Hard X-ray photoemission spectroscopy of transition-metal oxide thin films and interfaces

H. Wadati [a],*, A. Fujimori [b]

[a] Department of Applied Physics and Quantum-Phase Electronics Center (QPEC), University of Tokyo, Hongo, Tokyo 113-8656, Japan
[b] Department of Physics, University of Tokyo, Bunkyo-ku, Tokyo 113-0033, Japan

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ABSTRACT

Photoemission spectroscopy is a powerful experimental technique to study the electronic structures of solids, especially of transition-metal oxides. Recently, hard X-ray photoemission spectroscopy (HXPES) has emerged as a more relevant experimental technique to obtain clear information about bulk states. Here, we describe how HXPES can be conveniently applied to study the interesting subjects on oxide thin films such as the composition dependence and the film thickness dependence of the electronic structures and the interfacial electronic structure of multilayers.

1. Introduction

Photoemission spectroscopy has been a powerful experimental technique to study the electronic structures of solids, especially of strongly correlated materials such as transition-metal oxides. Since one uses a "photon-in-electron-out" process in photoemission spectroscopy, its probing depth is determined by the electron mean-free path of photoelectrons [1], which is only 5–10 Å in the soft X-ray region of 100–1000 eV, and is comparable to the unit-cell size of many complex oxides. Photoemission spectroscopy measurements in the soft X-ray region have been performed either by using soft X-ray beamlines in synchrotron radiation facilities or using laboratory X-ray sources of Mg Kα line ($h\nu = 1253.6$ eV) and Al Kα line ($h\nu = 1486.6$ eV). In order to obtain clear information about bulk electronic states, hard X-ray photoemission spectroscopy (HXPES) [2] is a more relevant experimental technique. In HXPES, the mean free path of photoelectrons is increased up to ~100 Å. The surface sensitivity can also be changed by changing the emission angle θ of photoelectrons because the probing depth of photoelectrons is given by $\lambda \cos\theta$, where λ is the electron mean-free path. By making use of bulk-sensitive hard X-rays, one can study the electronic structures of buried interfaces quite efficiently.

In this article, we give an overview of how HXPES can be conveniently applied to study the electronic structures of oxide thin films. We shall discuss the composition dependence and the film thickness dependence of the electronic structure as well as the interfacial electronic structure of oxide multilayers investigated using HXPES.

2. Experimental techniques

One serious problem of HXPES is the weak photoemission intensity due to the small photoionization cross-sections (σ) because the σ values rapidly decrease with increasing photon energy [3]. Since the mean free path of photoelectrons is much shorter than the X-ray attenuation length, grazing incidence of X-rays relative to the sample surface greatly increases the effective sample area irradiated by X-rays without losing the effective probing depth. On the other hand, to achieve a large probing depth, photoelectrons emitted in the direction normal to the sample surface should be detected. Therefore, the configuration shown in Fig. 1 is usually employed. The axis of the analyzer is placed perpendicular to the X-ray beam and the incidence angle relative to the sample surface is typically set to 1°.

The importance of the grazing incidence is clearly seen in Fig. 2, where the V 1s photoemission intensity of a LaVO$_3$ thin film is shown as a function of the X-ray incidence angle θ, which was varied by changing the sample angle, as shown in the inset. The intensity at $\theta = 1°$ is about 10 times larger than that at $\theta = 5°$, and about 100 time larger than that at 20°. To obtain the grazing incidence of X-rays, large flat surfaces of samples are necessary. Therefore, thin films can be quite efficiently studied by HXPES.

3. Composition dependence of the electronic structure

In studying the electronic structures of various transition-metal oxides, it is important to analyze the composition dependence, i.e.,

* Corresponding author. Tel.: +81 358410874; fax: +81 358410875.
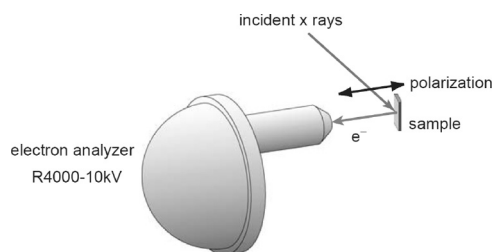E-mail address: wadati@ap.t.u-tokyo.ac.jp (H. Wadati).

Fig. 1. Schematic drawing of the experimental setup in hard X-ray photoemission spectroscopy (HXPES) experiments [2].
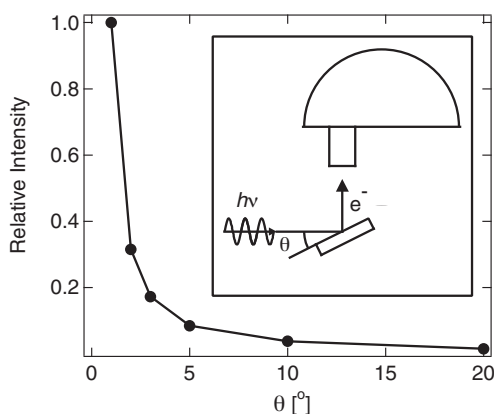

Fig. 2. V 1s photoemission intensity from a LaVO$_3$ thin film as a function of the X-ray incidence angle θ.

Fig. 3. Combined plot of the valence-band HXPES spectra and the O 1s XAS spectra of CaRu$_{1-x}$Mn$_x$O$_3$ (x = 1.0, 0.75, 0.5) [7]. HXPES spectra have been taken with the photon energy of $h\nu$ = 3.5 keV.

the effects of the substitution of some element for the original one [4]. First of all, one can achieve filling control, whose importance has been widely recognized since the discovery of high-temperature superconductivity. The typical example is La$_{2-x}$Sr$_x$CuO$_4$, where the band filling can be controlled by substitution of divalent Sr for trivalent La. One can also achieve band-width control by atom substitution. For example, the substitution at the B site of the perovskite oxides ABO$_3$ often leads to new physical properties. Bandwidth-controlled system RNiO$_3$, where the atomic radius of the rare-earth ion R at the A site of the perovskite ABO$_3$ is varied, was first studied by Torrance et al. [5]. LaNiO$_3$ with the maximal bandwidth W is metallic, while the other RNiO$_3$ compounds with smaller W are charge-transfer insulators with an antiferromagnetic ground state.

Substitution studies have also been made for the transition-metal atoms, which are directly involved in the electrical and magnetic properties of the compounds. As an example of B site-substituted perovskite oxides, CaRu$_{1-x}$Mn$_x$O$_3$ shows ferromagnetism with the maximum transition temperature T_c (150–210 K) and the maximum magnetization occurring at x = 0.5, although neither end member CaRuO$_3$ nor CaMnO$_3$ is ferromagnetic (CaRuO$_3$: paramagnetic metal; CaMnO$_3$: antiferromagnetic insulator). The origin of ferromagnetism has been explained by a double exchange mechanism between Mn^{4+} and Mn^{3+}, where Mn^{3+} ions are created when Ru atoms are replaced by Mn atoms [6]. However, this mechanism needs charge transfer from Ru to Mn, which seems difficult considering the higher electronegativity of Ru than that of Mn. In order to understand the unique physical properties of this system, the information about the electronic structure and its relationship to ferromagnetism has been studied by HXPES and X-ray absorption spectroscopy by Terai et al. [7]. Fig. 3 shows a combined plot of the valence-band HXPES spectra and the O 1s XAS spectra of CaRu$_{1-x}$Mn$_x$O$_3$ (x = 1.0, 0.75, 0.5), representing the electronic state below and above the Fermi level (E_F). The occupied Ru 4d states are more clearly observed than in the previous
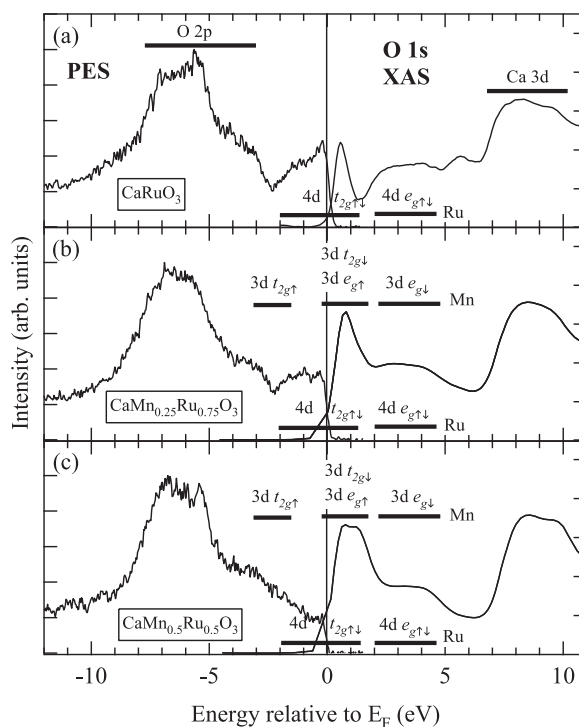
study [8], which implies that we succeeded in measuring the dominantly bulk electronic structure. The band between −8 and −3 eV is mainly composed of O 2p states. The peak intensities of the two peak structures between around −8 and −5 eV change with the Ru concentrations, and can be assigned to the Ru 4d – O 2p (−5.5 eV) and Mn 3d – O 2p (−7 eV) bonding states. On the other hand, the peak intensity at around −3 eV does not depend on the Ru/Mn ratio and, thus, can be assigned to O 2p nonbonding states. The intensity of the structure at around −2.5 eV increases as the Mn concentration increases. Hence, the structure can be attributed to Mn 3d t$_{2g}$ up-spin states by a comparison to the previous the configuration-interaction cluster-model calculation [9]. By the same token, the peak structures at around 0–2 eV above E_F can be assigned to the Mn 3d t$_{2g}$ down-spin and Mn 3d e$_g$ up-spin states. The concentration dependence of the peak structure around 0–2 eV is caused by the overlap between the hybridized O 2p-Ru 4d states and the hybridized O-Mn 3d states. The intensity of the structure near E_F in the HXPES spectra decreases as the concentration of Ru decreases. At the same time, the intensity of the structure near E_F in the XAS spectra increases as the Mn concentration increases. These structures are attributed to the Ru 4d t$_{2g}$ states. Together with the soft X-ray magnetic circular dichroism at Mn 2p and Ru 3p edges, the authors propose that the localized Mn 3d t$_{2g}$ states and the itinerant Ru 4d t$_{2g}$ band are antiferromagnetically coupled and give rise to the ferromagnetic ordering.

HXPES has been applied to another transition metal-substituted system V$_{1-x}$W$_x$O$_2$ by Sakai et al. [10]. VO$_2$ undergoes a metal-insulator transition (MIT) near room temperature associated with a structural phase change from metallic rutile to insulating monoclinic [11]. Although an MIT concomitant with structural change is reminiscent of the Peierls transition, the importance of strong electron correlations is also evident. Therefore, whether this transition is essentially Peierls type or Mott-Hubbard type has been debated for years. The substitution of other ions having a higher valence state than V ions makes the Peierls instability of VO$_2$ weaker as