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SITE SPECIFIC XPS: STRUCTURAL AND ELECTRONIC PROPERTIES INVESTIGATED BY X-RAY STANDING WAVES

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One of the powerful tools for surface science available at synchrotron light sources is the X-ray standing wave (XSW) method [1]. Its strength is the very high spatial resolution of the order of 0.01 Å, which the technique adds to common spectroscopic methods, like fluorescence, Auger, or photoelectron spectroscopy. The XSW technique is applicable if the wavelength of the X-rays is of the order of unit cell dimensions, which corresponds to an X-ray photon energy of typically few keV.

The X-ray standing wave method utilizes the spatial intensity modulation of an X-ray interference field, which can be generated by interference via Bragg reflecting an X-ray plane wave from a single crystal. By scanning the photon energy or the angle of the incident beam through the range of Bragg reflection, the intensity maxima of the wavefield are moved by half the wavefield period over the distribution of atoms in the unit cell. The X-ray absorption profile for specific elements, indirectly detected by the fluorescence, Auger, or photoelectron signal, exhibits a shape characteristic of the elemental distribution in the unit cell. Selecting the photon energy or the incident angle of the beam within the Bragg range allows positioning the wavefield to preferentially excite atoms at specific lattice sites.

This presentation will mainly focus on two recently established applications of the XSW method:

(1) XSW valence electronic structure analysis

X-ray photoelectron spectroscopy (XPS) is an important tool for investigating the density of occupied electronic states. Combined with the XSW technique, we can obtain electronic information spatially resolved on the atomic scale: It is possible to reveal how structure and chemical composition are related to the electronic structure of a solid.

We used the XSW method to exactly identify the site within the unit cell of the wide gap (3.2 eV) semiconductor $SrTiO_3$ from which the electrons from a specific region of the valence band arise [2].

XSW interference fields were established in the surface region of a $SrTiO_3$ single crystal for the (111) and (112) Bragg reflections. The period of these interference fields reflects the spacing of the diffracting planes, which for a (111) reflection are indicated with respect to the $SrTiO_3$ unit cell in Fig. 1. We can shift this wavefield by varying the X-ray energy within the range of the Bragg reflection, which occurs over a few 100 meV. In this way we can scan the planes of the interference field in a controlled way across the atomic positions. A maximum number of photoelectrons with a characteristic energy will be emitted when the maxima of the wavefield coincide with the centre of the atoms of a specific element in the unit cell, here Sr, Ti, and O. The emission will be strongly localised even for the largely delocalized valence electrons, since the dipole approximation applies, meaning that photoelectron emission occurs from the centre of the atoms exclusively.

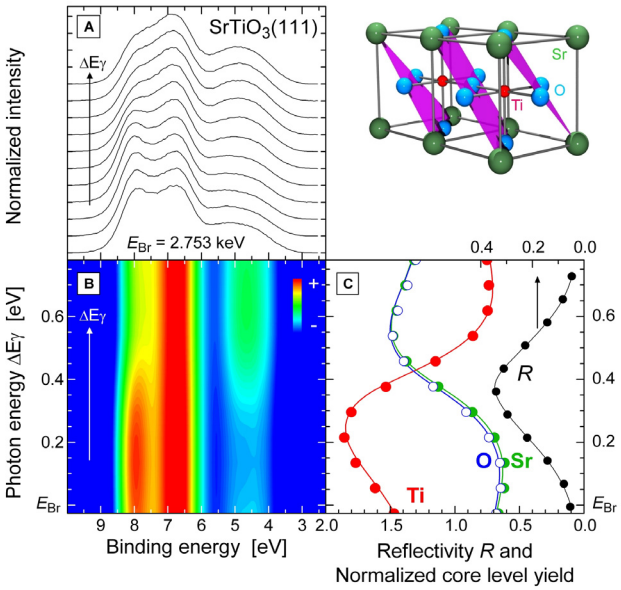

Figure 1. Two $SrTiO_3$ unit cells with the (111) diffraction planes indicated (top right). a) $SrTiO_3$ valence band for different standing wave positions while crossing the (111) reflection b) 2D colour rendering of a). c) $SrTiO_3$(111) reflectivity curve and simultaneously recorded Ti, O, and Sr XPS core levels emission.

For the $SrTiO_3$(111) reflection at around 2.753 keV, the valence band recorded for different positions of the standing wave within the unit cell exhibits a pronounced

variation in line shape, as Figs. 1a and 1b show. The simultaneously recorded reflectivity curve shown in Fig. 1c allows unambiguously determining the position of the wavefield within the unit cell of the $SrTiO_3$ crystal. Maxima in the O, Sr, and Ti XPS core level intensities are observed when the maxima of the wavefield are located at the position of the corresponding atoms.

Just by visible inspection of Figs. 1a and 1b and comparison with Fig. 1c one can conclude that the valence band at about 4.5 eV binding energy is dominated by emission from Sr and O sites, whereas at 8 eV binding energy the photoelectrons mainly arise from Ti sites. With respect to the (111) reflection, Sr and O are located on a common plane. However, utilising the (112) reflection, the contributions from the Sr and O sites can be disentangled.

The result of a quantitative XSW analysis is shown in Fig. 2 compared with the results of *ab initio* density functional theory (DFT) calculations in the local density approximation (LDA). The agreement is excellent. It should be noted that the density of states, which is determined by theory, must be weighted for comparison with experiment with the X-ray cross sections. This must be done for the individual elements and angular momentum states. As *a priori* unknown values for the solid state, valence band cross sections are a further important result of this study.

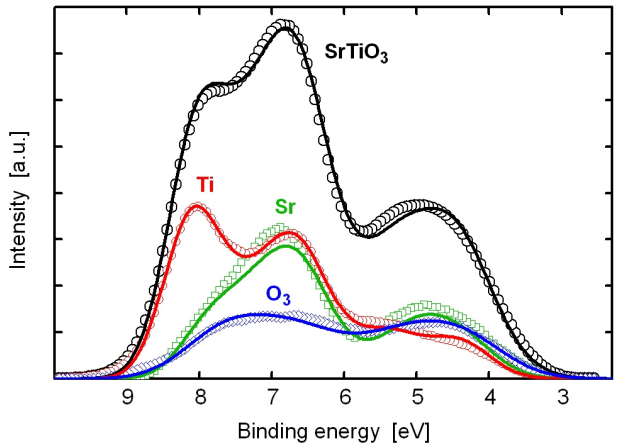

Figure 2. $SrTiO_3$ valence band spectrum and the determined partial contributions arising from the Ti, Sr, and O sites. Symbols: experimental results, lines: DFT/LDA calculations, weighted with cross sections.

(2) XSW real space imaging

The early stages of epitaxial growth processes can comprise complicated nucleation mechanisms. This can in particular be the case for multi-elemental compounds with a complex unit cell, such as high-temperature superconductors.

We employed XSW real space imaging for studying the atomic structure of 0.5 layers of $YBa_2Cu_3O_{7-\delta}$ deposited on the (001) surface of a $SrTiO_3$ single crystal by pulsed laser deposition. XSW core level photoelectron yield was recorded for all 6 elements present in film and substrate for 7 different Bragg reflections, each providing amplitude *and phase* of one Fourier coefficient of the elemental atomic distribution function. Assuming a 4-fold in-plane symmetry of the film yielded 29 Fourier coefficients. By direct Fourier inversion, a three-dimensional real space image of the atomic distribution for each of the elements was reconstructed, as shown in Fig. 3.

The study has contributed towards the understanding of the nucleation mechanism of a heteroepitaxially grown complex material: The images confirmed the formation of a $(Y/Ba)CuO_3$ mixed perovskite precursor phase prior to the formation of the $YBa_2Cu_3O_{7-\delta}$ phase during the growth of the first monolayer of the film.

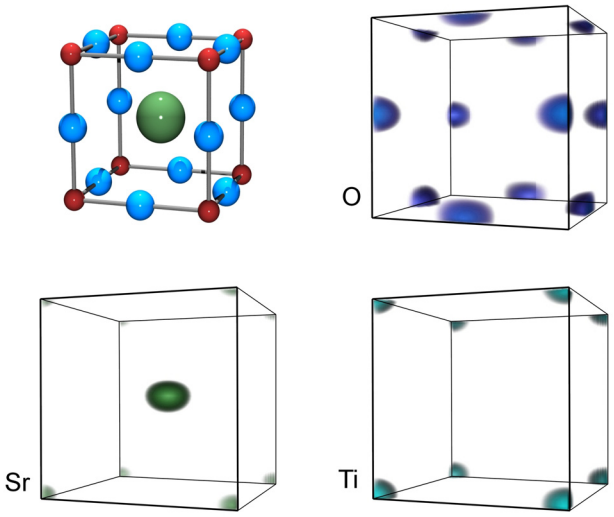

Figure 3. Sketch of the unit cell of $SrTiO_3$ (top left) and 3-dimensional images of the Sr, Ti, and O atomic distributions reconstructed from XSW data recorded from a $SrTiO_3$ single crystal covered with 0.5 monolayers $YBa_2Cu_3O_{7-\delta}$.

A hard X-ray XPS (HAXPES) instrument suitable for XSW studies is currently under commissioning at undulator beamline P09 at the new 6 GeV storage ring PETRA III at DESY in Hamburg, Germany. Two sets of focussing mirrors (the second yet to be installed) will allow beam spot sizes of about 2 × 2 microns on the sample surface. A SPECS Phoibos 225 spectrometer with an operational range of photoelectron energies up to 15 keV allows XSW experiments for high Bragg reflection orders of the sample.

References

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