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

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Scope of Research

We study crystallographic and electronic structures of materials and their transformations through direct imaging of atoms or molecules by high-resolution electron spectromicroscopy, which realizes energy-filtered imaging and electron energy-loss spectroscopy as well as high-resolution imaging. By combining this with scanning probe microscopy, we cover the following subjects: 1) direct structure analysis, electron crystallographic analysis, 2) elemental analysis and electronic states analysis, 3) structure formation in solutions, and 4) epitaxial growth of molecules.

KEYWORDS

STEM-EELS Spectrum Imaging Template Matching Nonrigid Registration Atomic-Resolution Anisotropic Spectroscopy

Selected Publications

Aso, R.; Kan, D.; Shimakawa, Y.; Kurata, H., Atomic Level Observation of Octahedral Distortions at the Perovskite Oxide Heterointerface, *Sci. Rep.*, **3,** [2214-1]-[2214-6] (2013).

Saito, H.; Kurata, H., Formation of a Hybrid Plasmonic Waveguide Mode Probed by Dispersion Measurement, *J. Appl. Phys.*, **117,** [133107-1]-[133107-7] (2015).

Haruta, M.; Hosaka, Y.; Ichikawa, N.; Saito, T.; Shimakawa, Y.; Kurata, H., Determination of Elemental Ratio in an Atomic Column by Electron Energy-Loss Spectroscopy, *ACS Nano*, **10,** 6680-6684 (2016).

Haruta, M.; Fujiyoshi, Y.; Nemoto, T.; Ishizuka, A.; Ishizuka, K.; Kurata, H., Atomic-Resolution Two-Dimensional Mapping of Holes in the Cuprate Superconductor $La_{2-x}Sr_xCuO_{4\pm\delta}$, *Phys. Rev. B*, **97,** [205139-1]-[205139-5] (2018).

Yamaguchi, A.; Haruta, M.; Nemoto, T.; Kurata, H., Probing Directionality of Local Electronic Structure by Momentum-Selected STEM-EELS, *Appl. Phys. Lett.*, **113,** [053101-1]-[053101-4] (2018).

Atomic-Resolution Two-Dimensional Mapping of Holes in the Cuprate Superconductor $La_{2-x}Sr_xCuO_{4\pm\delta}$

One of the key factors in understanding high-T_c cuprate superconductors is the spatial distribution of holes in the sample. Since electron-energy-loss spectroscopy (EELS) can directly measure the unoccupied 2*p* states of the oxygen, EELS combined with scanning transmission electron microscopy (STEM-EELS) has the ability to resolve different oxygen states with atomic resolution. However, since cuprate superconductors are extremely sensitive to electron irradiation, it has not been possible to characterize them with atomic resolution. Here, we succeeded in atomic-resolution two-dimensional mapping of holes in the high-T_c superconductor of hole-doped type $La_{2-x}Sr_xCuO_{4\pm\delta}$ by overcoming the problem of irradiation damage using an advanced integration technique.

STEM-EELS was carried out at room temperature on a JEM-ARM200F. In order to achieve atomic-resolution imaging without specimen damage, a low probe current (21 pA) and a short dwell time of 5 ms were used with a scan step of 0.651 nm/pixel and a relatively wide energy dispersion of 0.25 eV/pixel. Spectrum imaging (SI) is a technique that collects the spacial distribution of EELS data. SI data were acquired from a 32.55 × 130.2 nm^2 (50 × 200 $pixel^2$) region. The total acquisition time for a single SI data was 66 s and the total dose was 2.4 × 10^3 C/cm^2. Although the individual single spectrum was very noisy, if the many crystallographically equivalent positions could be integrated, we might be able to realize atomic-resolution spectroscopy under the present conditions. However, the atomic-scale HAADF-STEM image obtained in the SI mode is distorted due to sample drift during the long acquisition time. Therefore, we devised the following procedure. First, we obtained many SI data with atomic resolution from a wide single-crystal region using a low-current condition. Next, we obtained a nondistorted HAADF image with the same scan step using a fast dwell time (the template image of the unit cell). Then, we selected many crystallographically equivalent regions from a target HAADF-STEM image by judging the correlation with the template image (template matching) and applied rigid and nonrigid registration of these equivalent regions to fit the template image by using the SMARTALIGN software package (HREM Research) and finally applied them to the corresponding SI data. Upon repeating this procedure over many SI data, the S/N ratio improved dramatically, maintaining spatial resolution without causing irradiation damage. The total accumulation numbers of the spectra were 12008, 14348, and 4712 for the x = 0.15, 0.3, and 0.4 samples, respectively.

Figure 1(a) shows O *K*-edge spectra of $La_{2-x}Sr_xCuO_{4\pm\delta}$ averaged over the whole unit. The prepeak (528.5 eV) that appears for doped samples corresponds to holes in the oxygen 2*p* state. Figures 1(b) and 1(c) show the spectra for the center of the apical and purely planar oxygen sites [labeled planar1 in Figure 2(a)], respectively. Figure 2 shows the results obtained by template matching and nonrigid registration. Figures 2(c)–2(e) show atomic-resolution hole maps obtained using hole-peak signals (1.5 eV window) of the O *K* edge. In the case of x = 0.15, the hole map exhibits an anisotropic distribution, where only the planar oxygen sites are displayed brightly. Planar 2 oxygen columns appear darker than planar 1 oxygen columns. If, as in the planar 1 oxygen columns, the hole state ($2p_x$) in planar oxygen is perpendicular to the electron beam (parallel to the direction of momentum transfer upon inelastic scattering), the prepeak intensity must be higher than that ($2p_y$) at the CuO column. We have demonstrated the anisotropic chemical bond related to the difference between p_x and p_y orbitals was observed with atomic resolution. The present approach enables atomic-resolution anisotropic spectroscopy.

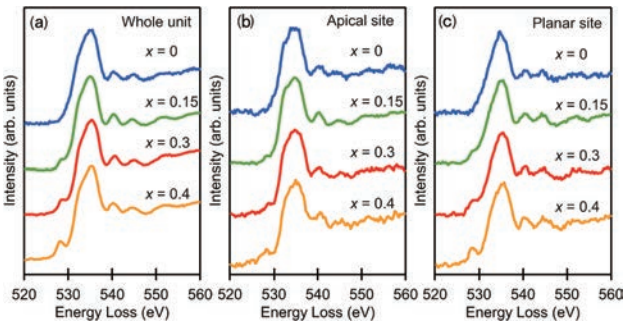

Figure 1. O *K*-edge spectra of $La_{2-x}Sr_xCuO_{4\pm\delta}$. (a) Atomic-resolution spectra averaged over the whole unit, and (b) apical and (c) planar oxygen site spectra after nonrigid alignment.

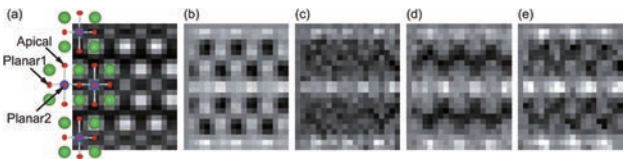

Figure 2. Atomic-resolution hole mapping. (a) Template HAADF image of $La_{2-x}Sr_xCuO_{4\pm\delta}$ observed along the [100] zone axis of the tetragonal phase. La (Sr), Cu, and O atoms correspond to green, blue, and red, respectively. (b) Atomic-resolution oxygen mapping of $La_{1.85}Sr_{0.15}CuO_{4\pm\delta}$. Atomic-resolution hole mapping of (c) x = 0.15, (d) x = 0.3, and (e) x = 0.4.