Total reflection hard x-ray photoelectron spectroscopy: Applications to strongly correlated electron systems

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We demonstrate that total reflection hard x-ray photoelectron spectroscopy (TR-HAXPES) is a versatile method for elucidating a difference between surface and bulk electronic states of strongly correlated electron systems, complementing conventional bulk sensitive hard x-ray photoelectron spectroscopy (HAXPES). To demonstrate the experimental feasibility of the method, we investigated $La_{0.6}Sr_{0.4}MnO_3$ and the electron-doped high-T_C superconductor $La_{1.9}Ce_{0.1}CuO_4$. From the incident angle dependence of the spectral line shapes, we found that the surface-sensitive TR-HAXPES measurement equivalent to soft x-ray photoelectron spectroscopy is possible in the total reflection condition. The results strongly suggest that this method allows us to measure both surface and bulk electronic states without making any changes to experimental setup such as the energy resolution, x-ray energy, and the beamline.

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I. INTRODUCTION

Photoelectron spectroscopy (PES) is an essential tool for studying the properties of solids. Over the last two decades the hard x-ray photoelectron spectroscopy (HAXPES) technique made a major impact in unraveling the electronic properties of solids, covering a large field of applications, from fundamental to applied science [1–3]. Recent advances in the development of synchrotron radiation beamlines made it possible to exploit HAXPES with an extremely large dynamic range in photon energy (2–15 keV) and the necessary high flux (10^{11}–10^{12} photons/s on the sample in a bandwidth of 50–300 meV) to overcome the strong reduction of the photoionization cross section at high energy [4–11]. Paying the price of a minimum energy resolution on the order of about 50 meV, which is still good enough to obtain a reliable comparison with the standard surface-sensitive PES experiments, HAXPES provides information up to 15–60 nm for electron kinetic energy $\geqslant$5 keV, corresponding to truly bulk sensitivity with chemical selectivity [4–11].

A typical example of the merit of HAXPES comes from the study of strongly correlated materials, such as transition metal oxides (TMOs) [12–19]. In these systems, general agreement has been reached on the fact that the surface sensitivity of conventional PES becomes a limitation when the need is to obtain information about bulk electronic structures; this limitation is particularly important when dealing with electron correlation, where structural distortion, stoichiometry changes, strong reactivity to an external agent, and major atomic and/or electronic reconstruction often appear at surfaces, preventing us from obtaining important and reliable information about the solid as a whole.

The analysis of the true bulk electronic structure in many oxides, Mott-Hubbard and mixed-valence systems, heavy Fermion compounds, and anomalous metals/doped semiconductors was successfully addressed by HAXPES in recent years both experimentally and theoretically [12–19]. HAXPES spectra show a totally new class of satellite peaks in the $2p$ core-level for many TMOs. Those additional peaks strongly depend on the doping and metallic or insulating states (bulk or surface).

The first observation of a bulk-only HAXPES feature in $3d$ TMOs was reported by Horiba *et al.* [12]. At $h\nu = 5.95$ keV, a clear shoulder appears on the low binding energy side of Mn $2p_{3/2}$. The intensity of such a shoulder decreases for larger emission angles (i.e., when surface sensitivity is enhanced) and almost disappears at low photon energy (e.g., increased surface sensitivity due to the lower kinetic energy). The observed behavior clearly points to a bulk feature. Interestingly, such a structure disappears above T_C, corresponding to the passage between a metallic ferromagnetic phase and an insulator paramagnetic one. Furthermore, dramatic changes with Sr doping have been also observed.

Another example is high-T_C cuprates. Theoretical studies have predicted that the Zhang-Rice singlet should show a signature in Cu $2p$ PES of the cuprates. The Zhang-Rice

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singlet state is considered very important for superconductivity and was observed by various valence band PESs but has not been observed by core-level PES with soft x rays. Furthermore, while many Cu $2p$ core-level soft x-ray PESs of high-T_C cuprates have been performed, the spectra show very little change upon doping. These puzzles bring into question the role of the depth sensitivity of PES. The HAXPES spectra of electron-doped $Nd_{1.85}Ce_{0.15}CuO_4$ (NCCO) and hole-doped $La_{1.85}Sr_{0.15}CuO_4$ and La_2CuO_4 are clearly different for each material, emphasizing their differences in their ground states [14]. Especially, the HAXPES for NCCO shows a sharp low binding energy feature which is not observed in NCCO soft x-ray PES.

A majority of HAXPES experiments employ a normal emission geometry with a grazing incidence of hard x rays to enhance the excitation probability of photoelectrons in the surface region by hard x rays. Their studies have so far focused on the bulk electronic state of the crystal or thin film by utilizing the bulk sensitivity and large proving depth, which are the main features of HAXPES. However, when we perform HAXPES measurements, it is often necessary to compare the difference between the bulk and the surface electronic states of the same sample. In that case, the reapplication of beam time to another soft x-ray photoelectron beamline in a synchrotron radiation facility is necessary in order to obtain the surface-sensitive spectrum. As a result, it will typically take more than half a year after the HAXPES experiment until the complete data set is available. Furthermore, since the energy resolution and detector are different for each beamline, the experimental conditions will also change, making direct comparison difficult.

On the other hand, total reflection x-ray photoelectron spectroscopy was proposed nearly 45 years ago [20] and has now reached a level of acceptance as a useful surface analysis technique. For the surface state analysis, x-ray photoelectron spectroscopy (XPS) measurement under the total reflection conditions has often been performed not only in soft x-ray PES but also in HAXPES [21], mainly for semiconductor materials, where x rays are incident at the total reflection critical angle under the total reflection condition, so that the penetration depth of the incident x ray is limited. The combination of total reflection HAXPES (TR-HAXPES) and conventional HAXPES can resolve all the issues mentioned above, as will be discussed later.

The aim of this paper is to show that the detailed intrinsic electronic properties in both the bulk and surface for strongly correlated electron systems can be obtained without requiring any additional experiment by combinations of TR-HAXPES and conventional HAXPES in a normal experimental setup (NR-HAXPES). To this end we applied this method to $La_{0.6}Sr_{0.4}MnO_3$ (LSMO) and the optimally electron doped high-T_C cuprate $La_{1.9}Ce_{0.1}CuO_4$ (LCCO) as typical examples of strongly correlated electron systems. We succeeded at measuring both the surface and bulk electronic states at the same beamline and with the same energy resolution just by slightly changing the incident angle of the x rays. The application of TR-HAXPES to strongly correlated electron systems with a focus on the well-screened peak allows us to extract the detailed electronic changes for both the surface and bulk very easily.

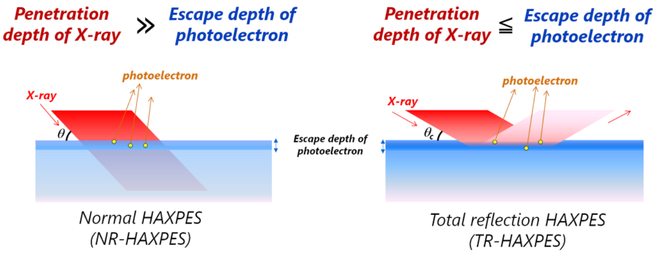

FIG. 1. Probing depths of HAXPES at a sample surface as functions of the glancing angle. Left: Bulk sensitive HAXPES (labeled "NR-HAXPES"): the penetration depth of x ray is much larger than the escape depth of the photoelectron. Right: Surface sensitive HAXPES (labeled "TR-HAXPES"): the penetration depth of the x ray is smaller than the escape depth of the x ray. The incident angles of the TR- and NR-HAXPES for LSMO (LCCO) are 1.3° and 1.8° (1.5° and 2.0°) from the sample surface, respectively. However, these values largely depend on how the sample is mounted on the sample holder.

II. EXPERIMENTS

The LSMO and LCCO thin films were grown epitaxially on $SrTiO_3$ and $NdScO_3$ substrates by laser molecular beam epitaxy, respectively. The thicknesses were accurately determined from grazing incidence x-ray reflectivity to be 40 nm (LSMO) and 185 nm (LCCO). The growth condition and the characterizations of the grown films details are described elsewhere [22,23].

Before discussing HAXPES spectra, it is useful to consider a general feature of the probing depth of HAXPES. As we mentioned earlier, one of the main aspects of the HAXPES experiment was the use of a grazing incidence geometry, with an incidence angle θ of the x-ray beam relative to the sample surface, typically set to 3° [24]. This experimental setup helps us to gain photoelectron intensity, where the penetration depth of x rays is much longer than the mean free path of photoelectrons. As a consequence, the probing depth of HAXPES is governed by the mean free path of photoelectrons, which is typically several tens of nanometers in HAXPES (see the left-hand side of Fig. 1). By contrast, in the total reflection, x rays are incident at the total reflection critical angle θ_c (e.g., $\theta_c \sim 0.5^\circ$ for LSMO and LCCO); therefore, the penetration depth of the incident x-ray beam is limited and is shorter than the mean free path of photoelectrons. Therefore, the probing depth of HAXPES is governed by the penetration length of the x rays (e.g., ~8.4 nm for LSMO and LCCO as determined by the reflectivity calculation [25]), resulting in high surface sensitivity and low background intensity caused by inelastic scattering (see the right-hand side of Fig. 1). It should be noted that the probing depth of TR-HAXPES is several nanometers, while it is several tens of nanometers for NR-HAXPES.

HAXPES measurements are performed in a vacuum of 10^{-7} Pa at undulator beamline BL47XU (also at BL16XU [26]), SPring-8 [27], using a Scienta R4000-10 kV (R4000 Lens 1 10 kV) electron analyzer, respectively. The energy width of incident x rays is 50 meV, and the total energy resolution ΔE is set to 300 meV. All PES measurements used normal emission geometry to maximize depth sensitivity. HAXPES for the LSMO and LCCO samples were measured

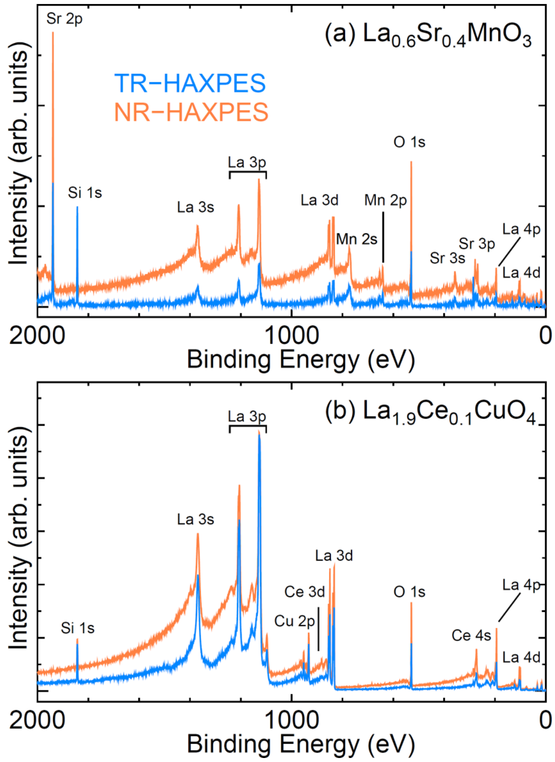

FIG. 2. Comparison of wide-scan HAXPES spectra between total reflection and normal conditions. (a) $La_{0.6}Sr_{0.4}MnO_3$. (b) $La_{1.9}Ce_{0.1}CuO_4$.

at 160 K and room temperature, respectively. The Fermi level of gold was measured to calibrate the energy scale.

III. RESULTS AND DISCUSSION

First, we present the wide energy scan spectra (from 0 to 2000 eV) for LSMO and LCCO in Fig. 2, which illustrates a basic aspect of TR-HAXPES. By comparison with NR-HAXPES, the spectral weight of the background in TR-HAXPES spectra is drastically reduced. This is because the penetration depth of the x ray has become shallower in total reflection, so that photoelectrons do not come out from deeper atoms, and secondary electrons forming the background will decrease. The reduction of the background in TR-HAXPES makes a distinction between TR- and NR-HAXPES, thereby confirming that the TR condition is satisfied

Next, we present experimental Mn 2p and Cu 2p core-level HAXPES spectra of LSMO and LCCO thin films at 160 K and room temperature obtained with photon energies of $h\nu = 7.94$ keV in Fig. 3(a) [see also Fig. 3(b)] and Fig. 4(a), respectively. The core-level spectra were normalized at the $2p_{3/2}$ main line. The NR-HAXPES spectra agree well with the reported results [12,14] and show a clear shoulder at ∼638 eV for LSMO and ∼932 eV for LCCO. The present TR-HAXPES result shows the same qualitative behavior as previous soft x-ray PES results [22]. By comparison, the spectral weight of the lower binding energy peaks labeled β in the main line is found to be strongly enhanced in the bulk-sensitive NR-HAXPES spectra. Its energy positions are the same as those of the weak shoulders observed in TR-HAXPES. The strong enhancement of the feature indicates the importance of the HAXPES measurements. It should be noted that these well-screened features were explained well by the configuration interaction model including a screening channel derived from states near the Fermi energy for a series of transition metal compounds [12–19].

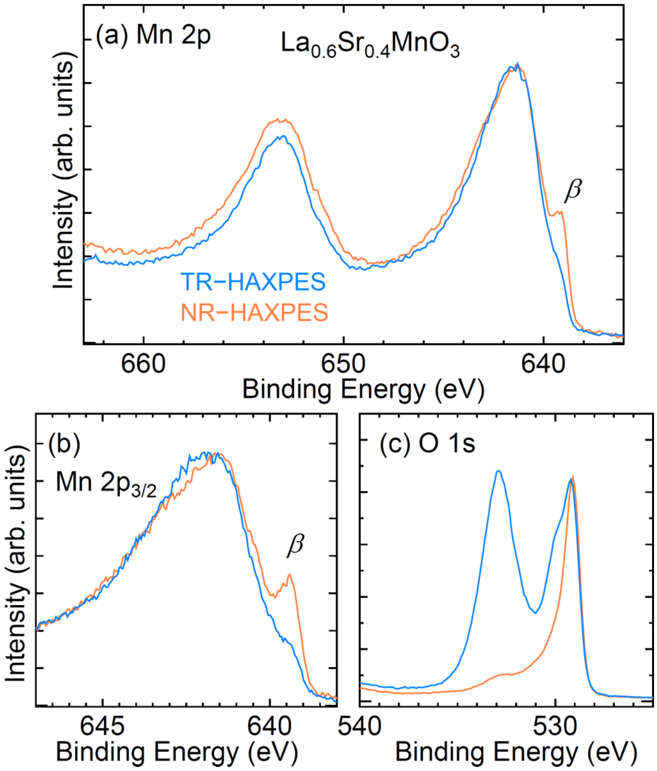

FIG. 3. Measured HAXPES spectra of a LSMO thin film at 160 K. (a) Comparison of Mn 2p core-level HAXPES spectra between surface-sensitive TR-HAXPES and bulk-sensitive NR-HAXPES. (b) Enlargements of the energy range corresponding to the Mn $2p_{2/3}$ line. (c) Comparison of O 1s core-level HAXPES spectra between TR- and NR- HAXPES.

Figures 3(c) and 4(b) show a comparison of O 1s core-level spectra between TR- and NR-HAXPES for LSMO and LCCO, respectively. Due to the lower probing depth of the photoelectron spectroscopy the TR-HAXPES data are much more surface sensitive than the NR-HAXPES data. This is most clearly illustrated by the contamination peak in the O 1s region, which is strongly enhanced on both the LSMO and LCCO samples, and is assigned principally to the atmospheric contamination components. Especially, in the O 1s spectra of the LSMO sample, this contamination peak dominates the spectrum, and a weak shoulder around 530 eV is not clearly resolved from the main peak, making line shape analysis very difficult and unreliable. This situation is greatly improved by employing NR-HAXPES, for which the sensitivity to the surface and therefore the contamination components are greatly reduced and can easily be separated from the main peak. It should be note that there is a difference in the O 1s peak compared to the previous result [22]. These peaks around 531–533 eV are mostly caused by a storage period and the condition of the sample, which lead to the difference from the previous results [22].

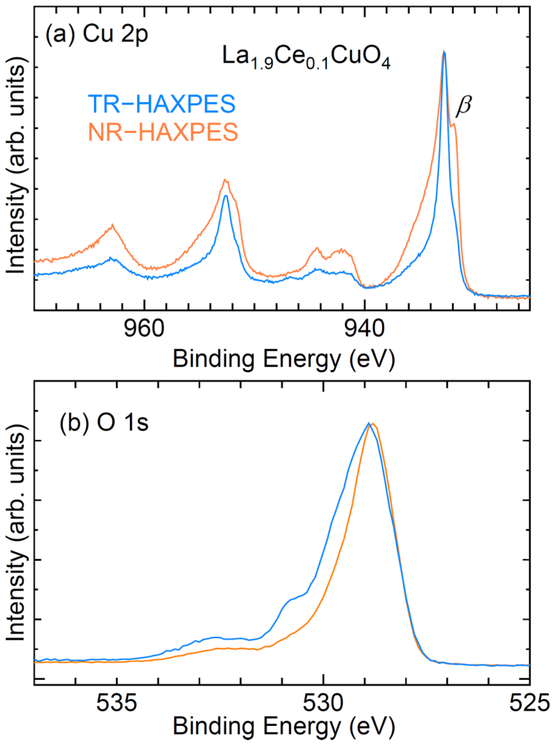

FIG. 4. Measured HAXPES spectra of the LCCO thin film at room temperature. (a) Comparison of Cu 2*p* core-level HAXPES spectra between surface-sensitive TR-HAXPES and bulk-sensitive NR-HAXPES. (b) Comparison of O 1*s* core-level HAXPES spectra between TR- and NR- HAXPES.

Since a strong polarization dependence has been reported in the Mn 2*p* spectra of LSMO [18] and we used linear polarized light of the incident photon in the present study, the polarization of the x ray will change the spectral shape with the change in the incident photon direction. However, the angle of incidence photon changes by only 0.5° in going from total reflection to normal conditions. Since the polarization dependence of the spectrum changes continuously as a function of the polarization angle, it is unlikely that a change of only 0.5° will result in such a dramatic change as we observed.

As mentioned above, the majority of HAXPES studies for strongly correlated electron systems have so far focused on the bulk electronic state of the crystal or thin film. However, it is often necessary to compare the electronic states between the bulk and the surface for the same sample, thereby requiring additional beam time for soft x-ray PES measurements at a synchrotron radiation facility. In addition, the experimental conditions such as the energy resolution, the sample condition, and the detector will also change. Simultaneous measurement of TR- and NR-HAXPES at the same beamline can resolve all the issues mentioned above.

Angle-dependent HAXPES is also a widely used alternative method to obtain information on surface and bulk states. However, the thickness of the dead surface layer in the strongly correlated electron system is usually very thin (typically ∼4 nm for LSMO [18]). In contrast, the minimum escape depth of the photoelectron in the conventional angle-dependent HAXPES is about 10 nm or more [18]. Therefore, it is hard to extract the surface-only component from the angle-dependent HAXPES data directly. In contrast, TR-HAXPES allows us to extract most of the surface components just by switching the incident angle to the critical angle.

IV. CONCLUSIONS

HAXPES has been used to study the surface and bulk electronic properties of LSMO and LCCO thin films. The use of total reflection geometry allowed us to discriminate the surface components from the bulk component at the same beam time without making any changes to the experimental conditions, such as the beamline, analyzer, and energy resolution. The well-screened peak disappeared, and the surface contamination peak appeared in total reflection HAXPES, suggesting that the surface-sensitive measurement equivalent to soft x-ray PES is possible in total reflection conditions. The results demonstrate a potential for TR-HAXPES to obtain information not easily accessible by conventional HAXPES for the study of strongly correlated electron systems and also semiconducting materials in general.

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