5 and 50 μm . Comparable sizes of microcrystals have recently been reported for undoped SrTiO₃(100) surfaces heated for 120 h at 1100°C by Sztot et. al from AFM measurements.¹¹

Comparing the respective MIEEM images and the PEEM images of Fig. 1, it appears that PEEM shows additional structures between the islands, which are only partly seen with MIEEM. The information depth for the PEEM corresponds to several atomic layers. The MIEEM information depth is zero. This suggests that the additional structures are located very near to the outermost surface layer, but do not necessarily appear on the very surface.

The surface work function of SrTiO₃(100) before and after oxidizing annealing was determined by MIES and UPS spectra. It is determined with an accuracy of ± 0.2 eV from the low-energy onset of the electron spectra and is found to be 4.0 eV for the original sample and 4.2 eV for the annealed surface.

The top of the valence band is estimated from the UPS spectrum to correspond to a binding energy (E_B) of (3.5 ± 0.2) eV with respect to the Fermi energy at $E_B = 0$, which is located close to the conduction band minimum due to donor doping. The band gap of pure SrTiO₃ amounts to 3.2 eV,¹² which is comparable to the value of (3.5 ± 0.2) eV evaluated from our UPS data.

The composition of the islands and of the subsurface structures was investigated by XPS comparing the surface before and after heat treatment. Spectra are shown in Fig. 2. After heat treatment the Sr(3d) intensity remains almost unaffected while the Ti(2p_{3/2}) emission is reduced. The relative ratios of the peak areas Ti2p_{3/2}/Sr3d are determined to be about 0.98 before and 0.63 after heat treatment. The primary O(1s) peak at a binding energy of 534 eV is reduced in intensity after heat treatment while a second O(1s) peak at 536 eV appears. This suggests that this additional peak corresponds to the islands appearing after heat treatment. In summary, these results are compatible with the assumption that the features arising during the heat treatment are due to a Sr–O complex. The XPS Ti2p_{3/2}/Sr3d ratio is reduced by 36%. A surface coverage with Sr-rich precipitates of about $(17 \pm 2)\%$ has been evaluated from optical micrographs. This result suggests that a Sr enrichment between the islands occurs, which most likely corresponds to the structures between the islands observed by the microscopic techniques.

The electronic structure of these islands is compared with the electronic structure of earth alkali oxides in Fig. 3. It shows the MIES difference spectrum of the surface state before and after heat treatment, which corresponds to the surface density of states of the islands together with the MIES spectrum for a polycrystalline and stoichiometric MgO surface.¹³ The difference spectrum is very similar to the MgO spectrum, but rather different from the spectra of TiO₂ single

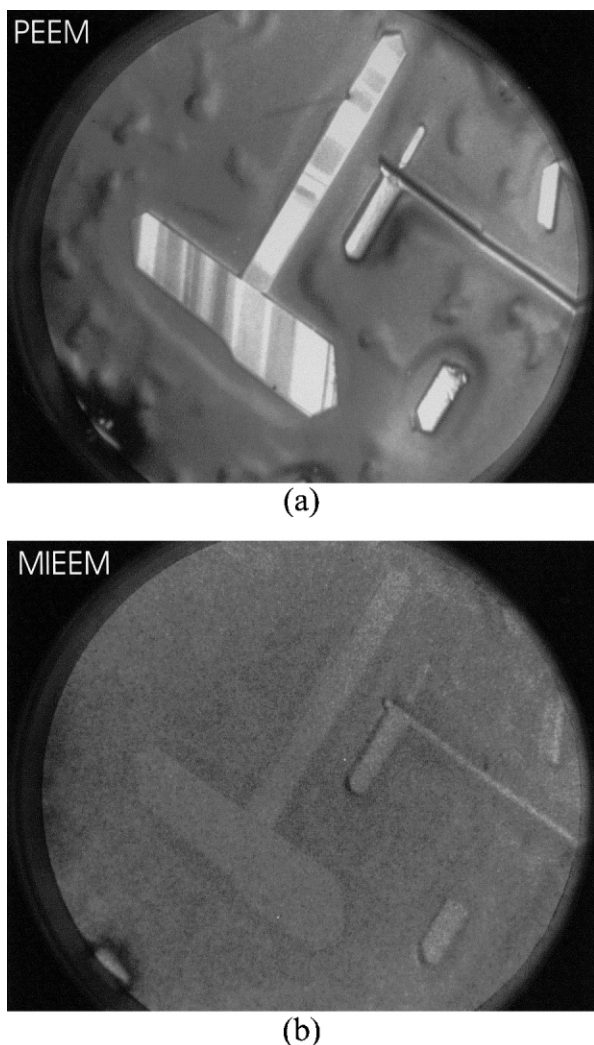


Fig. 1. PEEM (a) and corresponding MIEEM (b) images of the SrTiO₃(100) crystal heated at 1300°C in an ambient atmosphere for 120 h (corresponding to Fig. 2 after heat treatment). The field of view is 100 μm for all pictures.

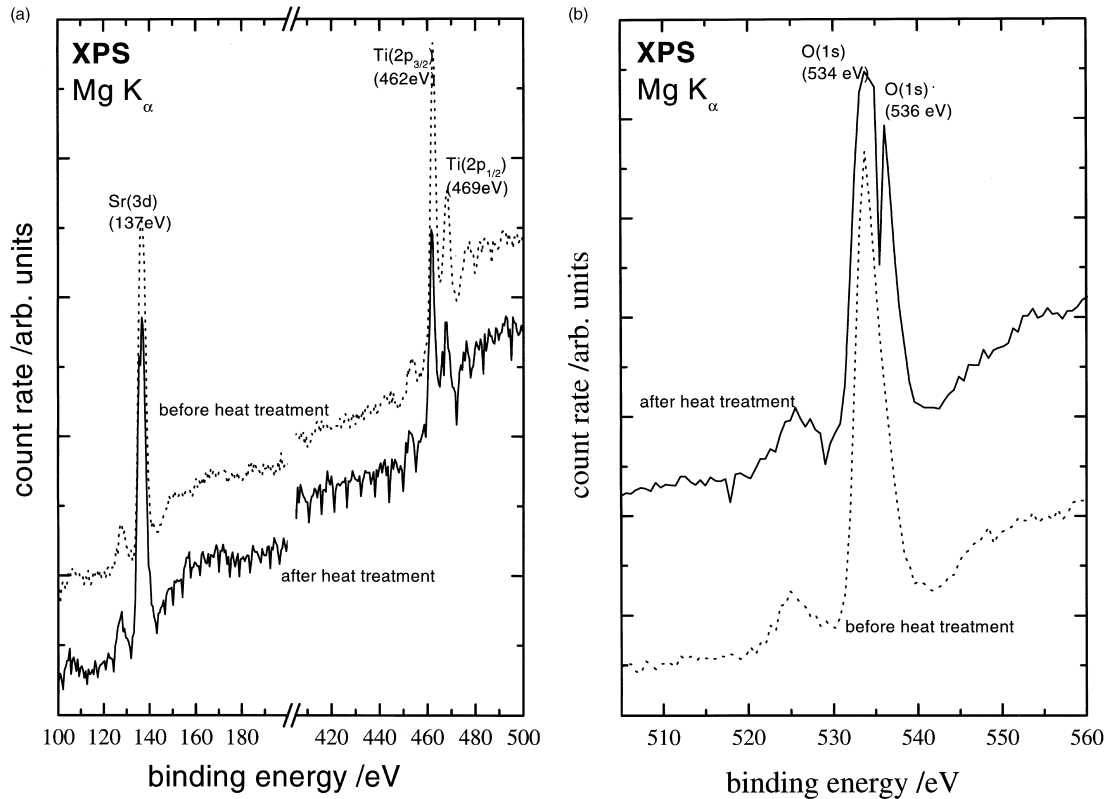


Fig. 2. XPS spectra of the SrTiO₃ surface before and after heat treatment: (a) Sr(3d) and Ti(2p) peaks and (b) O(1s) peaks.

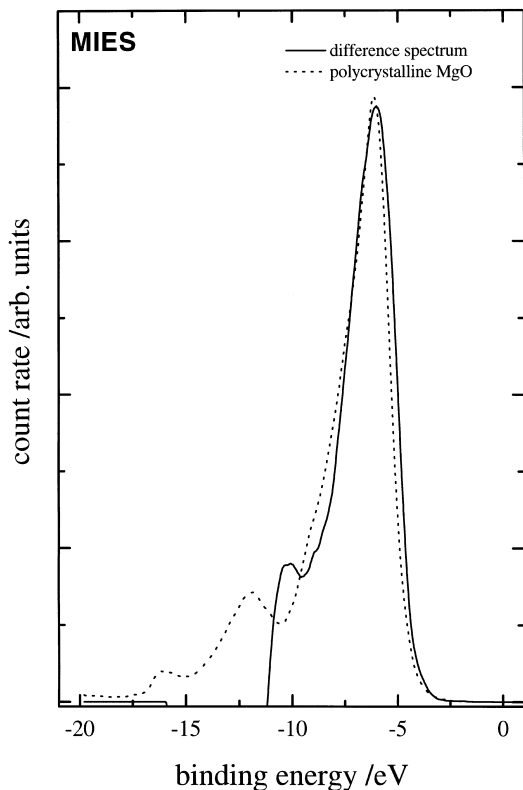


Fig. 3. MIES difference spectrum (before and after heat treatment, respectively) plotted together with a MIES spectrum for polycrystalline MgO (from Ref. 13).

crystal surfaces (not shown here).¹⁴ No features appear in the band gap below binding energies of about 3.5 eV. This indicates the development of a perfect insulator. We therefore assume that the islands formed on the SrTiO₃ surface after the heat treatment consist of stoichiometric SrO.

The presence of SrO islands on the SrTiO₃ surface will screen a considerable surface area from the oxygen incorporation process because earth alkali oxides do not interact with O₂.¹⁵

4. Summary

We applied several spectroscopic and microscopic techniques to investigate the electronic structure, the geometric structure and the chemical composition of insulating islands appearing on lanthanum doped SrTiO₃(100) single crystal surfaces after heat treatment in air. These islands consist most probably of stoichiometric SrO.

Acknowledgements

Financial support by the Deutsche Forschungsgemeinschaft under contracts DFG Li 813/1 and Bo 532/26 is gratefully acknowledged.

References

1. Ravikumar, V., Wolf, D. and Dravid, V. P., Ferroelectric-monolayer reconstruction of the SrTiO₃(100) surface. *Physical Review Letters*, 1995, **74**, 960–963.
2. Stäuble-Pümpin, B., Ilge, B., Matijasevic, V. C., Scholte, P. M. L. O., Steinfort, A. J. and Tuinstra, F., Atomic force microscopy study of (001) SrTiO₃ surfaces. *Surface Science*, 1997, **369**, 313–320.
3. Matsumoto, T., Tanaka, H., Kawai, T. and Kawai, S., STM-imaging of a SrTiO₃ surface with atomic resolution. *Surface Science*, 1993, **278**, L153–L158.
4. Liang, Y. and Bonnell, D. A., Atomic structures of reduced SrTiO₃ surfaces. *Surface Science*, 1993, **285**, L510–L516.
5. Szot, K., Speier, W., Herion, J. and Freiburg, Ch., Restructuring of the surface region in SrTiO₃. *Applied Physics A*, 1997, **64**, 55–60.
6. Helmbold, J., Borchardt, G., Meyer, R., Waser, R., Weber, S. and Scherrer, S., Oxygen diffusion in donor doped SrTiO₃: influence of thermal pretreatment. In *Proceedings of the NATO Advanced Research Workshop on Defects and Surface Induced Effects in Perovskites*, ed. G. Borstel, A. Krumins and D. Millers. Kluwer Academic Publisher, Dordrecht, 2000, pp. 461–466.
7. Wei, H., Beuermann, L., Helmbold, J., Borchardt, G., Kempter, V., Lilienkamp, G. and Maus-Friedrichs, W., Formation of SrO insulating islands on donor doped SrTiO₃(100) single crystals. *Journal of Electroceramics*, to be published.
8. Brause, M., Braun, B., Ochs, D., Maus-Friedrichs, W. and Kempter, V., Surface electronic structure of pure and oxidized nonepitaxial Mg₂Si layers on Si(111). *Surface Science*, 1998, **398**, 184–194.
9. Harada, Y., Masuda, S. and Ozaki, H., Electron spectroscopy using metastable atoms as probes for solid surfaces. *Chemical Reviews*, 1997, **97**, 1897–1952.
10. Stracke, P. R., *Elektronenspektroskopische Untersuchung der Metalladsorption auf MgO*. PhD thesis, TU Clausthal, 2000.
11. Szot, K. and Speier, W., Surfaces of reduced and oxidized SrTiO₃ from atomic force microscopy. *Physical Review B*, 1999, **60**, 5909–5926.
12. Pojani, A., Finocchi, F. and Noguera, C., A theoretical study of the unreconstructed polar (111) face of SrTiO₃. *Applied Surface Science*, 1999, **142**, 177–181.
13. Ochs, D., Maus-Friedrichs, W., Brause, M., Günster, J., Kempter, V., Puchin, V., Shluger, A. and Kantorovich, L., Study of the surface electronic structure of MgO bulk crystals and thin films. *Surface Science*, 1996, **365**, 557–571.
14. Brause, M., Skordas, S. and Kempter, V., Study of the electronic structure of TiO₂(110) and Cs-TiO₂(110) with metastable impact electron spectroscopy and ultraviolet photoemission spectroscopy (HeI). *Surface Science*, 2000, **445**, 224–234.
15. Ochs, D., Brause, M., Maus-Friedrichs, W. and Kempter, V., Interaction of small molecules with Mg and MgO surfaces studied with MIES and UPS(HeI). *Journal of Electron Spectroscopy Related Phenomena*, 1998, **88-91**, 757–762.