Looking Deeper into Buried Nanolayers and Complex Materials: Standing-Wave and Angle-Resolved Hard X-Ray Photoemission

Photoelectron spectroscopy (photoemission) is a well established and widely used technique for studying the atomic, electronic, and magnetic structure of materials, with in fact a history of over 100 years from Einstein's first explanation of it. However, it is only within the past decade that experiments have begun with energies in the hard X-ray regime above 2 keV and going up to 10 keV or more [1,2]. Such hard X-ray photoemission (HXPS or HAXPES) measurements are of high interest because they permit obtaining information from deeper below the surface of a solid sample, due to electron inelastic mean free paths (IMFPs) that increase roughly as (kinetic energy)$^{0.75}$. HAXPES is thus rapidly developing worldwide, and SPring-8 is a leader in this field, with many papers already published in leading journals.

The work described here involves exploring two new dimensions of HAXPES in order to enhance its power for the characterization of complex and nanoscale materials.

If the sample to be studied is grown as, or on, a synthetic multilayer mirror, then tuning the X-ray incidence angle to the mirror Bragg angle creates a strong standing wave (SW) in the mirror and above its surface. This nm-scale standing wave can then be moved vertically through the sample, by scanning the incidence angle through the Bragg angle (a rocking curve); by scanning the photon energy through the Bragg condition; or if one layer of the sample has been grown in a suitable wedge profile, also by moving the X-ray spot along the sample. In previous soft X-ray experiments, these techniques have been shown to provide a powerful new approach for studying buried layers and interfaces with sub-nm resolution [3]. However, soft X-ray measurements are limited in depth sensitivity due to the short IMFPs of ~10-20 Å involved. Recent experiments at beamline **BL15XU** have extended this technique into the hard X-ray regime with ~50-100 Å IMFPs, thus providing data that can reach into deeper layers and interfaces of technologically relevant multilayer nanostructures [4,5,6].

Some results of the rocking-curve type for a $SrTiO_3/La_{0.67}Sr_{0.33}MnO_3$ multilayer are shown in Fig. 1(a), based on SPring-8 hard X-ray data at 5.9 keV and analogous Berkeley ALS soft X-ray data at 833 eV [5]. These curves show effects both from the multilayer Bragg reflection (the large peaks at 1.9° and 14°) and from reflection at the top and the bottom of the multilayer (Kiessig fringes). From detailed X-ray optical simulations of this data, it has been determined that the bilayer distance has changed by about 6% in going from the top to the bottom of the multilayer. Further analysis of this data finally leads to the detailed surface and interface profiles shown in Fig. 1(b). Other studies at SPring-8 using the SW method in HAXPES have involved the Fe/MgO interface of relevance to spintronics, and the TiN/Si interface of relevance to semiconductor integrated circuits [4], thus demonstrating the broad applicability of this new approach.

Angle-resolved photoemission (ARPES) is a technique of choice in the soft X-ray regime for studying the valence-level electronic structure of solids and surfaces. Most measurements to data are done with photon energies below about 150 eV, and so are very surface sensitive. A limited number of studies have pushed this into the 0.5-1.0 keV range [7], thus achieving greater bulk sensitivity. In recent

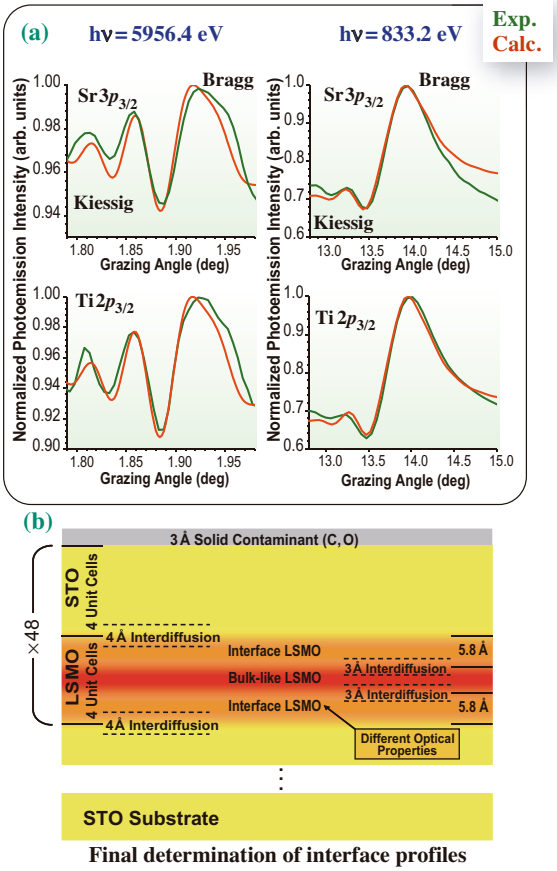

Fig. 1. **(a)** Standing-wave (SW) rocking-curves from Sr $3p_{3/2}$ and Ti $2p_{3/2}$ core levels excited by 5956 eV photons (data from SPring-8) and 833 eV photons (data from the ALS) from a $SrTiO_3/La_{0.67}Sr_{0.33}MnO_3$ multilayer, with both experiment and best-fit X-ray optical theory shown. **(b)** The detailed interface profiles of concentration derived from the best fit.

work at beamline BL15XU, it has been demonstrated that such measurements can be carried out at up to 6 keV [8], provided that the sample is cryogenically cooled to suppress phonon effects that tend to smear the data out over all occupied stated in the Brillouin zone [6,8]. Figure 2 shows such hard X-ray ARPES (HARPES) data obtained with 5.9 keV excitation for W(110): in (a) the data corrected for phonon effects and photoelectron diffraction, and in (b) the results of one-step theoretical calculations. Figure 3 shows similar data for 3.2 keV excitation of GaAs(100), here with its Brillouin zone (BZ) in (a), and the corrected data in (b). The more localized and core-like As 4*s* band at about 13 eV binding energy exhibits intensity modulation due to photoelectron diffraction instead of dispersing band structure, whereas the delocalized bands extending over 5-8 eV binding energy show clear dispersion that agrees well with band structure and one-step photoemission theory [8]. Hard X-ray photoelectron diffraction (HXPD) in fact promises to provide an additional new element-specific structural tool for complex materials, e.g. of dopant site determination [9]. Other theoretical calculations indicate that many materials should be amenable to such measurements in the 2-3 keV, if not higher, energy range [6].

These are thus first-of-a-kind HAXPES measurements of two different types that should permit future studies of the bulk, buried-layer, and interface compositions and electronic structures of various complex materials and nanostructures.

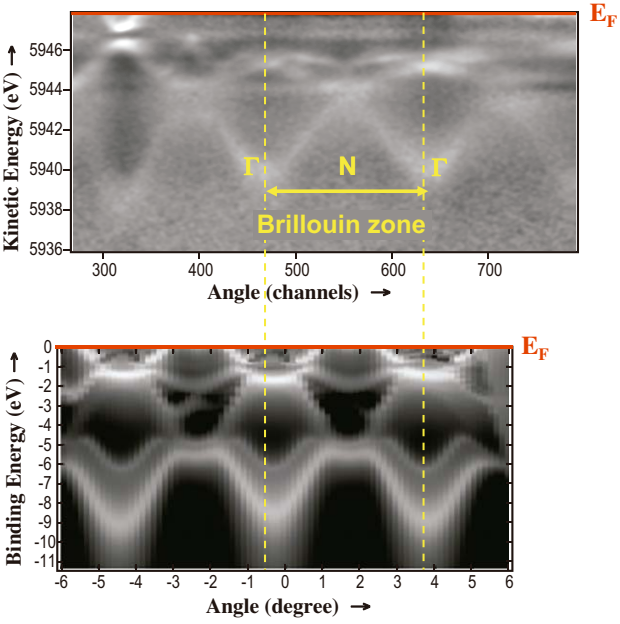

Fig. 2. HARPES data from W(110) at 30 K with excitation at a photon energy of 5956 eV. **(a)** The data at 30 K, corrected for DOS and HXPD effects, clearly exhibiting dispersive bands. **(b)** One-step photoemission theory, which exhibits good agreement with experiment.

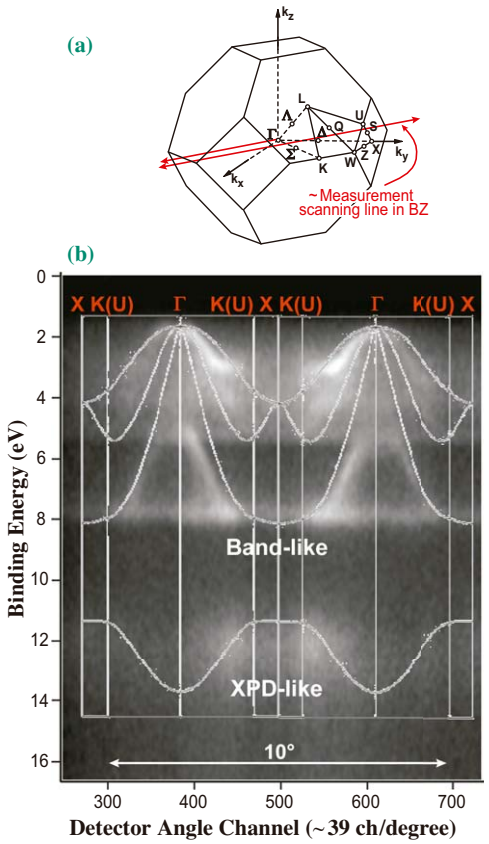

Fig. 3. HARPES data from GaAs(001) at 30 K with excitation at a photon energy of 3242 eV. **(a)** The Brillouin zone, with the expected sampling line shown in red. **(b)** The corrected data are overlaid with the band structure region that is predicted by a simple free-electron final-state calculation to be involved in direct transitions. The band at *ca*. 13 eV is mostly non-bonding As 4*s* and so is core-like, exhibiting HXPD effects. The bands above it are more delocalized, and show dispersion.

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