

## Site-specific valence atomic orbital characterization by detection of angular-momentum-polarized Auger electrons

Copper is nonmagnetic, while nickel, which has one less electron than copper, is ferromagnetic. Gold is chemically inert, while platinum, which has one less electron than gold, is an essential element in catalyst chemistry. If we can generate a valence hole with an arbitrary atomic orbital character in a solid, an excited state with new electronic properties can be created, which cannot be achieved by simple thermal excitation of valence electrons in the vicinity of the Fermi level.

Based on core-level photoelectron diffraction, element-specific atomic structure information can be obtained. Forward focusing peaks (FFPs) appearing in a photoelectron intensity angular distribution (PIAD) indicate the directions of atoms surrounding a photoelectron emitter atom. Upon a core-level excitation by circularly polarized light (CPL), the angular momentum of light, i.e., helicity, is transferred to the emitted photoelectron. This phenomenon can be confirmed by the parallax shift measurement of the FFP direction in a stereograph of the atomic arrangement [1,2]. The core hole may decay via Auger electron emission, where in this two-electron process the angular momentum also has to be conserved. Here we report the observation of angular momentum transfer from excitation light to resonant Auger electrons [3,4]. Note that FFPs also appear in the Auger electron intensity angular distributions (AIADs) [5]. We succeeded in detecting angular-momentumpolarized Cu LMM Auger electrons at the L absorption threshold, where the excited core electron is trapped at the conduction band. The FFP covers a solid angle of about 10°. By setting an analyzer at the corresponding position in the FFP direction, a photoelectron or Auger electron with a specific angular momentum can be selectively detected. Correspondingly, an orbitalmomentum-polarized hole state is created.

All the experiments were carried out using the twodimensional display-type analyzer installed at the circularly polarized soft X-ray beamline BL25SU. We measured full hemisphere PIADs and AIADs from the Cu(001) surface [3,4]. Figure 1(a) shows a Cu valence PIAD at a kinetic energy of 914 eV. PIADs excited by both helicities  $I^+$  and  $I^-$  were added and normalized. The incidence direction of CPL, i.e., the quantization axis, was aligned along the surface normal. Figure 1(b) shows a resonant Cu  $L_3M_{45}M_{45}$  AIAD at the kinetic energy of 914 eV excited by CPL with a photon energy of 934.2 eV. The energy window width of the displaytype analyzer was set to 5% of 914 eV and the whole valence band intensity or  $L_3M_{45}M_{45}$  Auger electrons were integrated. The FFPs at the four (101) directions correspond to the scattering by the nearest-neighbor atoms, while the center [001] direction corresponds to scattering by the second-nearest-neighbor atoms along the surface normal. Note that at this kinetic energy, FFPs are also present even for a delocalized valence band due to the majority of the excitation coming from electron density existing in the vicinity of the nucleus.



Fig. 1. (a) Cu valence PIAD at the kinetic energy of 914 eV. PIADs excited by both helicities ( $\sigma$ =±1) were added. (b) Resonant Cu  $L_3M_{45}M_{45}$  AIAD at the kinetic energy of 914 eV excited by CPL with photon energy of 934.2 eV. (c) Difference between the two valence PIADs excited by both helicities and normalized by their sum. (d) Same as (c) but for the AIAD shown in (b).

Figure 1(c) shows the circular dichroism angular distribution (CDAD) of the valence band, i.e., the difference between the two PIADs excited by both helicities and normalized by their sum;  $(I_1-I_{-1})/(I_1+I_{-1})$ . The suffix denotes the helicity. Figure 1(d) shows the CDAD of the resonant AIAD. This result indicates that at the  $L_3$  absorption threshold, where the excitation core electron is trapped in the conduction band, the angular momentum was partially transferred to the resonant  $L_3M_{45}M_{45}$  Auger electrons instead of the photoelectron.

As shown in Fig. 2, the azimuthal intensity profiles of the [101] FFPs excited by CPL were individually fitted by Gaussians centered at the  $\phi$  = 2.894° $m_f$  directions corresponding to the different angular momenta of emitted electrons. Note that the photoelectrons from the 3*d* valence band gain angular momentum  $\sigma$  by CPL excitation ( $m_f$  = 3, 2, ..., -1), while the angular momenta of *LMM* Auger electrons are the same as those of 3*d* valence electrons ( $m_i$ = ±2, ±1, 0). Components of  $m_f$  = ±3 do not exist in the FFP of the AIAD as shown in Fig. 2. The origin of circular dichroism in the resonant AIAD at  $L_3$  absorption threshold, where the excited core electron is trapped at conduction band, is attributed to the difference in transition to the final states  $m_f = \pm 1$  and  $\pm 2$ .

By combining Auger electron spectroscopy with the FFP shift measurements at the absorption threshold, element- and magnetic-quantum-number-specific hole states can be generated in the valence band. The Auger electron emission process that involves two valence electrons will allow, for example, the creation of a nickel-like  $3d^84s^2$  atom in a copper matrix. As we show here, the polarization of this  $3d^84s^2$  impurity may be controlled by the light incidence and polarization of the light used to create the core hole for the Auger decay process. The resonant Auger electron emission induced by CPL excitation is an excellent way to polarize a valence band with a specific orbital magnetic momentum and a specific atomic number in a controlled fashion localized in space and time. Furthermore, this phenomenon can be used for the atomic orbital characterization of the valence density of states at specific atomic sites in compound crystals and epitaxial thin films. For instance, we are now revealing the atomic orbital origin of the spin reorientation transition in a Ni perpendicular magnetized film [5] by applying this method.



Fig. 2. Azimuthal profiles of the [101] FFP intensity for valence photoelectron and Auger electrons.

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## References

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