Surface properties of polycrystalline Strontium Titanate analyzed by energy filtered photoemission electron microscopy

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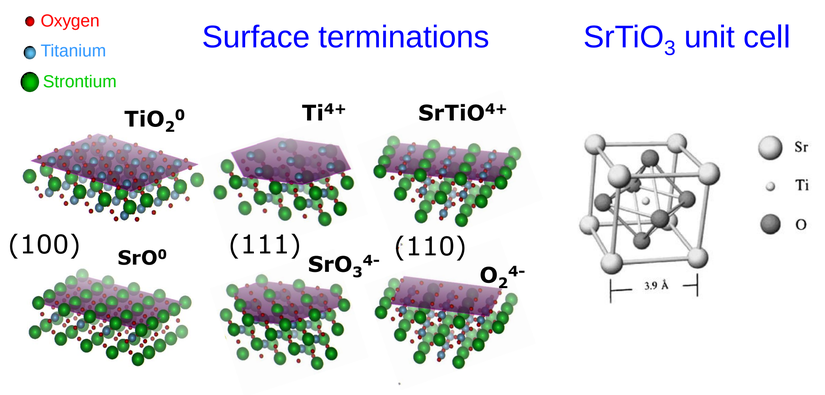
We present a study of surface termination and work function of a polycrystalline strontium titanate ($SrTiO_3$ - STO) ceramic doped with niobium. The samples were sintered polycrystals which were fine polished and annealed in situ at 1073 K in UHV. Surfaces were analyzed by energy filtered photoemission electron microscopy (PEEM) using soft x-ray synchrotron radiation. The experiments were performed at ID08 beamline at the ESFR using an Omicron NanoESCA microscope. We found that elemental maps of O 1s, Sr 3d and Ti 2p display intensity variations which are shown to depend on the orientation of each crystalline grain. A predominant termination is assigned to each major crystal orientation. Similarly, work function (WF) maps were measured. The surface WF is observed to depend on the orientation, being smaller for the <100> and bigger for the <111> (4.13 eV and 4.43 eV, respectively).[3] It is also observed that after annealing, the density of states just below the Fermi level is non-zero indicating that surface defects, likely to be oxygen vacancies, are present after annealing.

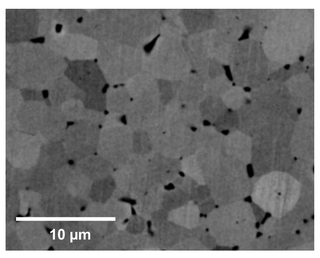
Introduction



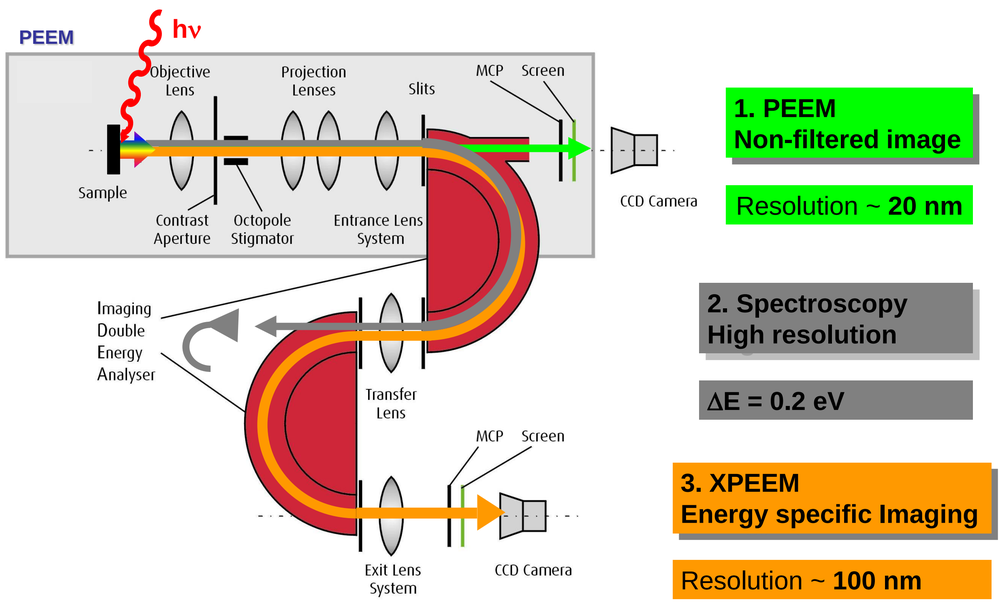
Sample preparation and Microstructure

Sintered (Poly-crystaline) Nb doped $SrTiO_3$

- $Sr_{0.994}Ti_{0.988}Nb_{0.012}O_3$
- Cold iso-statically pressed with 400MPa
- Sintered at 1420°C for 20 hours and quenched.
- Grain size ~1-5 µm
- Details: Bäurer et al. *Phys.: Conf. Series* 2008 **94** 012015; doi:10.1088/1742-6596/94/1/012015



Full-field XPS imaging with PEEM



Synchrotron Radiation (665 eV) at ESRF – ID08

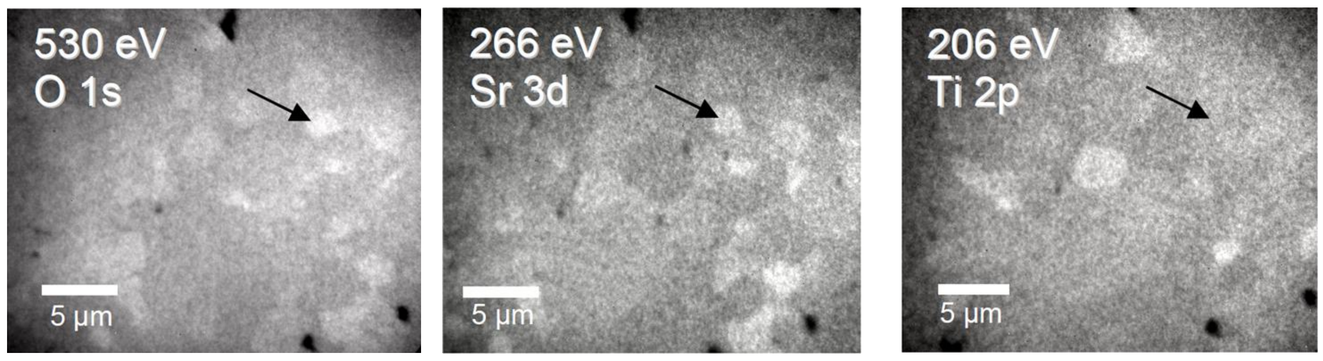
High surface sensitivity

[1] O. Renault, et al. **Surface Science**, Surface Science 601 (2007) 4727–4732. doi:10.1016/j.susc.2007.05.061
[2] M. Escher, et al. **J. Phys: Condens. Mat.** 17 (2005), p. 1329.

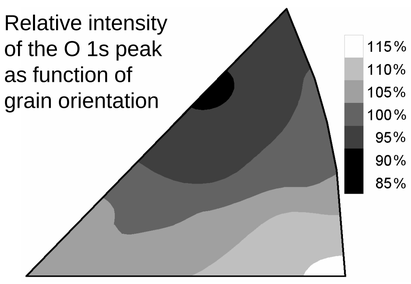
Find out more!

- *Orientation-dependent surface composition of in situ annealed strontium titanate*
  Zagonel et al., Surf. Interface Anal. 2008, 40, 1709. doi:10.1002/sia.2886
- *Orientation-dependent work function of in situ annealed strontium titanate*
  Zagonel et al., J. Phys.: Condens. Matter 2009, 21, 314013. doi:10.1088/0953-8984/21/31/314013.
- *Surface enhanced covalency and Madelung potentials in Nb doped SrTiO3 (100), (110) and (111) single crystals*
  Vanacore et al., Surface Science 2010, 604, 1674–1683. doi:10.1016/j.susc.2010.06.012

Surface Composition



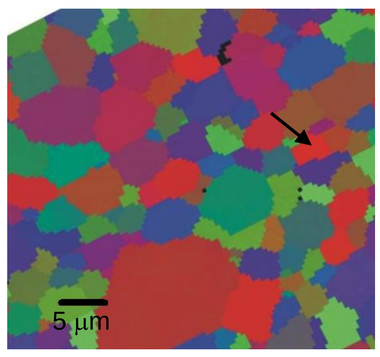
Relative intensity of the O 1s peak as function of grain orientation



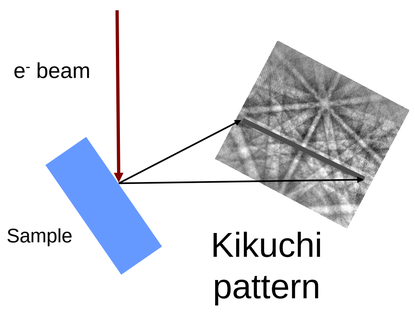
Energy filtered images at electron core levels O1s, Sr 3d and Ti 2p. The contrast shows the difference in surface composition with very high surface sensibility (~ 100 pm).

The orientation in observed to affect the surface composition: <101> surface is rich in O. <100> (see arrow) is made of SrO.

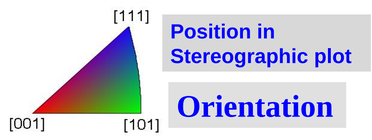
EBSD maps



The orientation of each grain on the surface is determined. This is done in the same region as PEEM measurements. The arrow indicates the same grain as in the Surface Composition figures.

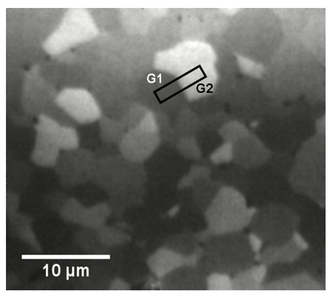


Electron Backscattered Diffraction was used to map the grain orientation. These experiments were performed on a SEM.

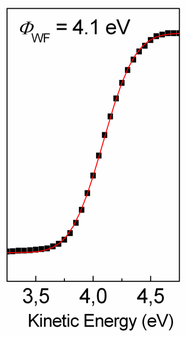


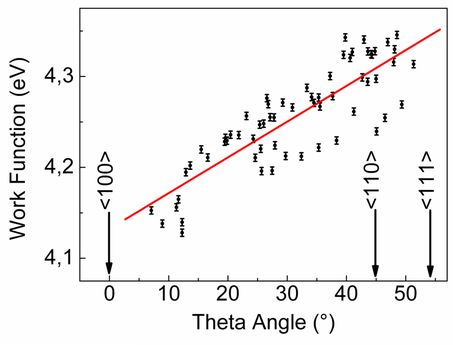
The color code indicated the orientation of each grain. The same type of plot can be used to see the intensity as function of orientation.

Electronic properties and Work Function

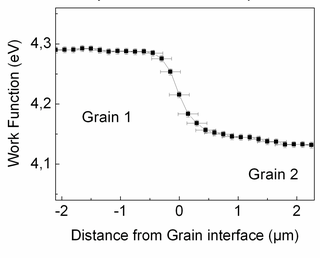


Raw data image acquired at the photoemission threshold ($E - EF = 3.85$ eV)



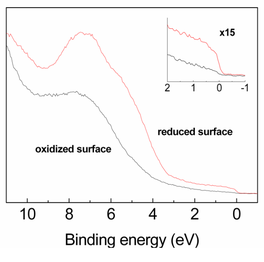


A correlation is observed between WF and grain orientation. Closer to the <100> surface, the WF is lower. <110> and <111> surfaces have higher WF. The difference is about 200 meV. This correlation is linked to the effect of orientation of the surface composition. <100> surface, for instance, is SrO terminated.



The surface work function can be determined from each pixel by fitting an error function to the photoemission threshold.

The WF variation across a grain boundary is observed to be smooth. According to the grain orientation, the WF changes from about 4.15 to 4.35 eV. This variation is possibly linked to the surface termination, composition and segregation.



UPS spectra have revealed that the surface is partially reduced during the annealing. This means that some grain orientation loose oxygen by desorption to the vacuum. Then, some grains are no longer stoichiometry.

Summary

In situ annealing cleaned the SrTiO3 surface providing a surface structure with different local compositions and electronic structures.

The surface composition is linked to the grain orientation and main compositions can be drawn.

The work function is affected by the surface composition and a variation of 200 meV was found.

Acknowledgments:

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