Advanced Research Center for Beam Science
– Electron Microscopy and Crystal Chemistry –

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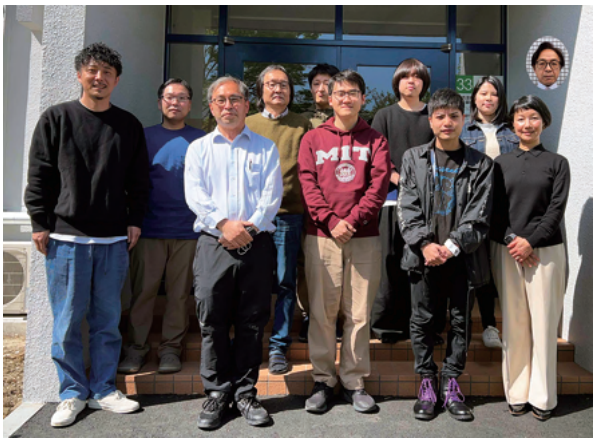
Scope of Research

In the field of nanotechnology, the importance of high spatial resolution analysis of materials further increases. We study the structure and the electronic state of materials at atomic scale through direct imaging of atoms or molecules by (scanning) transmission electron microscopy ((S)TEM) combined with energy dispersive X-ray spectroscopy (EDS) and electron energy-loss spectroscopy (EELS), which gives the information of elemental and electronic state. And we are studying with the aim of establishing new analytical methods using electron microscopes and evaluating materials using these methods.

KEYWORDS

STEM
EELS
HAADF
Elemental Mapping
Channeling



Recent Selected Publications

Lin, I-C.; Haruta, M.; Nemoto, T.; Goto, M.; Shimakawa, Y.; Kurata, H., Extraction of Anisotropic Thermal Vibration Factors for Oxygen from the Ti $L_{2,3}$-Edge in $SrTiO_3$, *J. Phys. Chem. C.*, **127(36),** 17802-17808 (2023). Supplemental cover

Iwashimizu, C.; Haruta, M.; Nemoto, T.; Kurata, H., Different Atomic Contrasts in HAADF Images and EELS Maps of Rutile TiO_2, *Microscopy*, **72(4),** 353-360, (2023). Editor's Choice

Haruta, M.; Kikkawa, J.; Kimoto, K.; Kurata, H., Comparison of Detection Limits of Direct-Counting CMOS and CCD Cameras in EELS Experiments, *Ultramicroscopy*, **240,** [113577-1]-[113577-6] (2022).

Haruta, M.; Nemoto, T.; Kurata, H., Sub-picometer Sensitivity and Effect of Anisotropic Atomic Vibrations on Ti $L_{2,3}$-Edge Spectrum of $SrTiO_3$, *Appl. Phys. Lett.*, **119,** [232901-1]-[232901-5] (2021). Featured Article

Iwashimizu, C.; Haruta, M.; Kurata, H., Electron Orbital Mapping of $SrTiO_3$ Using Electron Energy-Loss Spectroscopy, *Appl. Phys. Lett.*, **119,** [232902-1]-[232902-5] (2021). Editor's Pick

Different Atomic Contrasts in HAADF Images and EELS Maps of Rutile TiO_2

High-angle annular dark-field (HAADF) imaging and elemental mapping at the atomic scale by scanning transmission electron microscopy (STEM) combined with electron energy-loss spectroscopy (EELS) are widely used for material characterization. Recently, theoretical and experimental electron orbital mapping using STEM-EELS has been reported. Quantitative understanding of the contrast of the image is important to discuss the anisotropy of the orbital in an EELS map.

Figure 1 shows an experimental HAADF image with simultaneously measured Ti-$L_{2,3}$ and O-K elemental maps and the simulated elemental maps. Only the Ti atomic columns are visualized in the HAADF image due to its Z-contrast nature. The Ti and O elemental map measured using EELS show the respective atomic columns (Fig. 1c and d). The O map shows the distorted projected octahedral structure that agrees with the structure model (Fig. 1a), and the atomic shape is an isotropic distribution. On the other hand, the shape of the atom in the Ti map shows an anisotropic elliptical distribution that extends along the long axis of the octahedron, even though the HAADF image does not show such anisotropic contrast. Figures 1e and 1f show the simulated images of O and Ti elemental maps for the same sample thickness as experiment (32 nm). The Ti $L_{2,3}$-map shows anisotropic atomic shape along the long axis of the octahedron like the experimental one. This indicates that Ti maps of TiO_2 can show an anisotropic elliptical shape, regardless of the anisotropic electron orbital, because the simulation program (μSTEM) assumes (isotropic) isolated atoms without bonding character. We investigated the electron channeling process to elucidate the cause of the difference of the Ti atomic shape between the HAADF image and Ti $L_{2,3}$-map. Figure 2 shows the probe intensity propagating along the [001] axis of a rutile TiO_2 crystal as a function of the thickness, where the cross-section image is observed from the [110] direction along the black line indicated in Fig. 1. Figure 2a–e corresponds to the probe positions as numbered on the top. When the probe is located on a Ti (Fig. 2a and e) or O (Fig. 2c) column, strong electron channeling occurs, by which the incident electrons travel straight along each column. In the case of position 2 (Fig. 2b), the probe incident near an O column is quickly channeled onto the nearby oxygen atomic column. This can be confirmed by the high intensity in the O elemental map (Fig. 1c and 1e) and the low intensity in the Ti elemental map (Fig. 1d and 1f) at the yellow position, which corresponds to probe position 2. On the other hand, in the case of position 4 (Fig. 2d), the probe incident near a Ti column is also channeled onto a nearby Ti column. Therefore, the Ti $L_{2,3}$-edge is highly excited at position 4 due to the delocalization of inelastic scattering (Fig. 2d), whereas the excitation is suppressed at position 2 due to channeling onto the nearby oxygen column (Fig. 2b). It is considered that these processes are main reason for the anisotropic contrast in Ti $L_{2,3}$-map.

It is shown that considering the anisotropic shape of Ti atomic column observed in the Ti elemental map is essential for the quantification and visualization of electron orbitals. Consequently, much care must be taken in interpreting EELS maps.

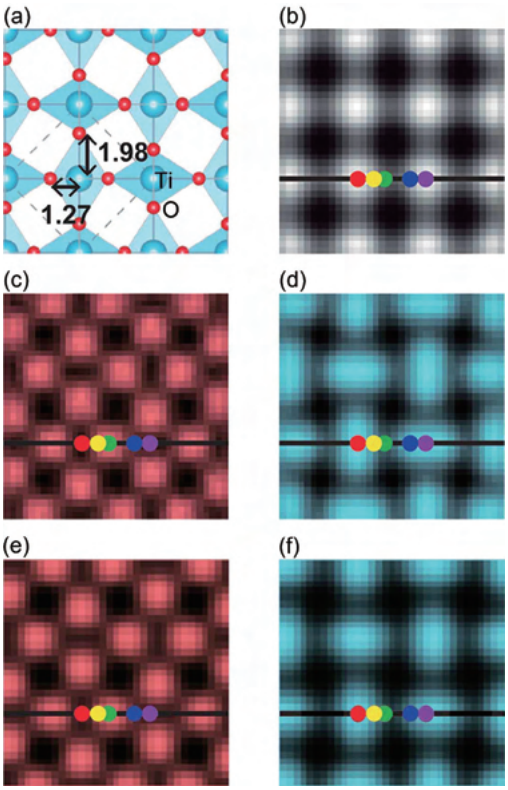


Figure 1. (a) Projected structure model of rutile TiO_2 along the [001] axis. The dashed line shows the unit cell. The lengths of the long and short Ti–O bond in the projected TiO_6 octahedron is written. (b) Accumulated experimental HAADF image. Elemental maps of (c) O K- and (d) Ti $L_{2,3}$-edges. Simulated elemental maps of (e) O K- and (f) Ti $L_{2,3}$-edges. The black lines in (b–f) and colour points correspond to the probe positions in Fig. 2.

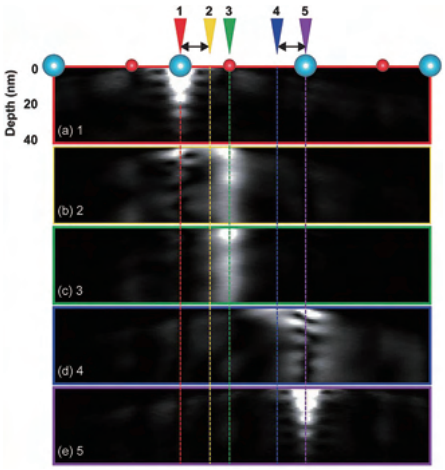


Figure 2. Probe intensity as a function of thickness in the [001]-oriented rutile TiO_2 crystal, where the cross-section image was observed from the [110] direction along the black lines indicated in Fig. 1. The electron probes are located on each triangle labelled 1–5, which correspond to the coloured dots in Fig. 1. (a, e) Probe located on the Ti column and (c) on the O column. The distances between positions 1 and 2 and between positions 4 and 5 are the same. This distance corresponds to the half width at half maxima of the short axis of the elliptical shape of the Ti map. Ti and O atoms are indicated as blue and red circles, respectively.