Depth resolved electronic structure of cuprate superconductor analyzed by two-dimensional X-ray Auger resonance emission spectroscopy

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Based on the measurements of emission angle and photon energy dependences of Auger electron intensity by using a display-type analyzer, two-dimensional X-ray Auger resonance emission spectroscopy (2D-XARES) method for depth resolved analysis of atomic and electronic structures has been developed. Here we applied this method to analyze the hole distribution at the surface region of high-transition-temperature cuprate superconductor (Bi2212).

The crystalline quality at each point on the sample surface was evaluated by Cu LMM Auger emission angular distribution (AEAD). Cu L-edge X-ray absorption spectra, especially the resonance peak structure of Cu $3d_{x^2−y^2}$ at absorption edge were shown to be quite sensitive to the surface quality. By combining AEAD with XANES, i.e. 2D-XARES, the vertical distribution of Cu $3d_{x^2−y^2}$ hole state at the surface region in conjunction with crystalline quality was revealed. [DOI: 10.1380/ejssnt.2007.143]

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I. INTRODUCTION

The progress of surface science has opened the door to the atomic level fabrication and chemical modification of superlattice and surface nanostructures. Transition temperature ($T_c$) of cuprate superconductor is altered by the change of carrier concentration and lattice distortion. Besides the bulk synthesis methods, the property of surface and thin film superconductivity can be changed by modification of the surface. Carrier concentration can be controlled by chemical decoration at the surface. Lattice distortion in the thin films is occurred at the surface and the interface. Property of surface superconductivity should be greatly affected by such a slight modification. This strategy is promising for realization of surfaces and thin films having higher $T_c$ [1, 2]. However, there was no direct method up to now for detecting the surface electronic structure in the depth direction at atomic level which is essential for these bottom-up technologies.

For this purpose, we have developed a new method, namely “Two-dimensional X-ray Auger resonance emission spectroscopy (2D-XARES)”. This method is based on the emission angle and the photon energy dependences of Auger electron emission intensity which are connected to the escaping depth of emitted electrons and the electronic structure of conduction state, respectively.

The angular distribution of the electron emitted from surface provides information on the atomic configuration around an excited atom. In the case of crystal surface, such angular distributions consist of forward focusing peaks in interatomic directions and diffraction patterns around them [3, 4]. Interatomic distances are deduced from the forward focusing peak parallax shifts observed in circularly polarized light excitation [5–8] or through the analysis of energy and angular dependence of diffraction patterns [9–13]. From another point of view, site-specific local information can be deduced by monitoring forward focusing peak intensity [14].

Auger electron emission which follows the diffraction process is also a site-selective probe. Furthermore, since the mean-free-path of Auger electron with kinetic energy of 500~1000 eV is in the order of 1~2 nm, Auger electron probing depth is dependent on the emission angle. Gross feature of Auger emission angular distribution (AEAD) is determined by Auger electron probing depth. Diffraction pattern is superimposed onto it as a modulation in the
order of several percent of average intensity.

On the other hand, X-ray absorption near edge structure (XANES) is a powerful element specific method for analyzing conduction states in the vicinity of the Fermi level. Partial density of conduction states can be measured for each element. However, it is difficult to specify the excited atoms individually in real space. Since Auger electron yield is proportional to the core-level excitation intensity, XANES spectra can be measured by monitoring Auger electron intensity while scanning photon energy [15]. We have combined X-ray absorption spectroscopy with AEAD measurements, and obtained depth resolved XANES spectra.

Here we report the application of 2D-XARES to the depth profile analysis of the hole density distribution of high \( T_c \) superconductor Bi\(_2\)Sr\(_2\)CaCu\(_2\)O\(_8\) (Bi2212). The depth resolved Cu L-edge XANES spectra were obtained from a series of Cu LMM AEADs using a display-type analyzer. Apart from other trials, we could check the quality of crystal from diffraction pattern and investigate the depth profile structure from emission angle dependence simultaneously at any position of sample surface. Combining with two-dimensional sample scanning mechanism, diffraction patterns and 2D-XARE spectra from each spot over the entire sample surface can be obtained. If the hole and electron doping to the surface electronic states at atomic level is clarified, then it will be a key for understanding relation between a superconductor super-lattice structure at the surface and its \( T_c \).

II. EXPERIMENTAL

The experiments were performed at the circularly polarized soft X-ray beamline BL25SU of SPring-8, Japan [16]. Bi2212 single crystalline sample (2×4 mm\(^2\)) was cleaved under atmospheric condition. No further treatment such as annealing and sputtering were applied. Fine structures in the reflection high energy electron diffraction (RHEED) pattern originating from the five time modulation along the \( b \) axis [17, 18] are used to determine the orientation of the crystal. The spot size of the synchrotron radiation beam on the sample was about 300×500 \( \mu \)m\(^2\).

AEAD from the sample at the specific kinetic energy is most efficiently measured by a two-dimensional display-type spherical mirror analyzer (DIANA) [19–21], which enables measurement of a two-dimensional angular distribution of specific kinetic energy electron at the same time [7–9, 14]. Figure 1 shows a schematic diagram of DIANA and measurement set ups. Light was incident from the direction 45\(^°\) inclined from the center of the analyzer. Auger electrons emitted from the sample were analyzed and projected onto the fluorescent screen. Acceptance angle of the analyzer is ±60\(^°\).

Outer hemisphere of analyzer act as a low pass filter while retarding grid in the front of the fluorescent screen act as a high pass filter. In the case of XPS measurements, we set the window width of pass energy to 2 eV. When measuring XAFS spectra and AEAD, the window width were optimized to achieve best angular resolution and signal to background ratio. In the present case, 5\% of the pass energy was appropriate for the window width. In the case of XPS measurements, the energy resolution is determined by the window width, while in the case of XAFS, the energy resolution is determined by that of monochromator. The energy resolution for XAFS measurement was one or two order better than that of XPS measurement.

Sample was mounted on a five-axis manipulator. Two measurement geometries used in the present investigation are depicted in Fig.1. In the case of 45\(^°\) incidence (\( \theta_{in} = 45^\circ \)), the sample surface normal direction (\( \theta_{out} = 0^\circ \)) is projected at the center of the screen. On the other hand, in the case of normal incidence (\( \theta_{in} = 0^\circ \)), we can obtain the emission angle (\( \theta_{out} \)) dependence from 0\(^°\) to 90\(^°\) respective to the surface normal simultaneously. Typical acquisition time for one AEAD pattern was several seconds to 1 minute. Since Auger intensity at absorption edge is so strong, one 2D-XARE spectrum consisted of 100 points were obtained within 10 minutes.

By using DIANA, one Auger pattern can be obtained with in several seconds. Sample rotation mechanism is needed for the acquisition of angular distribution when using conventional analyzers. In such cases, we need several hours which is 1000 times longer for the similar data acquisitions.

Sample scanning mechanism for the microscopy or real space mapping can be combined with DIANA. Then an AEAD pattern from an arbitrary point on the sample surface can be acquired in a short time. This can not be done by conventional apparatus which detects emitted electrons only in one direction at a time and requires sample rotation. Within one hour, we can obtain hundreds of Auger patterns from different points. However, if we use conventional analyzer, several months is needed to obtain the same volume of data.
III. RESULTS AND DISCUSSION

A. Cu LMM AEADs

Figures 2(a) - (f) show Cu LMM AEADs from various spot on the sample surface with the sample normal direction aligned to the analyzer center (θin = 45°). Center and periphery of the pattern corresponds to the polar angle (θout) of 0° and 60° from the surface normal, respectively. We set photon energy to 932 eV and the pass energy of analyzer to 914 eV. Orientations of the sample and corresponding directions in the AEAD are indicated in Fig. 3(a). Vertical and horizontal directions correspond to the a and b axes, respectively. Diagonal directions correspond to the x and y axes.

The AEAD shown in Fig. 2(a) was measured right after the cleavage. Clear Kikuchi bands in eight direction and sharp forward focusing peaks suggest fairly good quality of crystalline. Hereafter we label the position of this measurement as ‘α’. On the other hand, the pattern shown in Fig. 2(e) was the signal from the same sample but at different position (hereafter β) where cleavage did not succeed well. Contrast and feature of diffraction pattern were much small and diffuse. It suggests that the surface at position β had lower crystalline quality and/or contaminated.

‘Union Jack’-like Kikuchi patterns were observed as shown in Fig. 3(a) and 3(b). Peak at the center of the pattern corresponds to the forward focusing peak of O and Bi atoms in the surface normal c axis direction. This peak is broadened along the b axis direction due to the modulated structure of BiO plane. Vertical and horizontal Kikuchi patterns originate from ac and bc crystal planes. On the other hand, diagonal Kikuchi patterns originate from xc and yc crystal planes. Pink and yellow planes in Fig. 3(c) indicate ac and yc planes, respectively. Layer spacing of xc and yc planes are 1.92 Å, while that of ac and bc planes are 2.71 Å. Note that the xc and yc Kikuchi patterns running diagonally have larger width than that of the ac and bc Kikuchi patterns due to smaller layer spacing along the xc and yc directions than that of ac and bc directions.

Dots in Fig. 3(a) indicate directions of atoms surrounding excited Cu atom in the upper CuO2 plane. Four forward focusing peaks appearing within the ac and bc Kikuchi patterns correspond to the nearest Sr atoms. Large square formed by four forward focusing peaks coincide with direction of four Bi and four O atoms belonging to the first nearest Bi-O plane seen from the upper Cu atom. Inner square corresponds to the forward focusing peaks of four O and four Bi atoms belonging to the second nearest Bi-O plane seen from the upper Cu atom. These atoms are depicted in Fig. 3(d).

There are another set of squares formed by Bi and O atom forward focusing peaks seen from Cu atom in the lower CuO2 plane. They are indicated in Fig. 3(b). Directions of Cu atoms in the upper CuO2 plane seen from lower Cu atom overlaps with that of Bi atoms seen from
upper Cu atom. Main features observed in AEAD can be attributed to the forward focusing peak of heavy atoms such as Bi, Sr, and Cu.

B. Cu L-XANES and XPS

By scanning the photon energy around the core level excitation threshold region and measure a series of AEADs, we obtain Auger electron yield XANES spectra. Figure 4 shows Cu L-XANES spectra from sample positions α and β. We found that the absorption peak at 932 eV corresponding to the Cu 3d and 4s partial density of conduction band states in the vicinity of the Fermi level [22–24] appeared to be quite sensitive to the sample quality. This electronic state is closely related to the hole carrier which plays important role in the superconductivity. Spectrum from good crystal quality position has much larger peak intensity. This peak is attributed to the resonance transition between Cu 2p and 3d\(^{x^2-y^2}\) states [22–24], while several interpretations have been proposed for the origin of shoulder peak [23–27].

Furthermore, we have measured X-ray photoelectron spectra from two positions α and β for the comparison as shown in Fig. 5. Photon energy of 900 eV was used for the excitation. C1s peak is apparent in the latter case. O KLL Auger peak intensity at 510 eV was weaker while in the spectrum from position β. As emission angle increased, the peak intensity at 932 eV and 952 eV decreased. The peak intensity in the case of 85° emission angle was about half of that in the case of 0° emission angle. Since the 85° emission angle spectrum is more surface sensitive compared to that of 0° emission angle, the emission angle dependence of this peak suggest that the Cu atoms at the surface are reduced. The charge transfer back to Cu atoms by the O atom desorption from surface decreases hole concentration.

One Bi2212 layer (half unit cell) is 1.545 nm thick which is about the length of Cu LMM Auger electron mean free path. For qualitative discussion, we assumed the thickness of Bi2212 surface layer on top of ideal bulk Bi2212 crystal as same as that of half unit cell. In the case of 0° emission angle, the Cu Auger signal intensity from the first Bi2212 layer and the ideal bulk region are 1−exp(−1)=63% and exp(−1)=37% of the total signal intensity, respectively. On the other hand, spectra at the emission angles of 80° and 85° are representing mostly the surface electronic states. L\(_3\) peak intensity in the spec-
trum at 0° emission angle is 45% of that of the spectrum at 85° emission angle. Simple arithmetic teaches us that the 932 eV peak intensity of the surface layer at this particular position is 27% of that of the bulk. We can estimate the degree of reduction at the surface in such a way. Strictly speaking, there are slight intensity modulation in the emission angle dependence which comes from diffraction effect of Bi2212 crystal structure. Further quantitative analysis can be done by incorporating such effect into the consideration.

III. RESULTS

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IV. CONCLUSION

In conclusion, we have obtained Cu LMM AEAD from various point of the Bi2212 sample surface. The quality of sample surface was reflected in the contrast and sharpness of the diffraction pattern in the AEAD. We found that the Cu L$_3$ and L$_2$ absorption peak intensity in the L-XANES spectra is sensitive to the quality of the surface. Moreover, these absorption peak intensity decreased as the O KLL Auger peak intensity decreased. We explained decrease in the absorption peak intensity by the decrease of O atoms and charge transfer (reduction) back to Cu atoms. Newly developed depth-resolved 2D-XARES method revealed the desorption of O atoms from outermost surface layer. We expect this method to be widely applied to the depth analysis of carrier concentration distribution; in the case of high $T_c$ superconductor surface modification by alkaline metals for instance. The outcome will be a key for the construction of new super-lattice superconductor at the surface.

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