



Surface Structure of Oxygen Annealed Donor Doped SrTiO₃(100) Single Crystals Studied with Spectroscopic Electron Microscopy

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Abstract. Heating 5at.% (on A-site) La-doped SrTiO₃(100) single crystals in an ambient atmosphere at 1300°C for 120 h results in the formation of insulating islands on top of the surface with typical dimensions of up to 50 μm. The islands and the surface between them were investigated by spectroscopic Metastable Impact Electron Emission Microscopy (specMIEEM) and Photoelectron Emission Microscopy in order to determine its electronic and geometric structure.

The comparison of specMIEEM results with MIES (Metastable Impact Electron Spectroscopy) spectra from stoichiometric SrO shows that the insulating islands, which most likely consist of SrO, are at least partly covered by another species, probably SrO₂. All these islands are surrounded by 2–3 μm wide haloes. The electronic structure of these haloes is quite different from that of SrO and SrTiO₃ but similar to the electronic structure of TiO₂ or Ti₂O₃. It is suggested that the depletion of SrO from Ruddlesden-Popper (Sr_{n+1}Ti_nO_{3n+1}) phases results in the formation of SrO islands.

Keywords: strontium titanate, oxygen sensor, electron spectroscopy, electron microscopy

1. Introduction

The surfaces of SrTiO₃ single crystals 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 crystals in an ambient or oxygen atmosphere the appearance of Sr_xO_y and Ti_xO_y phases on top of or near to the surface has been reported, which will strongly reduce the sensitivity of SrTiO₃ sensors [5–7].

Applying Atomic Force Microscopy (AFM) Szot et al. suggest that the observed islands appearing on top of heated 5%La-doped SrTiO₃(100) consist of SrO [7]. Up to now the mechanisms of formation of these additional phases, also observed on SrTiO₃ powder [5], are not well understood. It is also not known how the formation of these phases may be influenced by the

dopants. Furthermore, the temperature dependence of the formation of these additional phases and the dependence on the atmosphere which may act as an oxygen source or as an oxygen sink, respectively, are not yet understood. SrTiO₃ oxygen sensors incorporate or release oxygen and thereby change their conductivity as a function of the ambient oxygen partial pressure. The first interaction step is the dissociation of O₂ molecules, which leads to the temporary formation of O²⁻ ions on top of the SrTiO₃ surface [8] with the subsequent diffusion of the oxygen ions into the sensor. Earth alkali oxides do not interact with O₂ [9]. Oxygen molecules impinging on SrO patches are therefore reflected without chemical interaction resulting in a strong reduction of the oxygen sensitivity.

The application of metastable rare gas atoms as an excitation source in electron spectroscopy has been developed into a powerful spectroscopic tool for surface analysis during the last years (Metastable Impact (or Induced) Electron Spectroscopy (MIES) or Metastable

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Atom Electron Spectroscopy (MAES)) [10]. We use MIES to obtain information of the reactivity of the outermost surface layer. The metastable He^* atoms, mostly in the $\text{He}^*(2^3\text{S})$ state, have thermal energies. They do not penetrate into the surface. The He^* atoms interact with the surface at distances between 3 Å and 10 Å in front of the surface [10]. The resulting electron emission is based on the interaction of the He^* wave functions with the very outermost part of the wave functions of the surface. Thus, techniques applying metastable rare gas atoms as excitation source are extremely surface sensitive.

Low Energy Electron Microscopy (LEEM) and Photoelectron Emission Microscopy (PEEM) have proved their usefulness for the investigation of surface structures with a resolution of better than 10 nm [11]. One of the main advantages of these microscopes is the fast image acquisition (video frequency is possible) due to direct image recording. Very recently, Harada et al. integrated Metastable Impact Electron Emission Microscopy (MIEEM) into a commercial LEEM/PEEM microscope [12, 13]. The spectroscopic type of this microscope allows energy dependent image acquisition.

In this work we extend our previous work [14] where we applied MIEEM, PEEM and XPS to investigate the composition of the insulating islands appearing on top of thermally treated $\text{SrTiO}_3(100)$ surfaces. Here we applied spectroscopic MIEEM (specMIEEM) for the very first time in combination with PEEM and supported by laterally averaging MIES in order to gather information on the electronic and geometric surface structure of heated $\text{SrTiO}_3(100)$ surfaces appearing on top of and between the insulating islands.

2. Experimental

The Spectroscopic Low Energy Electron Microscope (SpecLEEM) for the laterally resolved spectroscopy is based on the design by Veneklasen [15]; Figure 1 shows the principal setup. The basic principle is the parallel and energy filtered imaging of electrons emitted from a flat surface by any kind of excitation (photons, electrons or metastable rare gas atoms). The parallel image acquisition comparable to a light microscope renders small exposure times and a spatial resolution independent of the excitation source. A brief description

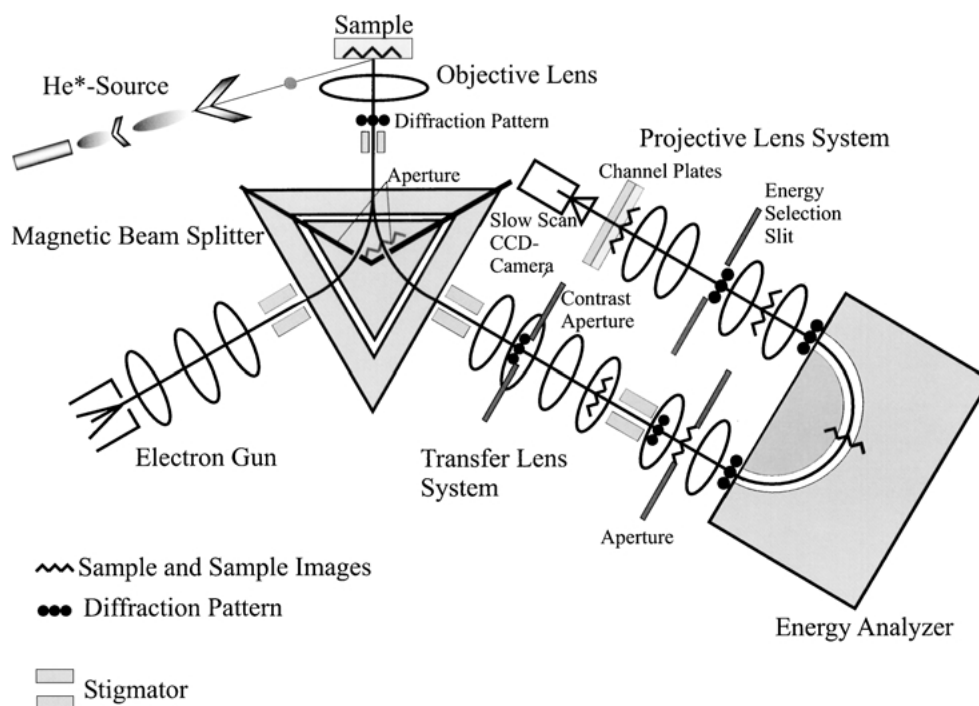


Fig. 1. Schematic setup of the specLEEM (see text).

of the present status of the instrument and results obtained with x-ray excitation can be found in [16]. Emitted electrons, which may be characteristic photoelectrons, Auger electrons, electrons from Auger processes interacting with He* or secondary electrons, can be imaged with spectroscopic and thus, chemical selectivity. The ultimate energy resolution of the SpecLEEM is better than 400 meV, the demonstrated lateral resolution is 25 nm in the energy filtered mode [16].

The emitted electrons are accelerated between sample and objective lens to about 18 keV thus making an energy integrated resolution limit of less than 10 nm possible. The objective lens forms an intermediate image which is transferred by the transfer lens system to a 180° electrostatic energy filter. Beam splitter (magnetic field, triangular) and electron gun are not important for the MIEEM mode. If the sample image is placed in the middle of the energy filter and the diffraction pattern (that is the intermediate image of the back focal plane of the objective lens) at its entrance, a high quality, energy filtered image of the sample can be achieved and projected onto the image amplifier. The amplification is performed by two channelplates in a chevron arrangement phosphorous screen. The image is recorded by a CCD camera (PCO Sencam) converts the image to visible light.

Chemical information via photoelectrons needs a strong X-ray excitation which is presently only supplied by synchrotron radiation sources which are expensive and have only limited access. In the present work we have illuminated the sample by metastable (2^3S) He* atoms with one electron in the 1s and the other in the 2s level. The transition to the ground state is dipole forbidden, thus the ground state can only be reached by an interaction of He* with other molecules or a solid surface. The potential energy of 19.8 eV of the He* is sufficient to emit valence electrons from a surface making a chemical analysis of the surface possible (MIES) [10, 17, 18]. One important difference to other valence band based spectroscopic methods like ultraviolet photoelectron spectroscopy (UPS) is the absolute surface sensitivity which is caused by the fact that He atoms cannot penetrate the surface and thus transfer their energy in front of the surface. In contrast to e.g. Auger and photoelectron spectroscopy, MIES is able to give answers to questions like termination of the surface and the oxidation state of the surface layer of the material which may be different to the bulk oxidation. The application of specMIEEM will be described in detail in a forthcoming publication [19].

The principle of the He* source has been described in detail previously [20]. Metastable He* ($2^3S/2^1S$) ($E^* = 19.8/20.6$ eV) atoms with thermal kinetic energies and HeI photons ($E^* = 21.2$ eV) are produced in a cold-cathode gas discharge. In order to increase the He* beam intensity a second discharge is ignited between source anode and skimmer [21]. Due to the special design of the He* source is excited by the HeI photons only a negligible percentage of all detected electrons.

For a reliable interpretation of the specMIEEM results additional MIES measurements on stoichiometric SrO and clean unheated 5%La-doped SrTiO₃(100) performed under defined conditions are necessary. These measurements were performed in a second apparatus described in detail previously [20, 22]. It consists of a He* source similar to that in the microscope with an additional time-of-flight technique to separate electrons emitted by He* (MIES) and HeI (UPS) interaction with the surface. The apparatus is equipped with a hemispherical analyzer (VSW HA 100) for data acquisition. MIES spectra are recorded with a resolution of 250 meV under normal emission. The angle of incidence for the mixed He*/HeI beam is 45°.

Polished La(5%)-doped SrTiO₃(100) crystals (Crystec) were heated in air for 120 h at 1300°C leading to the formation of Sr_xO_y islands on top of the surface [5–7, 14]. The crystals were only shortly flashed under ultrahigh vacuum conditions to about 700°C for several seconds to remove species from the ambient atmosphere. The cleanness was monitored by X-Ray Photoelectron Spectroscopy (XPS), Ultraviolet Photoelectron Spectroscopy (UPS) and the MIES measurements. Applying this procedure no enrichment or desorption from the surface occurs.

Stoichiometric SrO was produced on Si(100) by Sr exposure in an oxygen partial pressure of about 2×10^{-7} mbar. The correct stoichiometry was controlled by XPS. The cleanness of the surface was monitored by the MIES spectrum, which is very sensitive to pollution from the residual gas. The SrO layer thickness was evaluated to about 10 nm.

3. Results and Discussion

Figure 2 shows a set of corresponding PEEM (a) and MIEEM (b) images, respectively, which are typical for the surface after the heat treatment. The images are energy-integrated without spectral resolution. The field

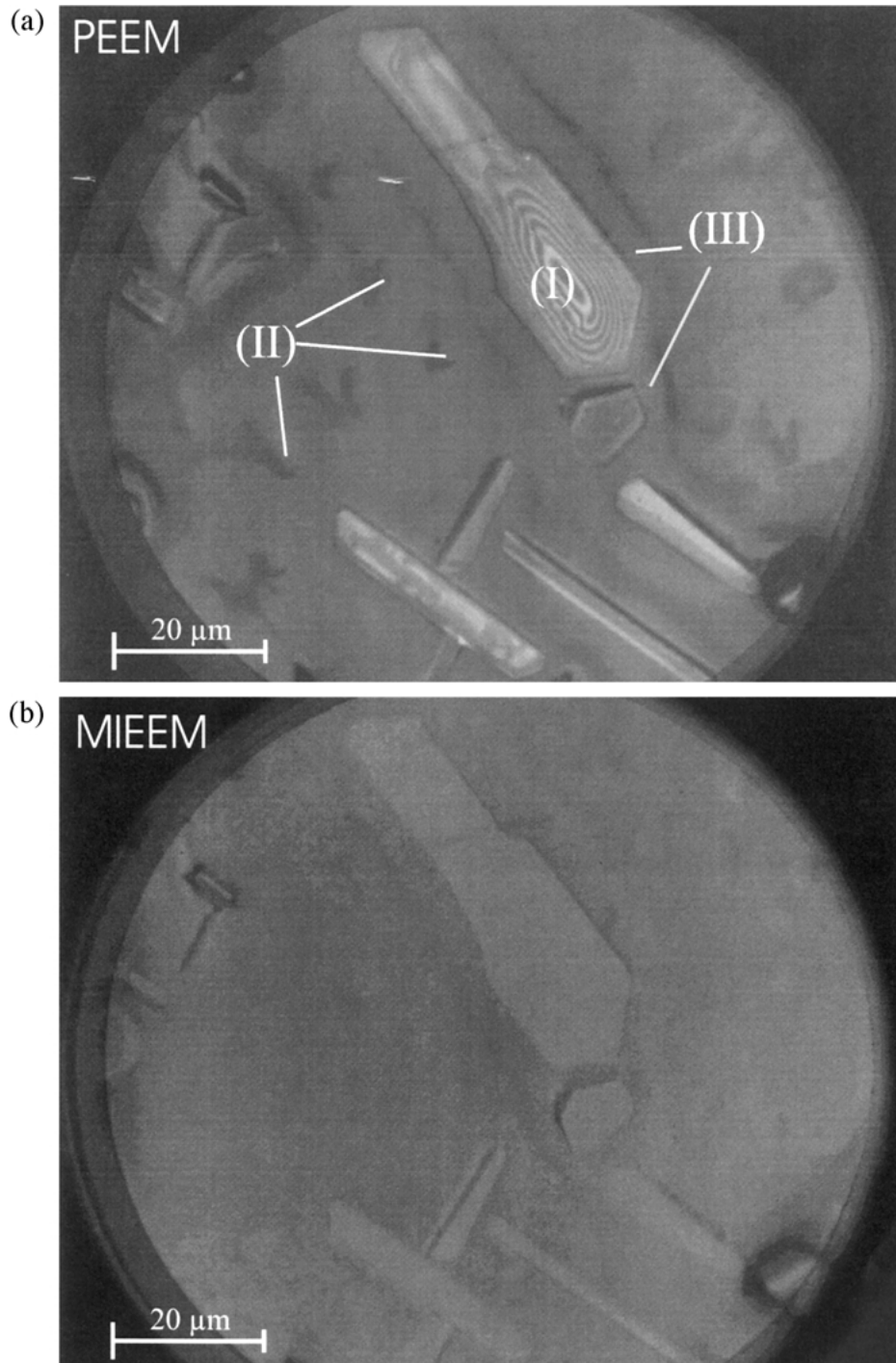


Fig. 2. PEEM (a) and corresponding MIEEM (b) images of SrTiO₃(100) crystal heated at 1300°C in air for 120 h; the field of view is 100 μm for all images.

of view is $100\ \mu\text{m}$ in both cases and the integration times are 0.5 s for the PEEM and 50 s for the MIEEM images. A number of microcrystals (denoted by (I) in Fig. 2(a)) is observed appearing during the heat treatment, which are distributed over the entire crystal surface. Typical island dimensions range from $5\ \mu\text{m}$ to $50\ \mu\text{m}$. Their typical heights are evaluated by Auger Electron Spectroscopy (AES) depth profile analysis (not shown here) to amount to several 100 nm. Interferences of the exciting UV light lead to the fine structure observable on top of the islands (I) in the photoemission images (Fig. 2(a)).

Microcrystals of comparable size have recently been reported for undoped $\text{SrTiO}_3(100)$ surfaces heated for 120 h at 1100°C in ambient atmosphere by Szot et al. from AFM measurements [5]. They identified these structures as SrO islands.

Both PEEM and MIEEM show the microcrystals although with different contrasts. Besides the islands two observations should be noted:

1. Comparing the MIEEM and the PEEM images of Fig. 2 PEEM shows additional structures between the islands (denoted by (II) in Fig. 1(a)), which are barely seen in MIEEM. Only a slight contrast due to shadowing (the metastable beam is impinging under 16° onto the surface) can be noted. The information depth for the PEEM pictures corresponds to the escape length of the electrons within the SrTiO_3 bulk which amounts to about 10 nm for kinetic energies around 2 eV [17]. The MIEEM information depth is zero because the impinging metastable He^* atoms interact with the very outermost surface wave function typically between $3\ \text{\AA}$ and $5\ \text{\AA}$ in front of the surface for Auger deexcitation (AD) processes. This suggests that the additional structures (denoted by (II)) are located near to the outermost surface layer, but not necessarily on top of the surface. Additional AES measurements (not shown here) and the results of Szot et al. [5–7] suggest that Sr enrichment occurs on top of the heated SrTiO_3 surface between the SrO islands resulting in the formation of Ruddlesden-Popper phases ($\text{Sr}_{n+1}\text{Ti}_n\text{O}_{3n+1}$) on top of the surface, but we cannot give direct evidence for this formation. Therefore it is reasonable to assume, that the observed structures (denoted by (II) in Fig. 1 (a)) are due to such SrO-rich phases forming on the surface.
2. All islands are surrounded by a region of reduced height (denoted by (III) in Fig. 1(a)). This is clearly

seen in the PEEM pictures, but to some extent also with MIEEM.

A series of spectrally resolved MIEEM images is shown in Fig. 3. E_B is the electron binding energy referring to the Fermi energy of the surface. The images have been taken after a 60 s flash at 700°C in ultrahigh vacuum. For the highest binding energies ($E_B = 13.8\ \text{eV}$) and very low binding energies ($E_B = 4.3\ \text{eV}$ and $3.8\ \text{eV}$) $2\text{--}3\ \mu\text{m}$ wide halo-like border regions surrounding the islands can be recognized very well. These regions correspond to the topographic structures around the islands displayed in Fig. 1, but appear to be somewhat smaller.

From those image series in Fig. 3 specMIEEM-MIES spectra were derived at the three different positions discussed previously: (I) on top of an SrO island, (II) between the islands and (III) in the region $2\text{--}3\ \mu\text{m}$ around the islands. The intensities were integrated from the squares shown in the first image of Fig. 3 for each of the pictures. The size of the squares is $2.2 \times 2.2\ \mu\text{m}^2$ for positions (I) and (II) and $1.1 \times 1.1\ \mu\text{m}^2$ for position (III).

The spectra evaluated in this manner are shown in Fig. 4 together with the MIES spectra for stoichiometric SrO and unheated 5%La-doped $\text{SrTiO}_3(100)$ [23]. The respective symbols mark the binding energies where the specMIEEM images were taken for the three different regions. The dotted lines between the symbols are obtained from a B-Spline. The MIES spectrum for pure 5%La-doped $\text{SrTiO}_3(100)$ and the specMIEEM spectrum of region (II) (triangles) correspond well. This means, that the electronic structure between the islands did not change dramatically during the annealing procedure. Obviously the electronic structures of pure SrTiO_3 and Ruddlesden Popper phases are very similar. The rise of the MIES intensity below a binding energy of 9 eV is due to secondary electron emission and will not be discussed.

The specMIEEM spectrum of region (I) (on top of an SrO island) (dots) shows a maximum at the same position as the stoichiometric SrO, but appears to be broader on both sides of its maximum. This means that the SrO islands are not terminated by a pure SrO top layer. Additionally, the position of the three peak structure of MgO_2 , calculated by Kantorovich et al. [24], is given in Fig. 4. The MgO_2 and the SrO_2 MIES peak positions are not expected to differ strongly [25]. Thus this comparison appears to be justified, suggesting that the observed broadening could partly be caused by the

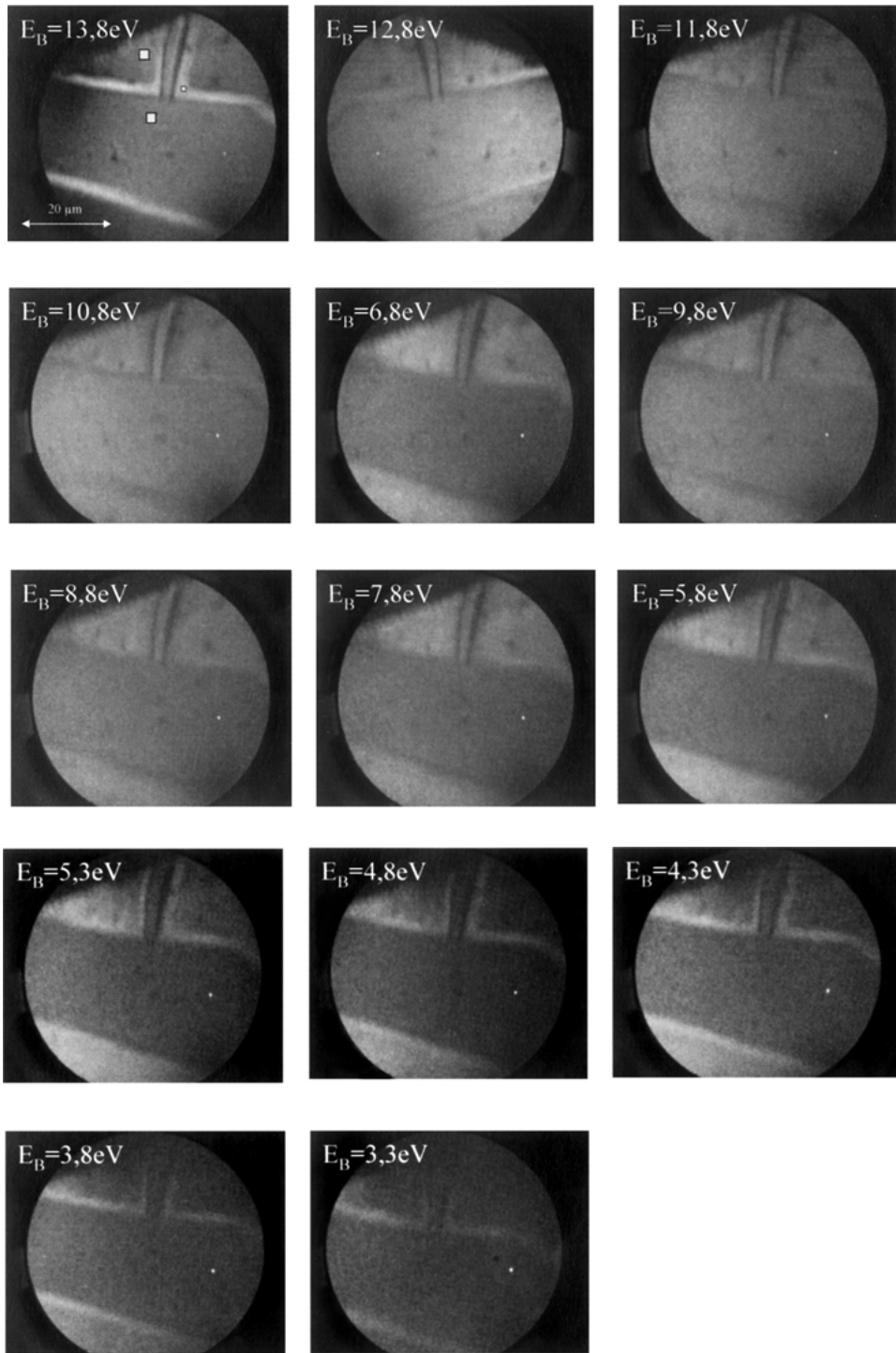


Fig. 3. specMIEEM images for different binding energies as indicated with each images; the field of view is 50 μm for all images.

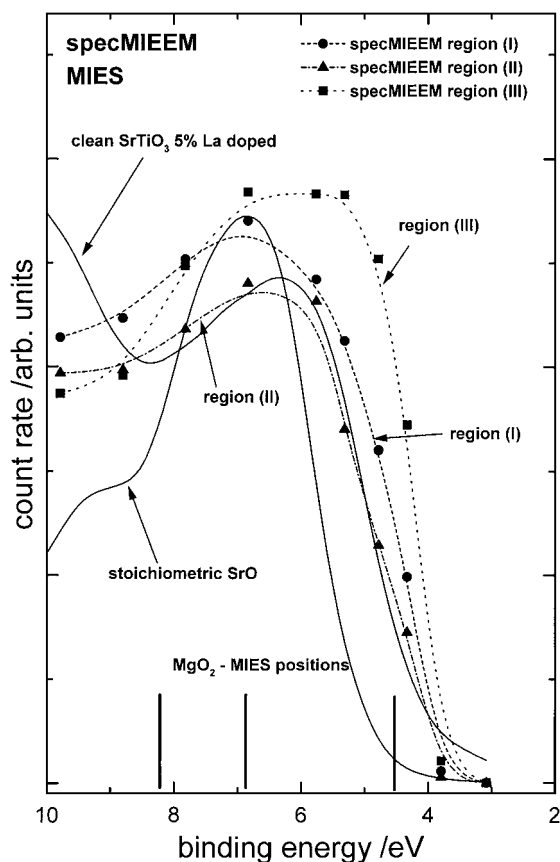


Fig. 4. specMIEEM spectra integrated in areas (I), (II) and (III) specified in the first image of Fig. 3 compared with the MIES spectra for clean La5%-doped $\text{SrTiO}_3(100)$ and stoichiometric polycrystalline SrO; the MIES spectra are plotted in solid lines while the specMIEEM spectra are plotted with squares and dotted lines.

formation of SrO_2 , which also is likely from a thermodynamic point of view [26]. We cannot give further evidence for this picture at the moment.

The specMIEEM spectrum of the the 2–3 μm wide border zone (III) around the islands (rectangles), where PEEM (see Fig. 2) showed some material loss, looks quite different from all other spectra shown in Fig. 4. Especially on the low binding energy side it is broader than the other peaks, although the spectral onset fits with the other spectra. Szot et al. observed dismantling of heated SrTiO_3 surfaces which leads to the formation of Sr-rich and Ti-rich regions on top of and underneath the surface [6, 7]. We are not able to confirm this observation, but it appears plausible that strontium and oxygen around the islands are consumed by the formation

of the SrO islands resulting in the appearance of Ti-rich phases. The observed electronic structure of the border zone surrounding the islands shows the highest width of the three different areas. Comparable broad and flat structures were observed with MIES on TiO_2 surfaces [27]. This indicates the formation of Ti-rich phases such as TiO_2 or Ti_2O_3 surrounding the islands. These border zones have not been detected with a scanning Auger microscope. At the moment we are not able to give further support for this hypothesis.

It is well known that during the heat treatment under oxidizing conditions Sr vacancies are created due to the Schottky equilibrium. This results in the Sr enrichment on the one hand and in the desorption of Sr from these surfaces on the other hand, which was reported by Szot et al. [7]. The Sr enrichment results in the formation of Ruddlesden-Poppers phases on the surface and in the near surface region being accompanied by a Sr depletion underneath the surface. The results presented here suggest that during prolonged heating SrO islands are formed consuming SrO from their surroundings. SrO transport takes place via surface diffusion. This will most probably finally result in large SrO islands consuming most of the enriched SrO being located on top or near the surface. This process may lead to the uncovering of TiO_x phases being responsible for the specMIEEM spectra from the border zones around the islands.

4. Summary

We applied spectroscopic Metastable Impact Electron Emission Microscopy (specMIEEM) and Photoelectron Emission Microscopy (PEEM) supported by Metastable Impact Electron Spectroscopy (MIES) to investigate the electronic and geometric structure of heated donor doped (La5%) $\text{SrTiO}_3(100)$ single crystal surfaces. The crystals were heated at 1300°C in an ambient atmosphere for 120 h. During this procedure SrO islands grow on top of the surface.

The surface termination of these islands does not consist of pure stoichiometric SrO but is most likely influenced by SrO_2 contributions. Surrounding the insulating islands, additional 2–3 μm wide border zones are observed which are assumed to consist of a Ti-rich oxygen containing phase. The depletion of SrO from the surroundings is most probably responsible for the formation of the SrO islands.

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