Journal of Electron Spectroscopy and Related Phenomena 190 (2013) 205–209

Contents lists available at ScienceDirect

Journal of Electron Spectroscopy and Related Phenomena

journal homepage: www.elsevier.com/locate/elspec

Determination of electronic and atomic properties of surface, bulk and buried interfaces: Simultaneous combination of hard X-ray photoelectron spectroscopy and X-ray diffraction

J. Rubio-Zuazo[a,b,*], G.R. Castro[a,b]

[a] SpLine, Spanish CRG BM25 Beamline at the ESRF, ESRF, B.P. 220, F-38043 Grenoble, France
[b] Instituto de Ciencia de Materiales de Madrid, ICMM, CSIC, Cantoblanco, E-28049 Madrid, Spain

ARTICLE INFO

Article history:
Available online 9 April 2013

Keywords:
HAXPES
Surface and bulk X-ray diffraction
Electronic and compositional depth profiles
La–Ca mixed-valence manganites

ABSTRACT

Hard X-ray photoelectron spectroscopy (HAXPES) is a powerful novel emerging technique for bulk compositional, chemical and electronic properties determination in a non-destructive way. It benefits from the exceptionally large escape depth of high kinetic energy photoelectrons enabling the study of bulk and buried interfaces up to several tens of nanometres depth. Its advantage over conventional XPS is based on the long mean free path of high kinetic energetic photoelectrons. Using the advantage of tuneable X-ray radiation provided by synchrotron sources the photoelectron kinetic energy, i.e. the information depth can be changed and consequently electronic and compositional depth profiles can be obtained. The combination of HAXPES with an atomic structure sensitive technique, as X-ray diffraction, opens a new research field with great potential for many systems in which their electronic properties are intimately linked to their crystallographic structure. At SpLine, the Spanish CRG Beamline at the European Synchrotron Radiation Facility (ESRF) we have developed a novel and exceptional set-up that combine grazing incidence X-ray diffraction (GIXRD) and HAXPES. Both techniques can be operated simultaneously on the same sample and using the same excitation source. The set-up includes a heavy 2S+3D diffractometer and UHV chamber equipped with an electrostatic analyzer. The UHV chamber has also MBE evaporation sources, an ion gun, a LEED optic, a sample heating and cooling device, an electron gun, a UV discharge lamp, a low and medium energy X-ray tube, leak valves and a load-lock port. The photon energy ranges between 7 and 45 keV. The HAXPES analyzer is an electrostatic cylinder-sector (FOCUS HV CSA), with a compact geometry and high transmission due to second order focusing. The analyzer is capable to handle kinetic energies both up to 15 keV and down to a few eV with the same analyzer setup and power supply.

1. Introduction

The photoemission and the Auger electron spectroscopies play a preponderant role in the study of the electronic properties of solids [1]. These techniques have been extensively used in the last 40 years and have reached a high degree of sophistication [1]. Overall, their application has been limited to the investigation of surface phenomena by using energies between 40 and 2000 eV for both the excitation sources and detected electrons. The low electron inelastic-mean-free-path (IMFP) and/or the effective attenuation length (EAL) [2] in the solid materials, at the energies used are responsible for their surface sensitivity. Particularly, buried interfaces are not accessible for the great majority of the techniques of surface physics. However, using hard X-rays as excitation source high kinetic energy photoelectrons can be produced. Consequently, HAXPES benefits from the exceptionally large escape depth of high kinetic energy photoelectrons increasing the information depth up to several tens of nanometres for 15 keV electron kinetic energy [3]. Using the advantage of tuneable X-ray radiation provided by synchrotron sources the photoelectron kinetic energy, i.e. the information depth can be changed and consequently electronic and compositional depth profiles can be obtained [4]. HAXPES is a novel method for non destructive and bulk sensitive electronic and chemical characterization of solids. However, in many materials, as e.g., high T_c superconductors, manganites, cuprates, nickelates, etc., their macroscopic properties result from an interrelated interplay between many degrees of freedom. Among them, the correlation between the atomic and electronic structure is of

* Corresponding author at: SpLine, Spanish CRG Beamline at the European Synchrotron Radiation Facility, B.P. 220, F-38043 Grenoble, France. Tel.: +33 476881782; fax: +33 476882816.
E-mail address: rubio@esrf.fr (J. Rubio-Zuazo).

0368-2048/$ – see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.elspec.2013.04.003

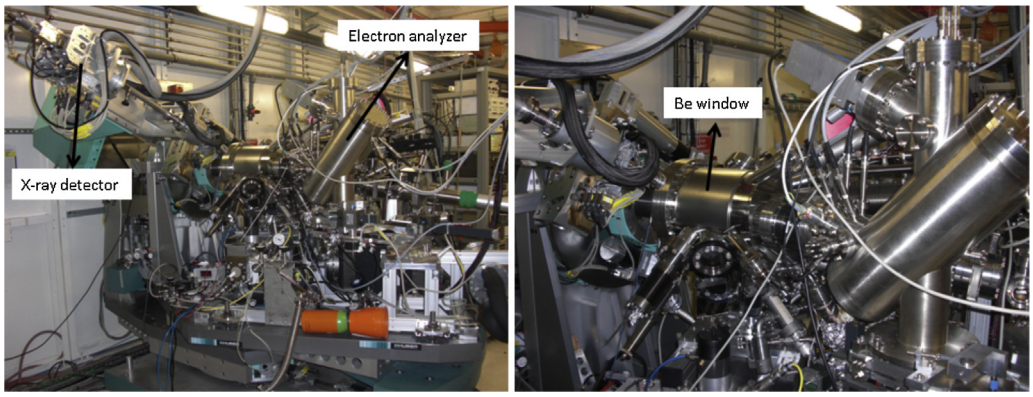

Fig. 1. (Left) Picture of the whole experimental HAXPES and GIXRD setup. The X-ray detector arm can be seen at the left side while the HAXPES electron analyzer can be seen at the right side. (Right) Close look to the X-ray outgoing Be window.

special relevance for the understanding of their magnetic, electric, multiferroic, half-metallicity, etc., behaviour. Hence, the complementation of HAXPES with an atomic structure sensitive technique, as X-ray diffraction, opens a new research field with major application on material science. At SpLine, the Spanish CRG Beamline at the European Synchrotron Radiation Facility (ESRF) we have developed a novel and exceptional set-up that combines HAXPES and grazing incidence X-ray diffraction GIXRD (surface and bulk X-ray diffraction and X-ray reflectivity). Both techniques can be operated simultaneously on the same sample using the same excitation source. A detailed description of the experimental set-up will be presented together with some examples that emphasize its outstanding capabilities.

2. Experimental HAXPES–GIXRD set-up

The experimental set-up is placed on branch B of the Spanish CRG BM25 Beamline SpLine [5] at the European Synchrotron Radiation Facility (ESRF), Grenoble, France. The Branch B is located on the hard edge of the bending magnet D25 device with a critical energy of 20.6 keV and a horizontal angular divergence of 2 mrad. Two Si (1 1 1) crystals placed at ~30 m from the source serve as a double-crystal monochromator, which gives an energy resolution of $\Delta E/E = 1.5 \times 10^{-4}$. The horizontal focusing is achieved by the second monochromator crystal through a sagittal cylindrical bending. A cylindrical bent mirror placed after the monochromator is used to focus in the meridional plane. In all the energy range the beam spot size is around 300 μm × 100 μm in the horizontal and vertical direction, respectively. A first mirror, Rh coated, is located before the monochromator that cuts-off the higher-order-harmonics reducing the heat load on the monochromator. The beamline photon energy ranges between 5 keV and 45 keV with an X-ray flux of 5×10^{11} photons/s (10^{-4} bw) that is well adapted for the HAXPES and GIXRD requirements.

A high-resolution channel-cut (Si(3 1 1), Si(3 3 3), and Si(4 0 0)) post-monochromator is located close to the vacuum chamber for cases where a better excitation source resolution in the HAXPES measurements is required. The experimental set-up includes a heavy 2S+3D diffractometer, a UHV chamber and an electrostatic analyzer [6,7]. The vacuum chamber has two Be windows so that the incoming and outgoing X-ray beam can hit the sample and the X-ray detector, respectively. The exit Be-window allows the out-going diffracted X-ray beam to cover 120° in-plane and 50° out-of-plane. The in-coming Be-window is wide enough to reach up to 50° X-ray incidence angles. A wide portion of the reciprocal space ($Q_{max} = 10$ Å^{-1} at 12 keV) is therefore accessible. The UHV chamber has also MBE evaporation sources, an ion gun, an electron gun (up to 15 keV), an X-ray tube (Mg and Ti anodes), a UV discharge lamp, a LEED optic, a sample heating (up to 1500 °C) and cooling device (down to 20 K on the sample), leak valves, mass spectrometer and a load-lock port. All these devices allow performing X-ray diffraction and UPS/XPS/HAXPES experiments during growth deposition or during different sample treatments. Fig. 1 shows a picture of the UHV experimental set-up. In our set-up design we have chosen an analyzer with the wider angular acceptance, keeping in mind that a great effort has to be done in optimizing the transmission and the energy resolution. The analyzer is an electrostatic cylinder-sector (FOCUS HV CSA), with a compact geometry and high transmission due to second order focusing [7,8]. The analyser is based on a cylinder sector with 90° deflection and 300 mm slit-to-slit distance. The sample-lens distance is maximized to 50 mm, allowing the simultaneous accomplishment of photoemission and diffraction experiments. The electron analyzer is mounted on a 3-linear motion (x, y, z) motorized table so that the analyzer focal point position can be adjusted on the sample. In this way, the detection geometry and consequently the counting rate can be optimized without changing neither the sample position nor the in-coming beam impact point, i.e., without disturbing the diffraction geometry conditions. This gives a very compact design of the analyser that is easily integrated into a multipurpose experiment with different techniques. The analyzer is capable to handle kinetic energies both up to 15 keV and down to a few eV with the same analyzer setup and power supply. Fig. 2 shows representative HAXPES spectra obtained at the SpLine HAXPES–GIXRD set-up demonstrating the excellent capabilities of the electron anlyzer to analyze electrons with kinetic energy up to 15 keV. HAXPES 3s, 3p and 3d Au core level spectra and Cu and Au valence band measured on a 21 nm thick Au film in situ grown on a Cu polycrystalline sample are shown in Fig. 2a and b, respectively. The spectra were obtained with a photon energy of $h\nu = 9$ keV ($E_{kin} = 5.4$–6.9 keV), $h\nu = 17$ keV ($E_{kin} = 13.4$–14.9 keV), $h\nu = 7.5$ keV ($E_{kin} = 7.36$–7.50 keV) and $h\nu = 15$ keV ($E_{kin} = 14.86$–15.00 keV), respectively. The bottom (Fig. 2a) and the upper spectrum (Fig. 2b) are multiplied by a factor 3 and 14.25, respectively. Note the absolute and relative cross section differences in the spectra.

3. Experimental results

Complex oxides have been widely studied since many years because they show exotic behaviours as superconductivity, colossal magnetoresistance, charge ordering, ferroelectricity or multiferroicity. In most of the cases, such phenomena are a consequence of an intricate interplay of charge, spin, orbital and lattice degrees of freedom. The growth of these materials in thin film form usually modifies its intrinsic properties hampering their potential application in industrial devices. This is the case of La–Ca mixed-valence manganites. Even the most stable manganites (1/3 doping)