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Recent Applications of Hard X-ray Photoelectron Spectroscopy (HAXPES)

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Abstract

Recent applications of hard x-ray photoelectron spectroscopy (HAXPES) demonstrate its many capabilities in addition to several of its limitations. Examples are given, including measurement of buried interfaces and materials under *in-situ* or *in-operando* conditions, as well as measurements under x-ray standing-wave and resonant excitation. Physical considerations that differentiate HAXPES from photoemission measurements utilizing soft and ultraviolet x rays are also presented.

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I. Introduction

X-ray photoelectron spectroscopy (XPS), also referred to as ESCA (electron spectroscopy for chemical analysis), is a highly developed technique for studying the chemical and electronic structure of materials, with applications in both academic and industrial research. Traditionally, XPS has been performed using either ultraviolet (UV) or soft x-ray excitation sources such as He discharge lamp (21.2 eV for He I and 40.8 eV for He II), Al K_α (1486.6 eV), and Mg K_α (1253.7 eV) sources, as well as synchrotron UV and soft x-ray beamlines with tunable energy ranges. However, in recent years, significant interest has turned to hard x-ray XPS, or HAXPES (sometimes referred to HXPS or HX-PES), defined here as XPS with photon energy, $h\nu$, greater than 2140 eV, which is the lowest energy typically accessible using a Si (111) double-crystal monochromator. This review will discuss several capabilities of HAXPES, focusing on recent scientific achievements.

While interest in HAXPES has expanded significantly within the last decade, hard x-rays have been used for XPS since its inception: The early work of Siegbahn measuring binding energies [1] and chemical shifts in oxidized copper [2] were performed using Mo K_α radiation (17,000 eV). However, the low count rates due to low photoionization cross sections (see, e.g. [3]) and the desire for high-energy resolution led to the adoption of lower-energy x-ray sources such as Al and Mg K_α . Synchrotron sources, however, are capable of providing higher count rates due to their high photon flux, simultaneously with better energy resolution. The use of synchrotron-source hard x rays for XPS was demonstrated by Lindau *et al.* using parasitic radiation from Stanford's SPEAR synchrotron [4] to measure the intrinsic linewidth of the Au 4f orbitals [5]. However, even here the count rate was deemed too low for low cross-section orbitals, particularly those in the valence region of the spectrum [4]. With the development of second and higher-generation synchrotron-light sources, however, HAXPES measurements have become extremely practical, especially with the advent of commercial hemispherical analyzers dedicated to HAXPES.

This critical review describes the physics necessary for HAXPES analysis, and especially how it differs from lower-energy XPS. Recent experimental results which demonstrate the utility of HAXPES for materials measurements, including the measurement of buried interfaces, measurements of “real” (i.e. without surface preparation) and *in-operando* samples, *site* and *interface* specific measurements using standing waves, and measurement of electron-orbital structures using resonant XPS follow. The review will conclude with exciting new developments in time-dependent HAXPES and hard x-ray photoelectron microscopy.

II. Physics of HAXPES

Photoelectron spectroscopy is based on the photoelectric effect: When photons of sufficient energy strike an atom, they can be absorbed, and photoelectrons emitted. The kinetic energy of a photoelectron, E_k , is equal to the difference between $h\nu$, the photon energy, and the sum of the electron binding energy, E_B , and material work function, φ , according to Einstein's famous equation:

$$E_k = h\nu - (E_B + \varphi). \quad (1)$$

It is this conservation of energy that gives photoemission the unique ability to directly measure the electronic and chemical structure of atoms, molecules, and solids.

In a photoemission experiment, the peak intensity, I_A , of an electronic core level "A", may be written as:

$$I_A = C \int \Phi \rho \frac{d\sigma_A}{d\Omega} \exp\left(-\frac{z}{\lambda_A \sin \theta}\right) \Omega d\tau. \quad (2)$$

Here C is a constant that accounts for instrumental effects such as the electron-detector transmission function, Φ is the incident x-ray flux, $\frac{d\sigma_A}{d\Omega}$ is the differential photoionization cross section of the core level, z is the electron-emission depth defined from 0 at the surface increasing into the bulk, λ_A is the electron-attenuation length (discussed further below), θ is the electron-emission angle, Ω is the spectrometer acceptance solid angle, and $d\tau$ is the volume element.

The underlying physics of HAXPES is general to conventional photoelectron spectroscopy, and this physics is well established (see, e.g. [6]). However, as $h\nu$ increases from the ultraviolet and soft x-ray ranges to higher energies, the practical effects of some of the physics changes, which leads to both unique capabilities and necessary considerations for HAXPES.

A. Depth Sensitivity

The most obvious difference between HAXPES and conventional photoelectron spectroscopy is the enhanced probing depth achievable with HAXPES. Because the x-ray absorption length is typically much longer than the photoelectron inelastic mean free path (IMFP), the information depth (ID) is restricted solely by the IMFP. The calculated IMFP vs photon-energy curve for the Si $2p$ core level in elemental Si is shown in Figure 1. Above a certain low-energy threshold, as $h\nu$ increases, so does the

IMFP and hence ID. For example, the Si 2p IMFP approximately doubles between 1486 eV (Al K_α) and 5000 eV excitation energy (Figure 1).

Figure 1: The IMFP for Si 2p photoelectrons in Si as a function of photon energy.

The IMFP may be calculated semi-empirically by the Tanuma-Powell-Penn equation (TPP-2M) [7], which depends on the material molecular mass (M), band gap (E_g), density (ρ), and number of free valence electrons (N_V). IMFP predictions using TPP-2M are accurate to within 10% with respect to optical data [8]. An alternative approach by Seah [9] utilizes a power law with reduced parameters, the ‘atomic volume’, a , and atomic number, Z :

$$IMFP = (4 + 0.44Z^{0.5} + 0.104E_k^{0.872})a^{1.7}/Z^{0.3}. \quad (3)$$

Here, a is given by:

$$a^3 = \frac{10^{21}M}{\rho N_A}, \quad (4)$$

where N_A is Avogadro’s number. Accuracies for this equation are similar to TPP-2M. A further simplified equation with only one parameter was also given by Seah [9], albeit with slightly lower accuracy:

$$IMFP = (0.73 + 0.0095E_k^{0.872})/Z^{0.3}. \quad (5)$$

Equation 3 and Equation 5 determine the IMFP in nm.

While the IMFP provides a first-order estimate of the depth sensitivity realized by HAXPES, elastic scattering also plays a significant role. The effective attenuation length (EAL), to be used in place of λ_A in Equation 2, is constructed to take elastic scattering into account [10] and is modeled as a linear relationship with the IMFP and the single-scattering albedo, ω , for photoelectron energies up to 5000 eV [11]:

$$EAL = IMFP(1 - 0.738\omega) \sin \theta. \quad (6)$$

The single-scattering albedo depends on the IMFP and the transport mean free path; it can be fitted according to the following exponential [12]:

$$\omega = \exp\left(\sum_{i=1}^4 B_i (\ln E_k)^i\right). \quad (7)$$

A list of the fitted coefficients, B_i , for elemental solids is given in Ref. [12].

The information depth (ID) in an XPS measurement is defined as the depth normal to the surface from which useful information can be obtained [10]. The ID is specified as the percent of detected signal, P , from within that depth, e.g. the depth from which 90% of the total signal derives. The IDs for a number of materials were calculated by Jablonski and Powell [13] and found to follow a trend similar to the EAL:

$$ID = IMFP(1 - 0.787\omega) \sin \theta \ln \left[\frac{1}{1 - (P/100)} \right]. \quad (8)$$

A comparison of the IMFP calculated by the TPP-2M equation, the EAL (Equation 6), and ID for 90% (ID-90) and 99% (ID-99) of the signal (Equation 8) is shown in Figure 2. Calculations were made for SiO₂ measured at an 85° takeoff angle. At low photoelectron E_k , the EAL and IMFP differ significantly, but as E_k increases, elastic scattering effects are minimized and the EAL and IMFP become equivalent. 90% of the photoemission signal arises from within approximately twice the EAL, and 99% of the signal from within four times the EAL.

Figure 2: Comparison of IMFP, EAL, and ID for 90% and 99% of information (ID-90 and ID-99, respectively) calculated for SiO_2 measured at an 85° electron takeoff angle.

B. Bulk vs Surface Sensitivity

The increased IDs in HAXPES permit the analysis of bulk electronic structure, buried interfaces, and depth profiling through modeling based on Equation 2, as shown schematically in Figure 3. IDs greater than 50 nm have been measured [14]. From Equation 1, it is also evident that HAXPES permits the measurements of deeper core levels: Only photoelectrons with $E_k > 0$ can be measured; thus with higher $h\nu$, higher E_B core levels can be studied, such as the $1s$ states for elements with $Z > 15$ that are not accessible with either UV or soft x-ray sources. Clearly, access to these additional core levels allows the investigation of new physics. For example, measurement of the Fe $1s$ core level combined with charge-transfer multiplet calculations gives an estimate of charge-transfer parameters in Fe_2O_3 [15]. Also, resonant photoemission measurements around the Ti $1s$ to $3d$ transition has been used to determine the nature of charge transfer in SrTiO_3 [16] (which will be discussed further below).

Figure 3: Schematic of the information depth (ID) of the photoemission process using soft (left) and hard (right) x-ray excitation for a surface/interface/bulk system.

The accessibility of deeper core levels also allows the *simultaneous* measurement of “bulk” and “surface” sensitive structural information. In the Si example below, at $h\nu = 2500$ eV, the IMFP of the Si $2p$ core level is 4.9 nm, while for the Si $1s$ ($E_B = 1840$ eV) it is only 2.2 nm, corresponding to a 99% ID of 22.5 and 8.7 nm, respectively. Figure 4 shows the Si $1s$ and $2p$ core levels for a 4 nm thick Nb_2O_5 film deposited on silicon. An interfacial SiO_x interlayer is evident in both; however, the large difference in surface sensitivity can be seen by the different sensitivity to the interfacial SiO_x : In the bulk sensitive Si $2p$ spectrum, the SiO_x contribution is minor, whereas it dominates the surface sensitive $1s$ spectrum.

Figure 4: Si $1s$ and $2p$ for a 4 nm Nb_2O_5 film deposited on Si. The different probe depths for the two core levels is evident from the difference in the relative intensities of the interfacial SiO_x and the substrate Si contributions. Data were collected with photon energy $h\nu = 2500$ eV.

Such multi-core-level analysis is only possible, however, for certain photon energy/material combinations. For example, measurements of lighter elements such as C and O, with E_B for all core levels less than 1000 eV, will always be relatively bulk-sensitive in HAXPES. Hence it is essential to consider the relevant material depths, IMFPs, core-level binding energies E_B , and available photon energies in the experimental design to ensure meaningful data. This situation can be realized by considering a simple three-layer model consisting of a 3 nm-thick surface, an interface with varying thickness, and an infinite bulk substrate (Figure 3). The calculated relative contributions to the overall signal from the three regions are shown in Figure 5 as a function of photon energy for two interface thicknesses equal to 3 nm and 0.5 nm, respectively. A core-level binding energy of 30 eV (equivalent to the Ge 3d core line) was assumed. As expected, at the lowest photon energies the signal is dominated by the surface; i.e., the ID is smaller than the surface-layer thickness. As the photon energy increases, the surface contribution decays exponentially while the interface contribution increases with photon energy until it hits its maximum, after which it decays. Note that the photon energy corresponding to the interface maximum increases with layer thickness, and the contribution from the bulk component increases monotonically with photon energy. An obvious benefit of HAXPES as seen from this analysis is that the signals from the different layers can be maximized by the judicious choice of photon energy.

Figure 5: Calculations of individual contributions from a 3nm-thick surface, an interface, and a bulk component to the total signal from a three-layer model system. Contributions for 2 interlayer thicknesses are displayed: 0.5 nm (open symbols) and 3 nm (filled symbols).

The enhanced depth sensitivity of HAXPES over lower photon-energy measurements and its unique ability to depth profile does not, however, come without a cost. Figure 6 shows data from an $\text{Al}_2\text{O}_3/\text{Ge}$ film system recorded with both soft and hard x rays. The study was designed to assess the passivation of interface defects at the GeO_2/Ge interface [17]. The soft x-ray spectrum shows a significant contribution from germanium oxides. The HAXPES spectrum, on the other hand, shows no such measurable oxide, because for photon energy $h\nu = 4000$ eV the bulk Ge signal overwhelms the signal from the thin interfacial oxide. Clearly, the deeper an interface lies within a given structure, for a measurement to be successful, the “thicker” its affect must be ($\sim 1/10$ times the electron escape depth for the choice of core level and photon energy).

Figure 6: Ge 3d spectra for p-type Ge with Al_2O_3 overlayer, collected at $h\nu = 120$ eV (left) and $h\nu = 4000$ eV (right). The Al_2O_3 film thickness was 1 nm in the left panel and 2.5 nm in the right panel, but the ratio of GeO_x to Ge is assumed equal for both. Figure from [17].

C. Recoil

While HAXPES offers various advantages over UV and soft x-ray photoemission, care must be taken in data analysis due to the possibility of recoil effects at the high kinetic energies [18–21]. Recoil is present in all photoemission processes, as momentum is transferred from the photoelectron to the emitting atom. Using a classical model of an atom at rest in vacuum, the recoil energy, ΔE , defined as the loss in photoelectron kinetic energy due to recoil, is dependent on the photoelectron kinetic energy and the ratio of the electron mass, m_e , and the mass of the emitting atom, M :

$$\Delta E = E_k \left(\frac{m_e}{M} \right). \quad (9)$$

In a solid, the recoil energy is absorbed through the generation of phonons. From Equation 9, it is clear that the recoil effect will be more prominent for lighter elements and higher photoelectron kinetic energies. For example, for C 1s emission at 5000 eV, the recoil energy will be over 0.2 eV – easily resolvable in a modern HAXPES measurement.

Takata *et al.* [18] demonstrated recoil effects in graphite, as shown in Figure 7, that compares C 1s data collected at different photon energies. At HAXPES photon energies, the C 1s peak shifts to higher binding energies, demonstrating the recoil loss; it also exhibits an asymmetric broadening. (The shift to lower binding energy observed between $h\nu = 340$ and 870 eV is attributed to surface vs bulk effects.) Similar recoil effects were observed for Al at the Fermi level [19] and also for the valence bands of vanadium oxides [20]. In the case of Al, that is usually assumed to be a “free-electron” metal, the presence of recoil at the Fermi level suggests strong electron coupling to the crystal lattice. At first, this observation may seem surprising, but it is important to remember that photoemission only occurs in the vicinity of an electronic core [22] (i.e. a truly free electron cannot photo-emit as the atomic core is required to absorb the photon momentum). For vanadium oxides, the extent of the recoil shift was dependent on the specific oxide (VO_2 , LiV_2O_4 , V_5O_9 , or V_2O_3) and on the relative contribution of the O 2p states to the valence band [20]. These results demonstrate that the recoil effect must be considered for the accurate interpretation of HAXPES data, especially in the case of the valence bands of light atoms and complex materials where different elements may show significantly different recoil shifts.

Figure 7: (Color online) Recoil effect in graphite: experiment (a) and theory (b). Figure from [18].

D. Photoionization cross sections

The photoionization cross section; i.e., the probability of a photon causing ionization of an atomic core level, must also be considered in the analysis of HAXPES data. For a fixed-energy laboratory source, relative sensitivity factors are easily obtained (e.g. [23]). However, as the photoionization cross sections depend strongly on the photon energy, for tunable-energy-source experiments they must be properly accounted for. Indeed, in the HAXPES regime, photoionization cross sections decay rapidly with increasing $h\nu$; this decay is even more pronounced for higher-orbital angular-momentum subshells [3,24,25]. Low photoionization cross sections are one reason why HAXPES is typically only performed at synchrotron facilities, where the high brightness of the photon source can overcome this limitation.

Angular anisotropy of the differential photoionization cross section is also observed in the HAXPES regime. In the dipole approximation, the differential photoionization cross section is cylindrically symmetric about the photon polarization; first- and second-order corrections to the dipole approximation are necessary to more accurately represent HAXPES cross sections and hence intensities [26,27]. In one parameterization [3], the differential photoionization cross section for linearly polarized radiation is given as:

$$\frac{d\sigma}{d\Omega} = \frac{\sigma}{4\pi} [1 + \beta P_2(\cos \theta) + (\gamma \cos^2 \theta + \delta) \sin \theta \cos \varphi] \quad (10)$$

The dipole parameter β and the non-dipole parameters γ and δ have been tabulated [3,25,28]. θ is defined as the angle between the photon-polarization vector and the photoelectron-momentum vector, and φ is defined as the angle between the projection of the photoelectron momentum orthogonal to the photon polarization and the photon-propagation vector. Recent Monte-Carlo calculations of photoelectron transport showed large deviations between the dipole approximation and these first order corrections, while there were smaller differences between first- and higher-order corrections [27].

III. Applications of HAXPES

A. *In Situ* Measurements

Perhaps the most obvious and important “new” practical application of HAXPES is the ability to chemically analyze “real” samples; i.e., samples that have been taken directly from air with no *in-situ* surface or other ultra-high vacuum preparation, as well as the ability to measure real samples under *in-operando* conditions; i.e., under actual device and/or catalytic-reaction conditions. This is made possible by HAXPES due to the large photoelectron IMFPs that assure significant signal from the bulk of the sample itself [29,30]. The enhanced bulk sensitivity also leads to the ability to study samples with intentional surface and/or overlayer modification, either for chemical protection (see, e.g. [31], where a passive SiN capping layer was used to prevent oxidation of Ni films deposited on InGaAs), or for *in-situ* and *in-operando* measurements.

Another example is the HAXPES-based electrical characterization of metal-oxide-semiconductor structures on both silicon [32] and GaAs [33]. Direct measurement of band bending via HAXPES can be advantageous in materials with high densities of interface defects, due to the complex interpretation required by capacitance-voltage measurements. In these works, Fermi-level shifting was achieved by the deposition of high work-function (Ni) and low work-function (Al) metals on substrates with oxide interfaces. The different work-function metals act as a built-in bias that shifts the semiconductor and oxide bands. In the case of Si with SiO₂ as the oxide layer, the different metals shift the work function as expected, but partial Fermi-level pinning was also observed and attributed to defects at the untreated Si/SiO₂ interface. For GaAs, Al₂O₃ was used as the oxide layer. Here again, partial Fermi-level pinning was observed and attributed to a high density of interfacial defect states.

The ability to measure substrate core levels through metal/oxide systems also allows HAXPES to study samples under the condition of *in-situ* electrical biasing. In these cases, the metal electrode deposited over the analysis area must be thick enough to ensure both continuity and low sheet resistance to avoid a potential drop across the sample. Such measurements have been performed to determine interface defect-state densities at SiO₂/Si interfaces [34] and the chemical and electronic modifications responsible for the resistive switching in resistive random-access memory (ReRAM) [35–38]. In the latter application, films of Pt/Zr/HfO_x/Si were studied by HAXPES with *in situ* biasing [38]. *Ex situ* electrical characterization showed switching between high and low resistive states; i.e., ‘OFF’ and ‘ON,’ respectively, with applied bias. HAXPES of the as-deposited films showed significant Zr oxidation and a small presence of metallic Hf suggesting a reaction between Zr and Hf at the interface. With *in situ* biasing to the “ON” state, subtle changes were found, as shown in Figure 8. Specifically, the ratio of ZrO_x to metallic Zr increased, while the ratio of HfO_x to metallic Hf decreased. The authors therefore attributed the resistive switching to the formation of oxygen vacancies in the HfO_x layer.

Figure 8: (Color online) Zr $2p_{3/2}$ and Hf $4f$ spectra for Pt/Zr/HfO_x/Si film stacks. As-deposited films show a high-resistivity state ("OFF"). With in situ biasing, the films are switched to a low-resistivity state ("ON"). Data were collected at $h\nu = 6000$ eV. Figure from [38].

The large photoelectron IMFPs in HAXPES also allow *in-situ* measurements of materials at significantly higher pressures than ultra-high vacuum; i.e., ambient-pressure photoelectron spectroscopy (AP-XPS) [39]. Problems associated with high pressures and gas discharge into the electrostatic lens of the hemispherical analyzer have been mitigated by multi-stage differential pumping [40], and the problem of photon-electron interaction with the gas can be addressed by minimizing the working distance between the sample surface and the analyzer aperture. The technique is ideally suited for the development of novel catalysts that requires the direct observation of electronic-structure changes during *in-operando* chemical reactions. HAXPES based measurements therefore overcome the limitations of lower-energy AP-XPS that arise from the surface sensitivity of the measurement.

An interesting and technologically relevant applications towards the study of catalysis focuses on behavior at liquid/solid interfaces. Such measurements pose additional complications with their biggest challenge currently the preparation of liquid/solid interfaces that are accessible to electron spectroscopy. Experiments require either the preparation of very thin (~ 10 nm) solution layers or the use of ultra-thin solid films through which the electrons from the liquid/solid interface may be detected. HAXPES has succeeded in studying a liquid/solid interface using a microcell with an ultra-thin silicon membrane to separate the liquid from the vacuum as shown in Figure 9 [41]. By applying a potential across the microcell, the evolution of SiO_2 at the silicon-water interface was studied as a function of the applied bias (Figure 10).

Figure 9: (Color online) Schematic illustration of microcell and experimental set up for AP-XPS. Figure from [41].

Figure 10: (Color online) Si 2p photoelectron spectra measured as a function of applied bias. Data collected at $h\nu = 6000$ eV. Figure from [41].

B. Standing Waves

In 1964, Batterman used the Ge K -fluorescence emission from a Ge single crystal to experimentally demonstrate that dynamical-diffraction theory not only predicts the energy reflected by a crystal, but also the distribution of this energy inside the crystal with respect to the scattering planes of atoms [42]. Since then, the x-ray standing-wave technique has developed as a crystallographic tool for the study of numerous topics relevant to single-crystal physics: surface adsorbed layers [43], overlayer structure [44], surface reconstruction [45], strain accommodation [46], and chemical bonding [47]. A review of the x-ray standing-wave technique can be found in Ref. [48]. These applications have historically utilized hard x-ray wavelengths where the wavelength is equal to the crystallographic spacing of the unit cell (single-crystal Bragg diffraction as in Figure 11), but it has also been demonstrated that multi-layered thin-film structures [49,50] and total external reflection from polished surfaces [51] can be used to generate x-ray standing waves, thereby opening the technique to arbitrary energy [52].

Unlike early standing-wave studies that utilized fluorescence detection to monitor the x-ray standing-wave interference field, more recent work has focused on the high-energy-resolution analysis of the photo-emitted electrons [47,52,53]. By combining both x-ray standing waves and high-energy-resolution photoelectron spectroscopy to create standing-wave photoelectron spectroscopy (XSW-XPS), spatially and chemically resolved atomic and electronic structural information may be directly obtained by this unique, non-destructive probe.

Figure 11: (Color online) Bragg reflection from of a plane wave, characterized by momentum k_0 and electric field E_0 with the reflected wave k_h and E_h . The formation of a standing wave can be seen in the overlap region. Figure from [54].

Site-specific atomic and electronic structure

A unique application of XSW-XPS is its ability to determine site-specific valence electronic structure. Because the photoemission process conserves both energy and angular momentum, the valence photocurrent from a solid can be written as [55]:

$$I(E, hv) \propto \sum_{i,l} \rho_{i,l}(E) \sigma_{i,l}(E, hv). \quad (11)$$

Here E is the photoelectron binding energy, $h\nu$ is the x-ray photon energy, $\rho_{i,l}(E)$ are the individual, angular momentum l -resolved electronic single-particle partial densities of states of the i^{th} atom of the crystalline unit cell, and $\sigma_{i,l}(E, hv)$ are the angle integrated, angular momentum dependent photoionization cross sections. By systematically placing the maximum and minimum of the x-ray standing-wave interference field on the different atoms within the unit cell of a heteropolar crystal, the dipole approximation may be used to extract the individual partial densities of states [56].

Figure 12 shows the photoelectron spectra of rutile TiO_2 (110) recorded at two different photon energies (and hence phase conditions) within the photon-energy width of the TiO_2 (200) Bragg back-reflection condition. The standing-wave field clearly modulates the intensity of emission from the Ti and O atoms, as well as the crystal valence band.

Figure 12: Photoelectron spectra from rutile TiO_2 surface. The spectra are collected within the photon energy width of TiO_2 (200) Bragg reflection condition. The photon energies were chosen to maximize electric field on either Ti (solid curve) or O (dotted curve) atomic plane. Figure from [47].

Figure 13 shows the standing-wave decomposition of the valence band; the experimental data has been compared with theoretical Ti and O partial density of states weighted by the relative photoionization

cross sections of the different orbital components (Equation 11). It is commonly understood that stoichiometric TiO_2 has a formal Ti^{4+} charge state with its valence band consisting primarily of O $2p$ -derived states [57]. However, a significant amount of Ti $3d$ ad-mixing is clearly observed in the valence band. Note that excellent agreement is found between the experimental data and theoretical density of states once the photoionization cross sections have been properly taken into account.

This technique was later used to analyze the SrTiO_3 valence band [58]. It was determined that the dominant weight of the valence band signal arises from the Sr and Ti levels. Comparison of the site-specific HAXPES valence-band spectra with theoretical partial density of states demonstrated that broadening was different for the O and metal states, consistent with earlier work [59]. The binding energy of the Ti states was found to be higher for SrTiO_3 than for TiO_2 [47] and attributed to the more perfect octahedral TiO_6 symmetry around the Ti atoms of SrTiO_3 versus TiO_2 .

Figure 13: Theoretical partial density of states corrected for individual angular-momentum photoelectron cross sections and the experimental data. Figure from [47].

XSW-XPS can also determine the bonding geometry of chemically distinct species to a local adsorption structure. This approach has been used, for example, to study the chemical reaction of CH_3SH on $\text{Cu}(111)$ [53] as well as more recently the structure of epitaxial graphene on SiC surfaces [60].

Probing buried interfaces

As mentioned above, synthetic multilayer mirrors can be used to produce standing waves [52]. This approach has been used to elucidate structure and inter-mixing in a variety of systems, such as ambient-pressure measurements of hydrated NaOH and CsOH on $\alpha\text{-Fe}_2\text{O}_3$ [61] and $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3/\text{SrTiO}_3$ interfaces for magnetic tunnel junction (MTJ) applications [62].

An illustrative example can be found in the XSW-XPS study of the interface properties of MgO/Au (monolayer)/ Fe tri-layer system [63]. MgO-based MTJs have shown remarkably high magneto-resistance; however, to achieve this high magneto-resistance high-temperature annealing is required. The post-growth anneal and the evolution of crystalline and electronic structure of different constituents of tunnel junctions have been extensively studied [64–67], but the nature of the interface of CoFeB with MgO is still debated. The formation of an Fe or Co oxide at the MgO interface can lead to a significant drop in the tunneling magneto-resistance (TMR). It has been assumed that an ultra-thin layer of a noble metal on the metal electrode can reduce the possibility of oxide formation and hence enhance TMR [68]. XSW-XPS was used to investigate the possibility of oxide formation in a model Au-decorated Fe/MgO structure. The chemical sensitivity of XPS combined with the position sensitivity of XSW allows precise characterization of this complex tri-layer system.

The sample structure consisted of a MgO film atop a monolayer of Au on a wedge of Fe; all layers were deposited on a multi-layer mirror. The intensities of the Fe $2p_{1/2}$ and $2p_{3/2}$ spin-orbit doublet were measured about the rocking-curve at a given position on the sample. Similar measurements were performed for Mg and O 1s core levels. The incidence angle was tuned to the first order Bragg angle; the sample was then moved laterally along the Fe wedge. Thus by locking the phase of the standing wave, scanning of the sample essentially leads to the movement of the different layers through the standing-wave. By recording the XPS signals of each element along the scan, a detailed model of the tri-layer structure can be extracted. Figure 14 shows the modulation of the three layers along the wedge compared to a simulated structure. It was concluded from the work that the inclusion of Au between Fe and MgO hinders the formation of FeO.

Figure 14: (Color online) Wedge scan of Fe 2p, Au 4d, and O 1s measured at $h\nu = 4000$ eV. Figure from [63].

C. Analysis of Buried Interfaces:

A major technical application of HAXPES is the measurement of the chemical and electronic structure at buried interfaces. Interfaces are key components of modern electronic devices with applications including complimentary metal-oxide-semiconductor structures (CMOS), the basis of modern computers, and p - n junctions for solar-energy applications. The ability to engineer interfacial materials, through chemistry, alloying, and strain gives the device designer the ability to tailor important electronic properties such as carrier mobility and band gap. Thus the overall understanding of the chemistry and electronic structure of interfaces is paramount for modern device design. Soft x-ray and UV photoelectron spectroscopy has made significant contributions to this field; however, due to the limited electron escape depths present in these measurements, these techniques are applicable only to surfaces and ultra-thin films, often requiring significant *in-situ* preparation that can significantly alter their atomic and electronic structures.

Band Alignment at semiconductor interfaces

An important physical parameter is the band alignment between two interface layers of a device. How the valence and conduction bands align across an interface is responsible for both charge transfer and leakage current. HAXPES measurements of band alignment are therefore becoming more and more

important to understand and optimize hetero-structures [69]; a brief overview of the underlying theory behind the technique as well as several examples will be presented below.

One of the earliest and still frequently employed theoretical models of interfacial band alignment is the “Anderson” or “electron-affinity” rule [70]. In this model, the natural conduction-band alignment is determined by the difference between the electron affinities of the two materials; i.e. across the two materials the vacuum level is assumed constant. The valence-band offset can then be found from the band gaps of the two materials. Other electrostatic models were later developed that take the intrinsic Fermi level to be constant [71], or the conduction band to be continuous [72]. *Ab initio* approaches were also applied to the problem [73–76], but these were often limited by the lack of a common theoretical energy reference between the two materials. To overcome this limitation, multilayer calculations were used, wherein the average potential on either side of the interface is used to reference the valence and conduction bands [77], leading to the concept of a “model surface,” where a common absolute energy scale was determined from bulk calculations of different materials [78]. A further approach was also developed, considering the formation and alignment of gap states when the interface is formed [79]. While considerable effort has been made to develop a theoretical model for interfacial band alignment, no single approach is universally consistent with experimental data, and this situation is likely due to the complex chemical and morphological interactions that occur at interfaces, and especially for the more complex interfaces that are now utilized in modern technologies.

Photoelectron spectroscopy can directly probe valence-band states, allowing for a straightforward measurement of band alignment, as was elegantly demonstrated by Katnani and Margaritondo [80] in Figure 15. Si was deposited at various coverages on a clean CdS sample. At lower coverages, the valence-band maxima from both CdS and Si are clearly seen, allowing for the direct measurement of the valence-band alignment between the two materials, as well as the observation of band bending in the CdS with Si coverage. However, it is also evident that such measurements are only so straightforward when: (1) samples are deposited *in situ*, and (2) a large offset exists between the two valence bands. Kraut’s method [81] overcomes these limitations by allowing valence-band alignment measurements via the measurement of core-level shifts. This method is predicated on the fact that, for a semiconductor, the energy difference between a core level and its valence-band maximum are physically fixed, analogous to a core level and its vacuum level for a gas; thus by measuring this energy difference in reference materials, the valence-band alignment for a layered structure can be measured simply from the energy difference between the respective core levels as shown in Figure 16. At HAXPES photon energies, core levels of several buried layers can be measured, making Kraut’s method with HAXPES a widely applicable tool for band-alignment measurements.

Figure 15: Photoemission valence-band measurements of Si on CdS. Figure from [80].

Figure 16: Diagram of energy levels for semiconductors A and B and metal. Figure from [69].

For semiconductor/semiconductor interfaces, the valence-band alignment, ΔE_V , is given by:

$$\Delta E_V = (E_{CL}^A - E_V^A) - (E_{CL}^B - E_V^B) - (E_{CL}^A - E_{CL}^B), \quad (12)$$

while for metals, the Schottky-barrier height, ϕ_B is:

$$\varphi_B = (E_{CL}^B - E_V^B) - (E_{CL}^M - E_F) - (E_{CL}^B - E_{CL}^M). \quad (13)$$

Here, E_{CL}^i and E_V^i are the core-level and valence-band energies, respectively, for material 'i', and E_F is the metal Fermi level. Conduction-band alignment can then be determined from the known band gaps.

An important aspect of Kraut's method is the accurate determination of the valence-band maximum from comparison of the theoretically derived density of states with the experimental valence-band spectrum. Due to the different energy dependences of the photoionization cross sections for different electron energy levels (see above and [3,25]), the density of states must be modulated by the cross section and broadened to account for experimental effects as in Equation 11. As illustrated for the diamond valence band [82] in Figure 17. After accounting for the C 2s and 2p photoionization cross sections [3], convolution with a Gaussian (full width at half maximum of 0.3 eV to account for experimental broadening) produces a theoretical density of states that matches the experimental valence-band measurement. The valence-band maximum is found by aligning the experimental and theoretical curves. It can be seen from the inset in Figure 17 that a simple linear extrapolation would produce an erroneous valence-band maximum that is several eV lower than that determined by this procedure.

Figure 17: Theoretical partial and total density of states for the diamond valence band (a). HAXPES valence band ($h\nu = 2140$ eV) and reconstructed weighted density of states (b). See text for details. Figure from [82].

HAXPES and Kraut's method have been used for band-alignment measurements of many materials systems, including Pt and Ag contacts on diamond for high-flux beamline monitors [82],

Pt/BaTiO₃/Cr film stacks for ferroelectric tunnel junctions [83], Ge/high dielectric constant oxide interfaces [84,85], and diamond/Cu(InGa)Se₂ [86] and poly(3-hexylthiophene-2,5-diyl)/ZnO [87] interfaces for applications in photovoltaics.

Band alignment at Fe-doped SrTiO₃ (STFO) interfaces with metal contacts was investigated for applications in “memristive” devices [88]. Memristors (memory resistors) provide non-volatile memory through changes in resistance. With STFO, this is accomplished through current-induced changes in the oxygen stoichiometry, which leads to conductive oxygen-deficient filaments [89–91] to allow conduction between the top metal contact and the underlying film, in this case Nb-doped SrTiO₃ (STO). The behavior of these systems, however, can be different according to the choice of metal contact. Thus investigating the metal/STFO band alignment is imperative to reach a fundamental understanding of these systems. After deposition of a Pt electrode, the STFO was initially in a high resistivity state and shows rectifying behavior. HAXPES results showed an STFO conduction-band to Pt Fermi-level offset of 0.9 eV, suggesting a significant conduction barrier between the underlying STO and Pt. With the insertion of a thin (5 nm) Ti layer between STFO and Pt, however, the system is found to be initially in a lower resistive state and non-rectifying. With a thicker (20 nm) Ti layer, ohmic behavior is observed. In these cases, HAXPES showed no gap (within experimental uncertainty) between the STFO conduction band and the Pt Fermi level; that is, the implied barrier between STO and Pt contacts is nearly eliminated. These results suggest that charge transport in the low-resistivity cases is determined by the different alignment of the energy levels.

HAXPES was also used to probe the band alignment and band bending at the interface of STO and spinel γ -Al₂O₃ [92]. Interest in this interface has arisen due to the electrical conductivity observed at similar interfaces of insulating materials such as STO and LaAlO₃ (LAO) [93]. HAXPES studies of these interfaces will be discussed in the next subsection. This research has led to the observation of a two-dimensional electron system at the γ -Al₂O₃/STO interface [94,95]. Understanding the band alignment may help elucidate the formation of the conductive interface. Using HAXPES [92], a 0.6 eV valence-band offset between STO and γ -Al₂O₃ was found. The γ -Al₂O₃ bands were found to be flat, but a small amount of band-bending was observed in the STO, determined from peak shifts with takeoff angle. The resulting band diagram is shown in Figure 18. The band bending measured leads the STO conduction band to dip below the Fermi level, consistent with the electron confinement at the interface. This electron confinement at the interfacial STO layers leads to the observed interfacial conductivity.

Figure 18: (Color online) Band diagram for STO/ γ -Al₂O₃ system as determined by HAXPES. Figure from [92].

Novel Interfacial Properties: LaAlO₃/SrTiO₃ Interfaces

In addition to the band alignment problem just discussed, HAXPES is uniquely suited to study novel interface phenomena. An example that has been heavily studied is the formation of a thin conductive layer (or “2 dimensional electron gas”) at the interface between LAO and STO, two band insulators [93]. Conductivity only occurs when the LAO film is deposited on TiO₂-terminated STO and when it is above a critical thickness of about 4 unit cells [93,96,97]. Multiple mechanisms have been proposed to describe the conductivity seen at the interface, the earliest of which was the presence of an electronic reconstruction driven by the polar discontinuity at the interface [93,96,97]. In this model, an electric field is present in the LAO, increasing with thickness until the LAO valence band is iso-energetic with the STO Fermi level; at this point charge can flow from the LAO surface to the interface and the Ti 3d bands become populated. The electronic reconstruction may also be effected in part by off-stoichiometry related defects in the LAO film [98]. In this work it was seen that conductive interfaces only occur when the LAO film was Al-rich. First principles calculations demonstrated that interfacial defects in stoichiometric and La-rich LAO films screened the charge present due to the polar discontinuity, thereby removing the built-in potential. In the case of Al-rich LAO, however, the charge is only partially screened, leading to a (reduced) electric field in the LAO and eventual electronic reconstruction from electron-rich LAO surface states.

Alternative mechanisms for the conductivity at LAO/STO interfaces involve oxygen vacancies, either in the interfacial STO layer [99,100], or at the LAO surface [101]. In the former case, the electrons liberated from the oxygen vacancies populate the Sr 3*d* bands leading to conductivity. In the latter case, the charge liberated at the LAO surface is transferred to the interface. Another potential mechanism for interfacial conductivity involves the diffusion of ionic La into the STO layer [102], leading to a thin layer of La-doped STO, which is known to be conductive [103]. HAXPES has been applied by multiple research groups to LAO/STO systems in an attempt to elucidate the precise mechanism of conductivity. While this research has not unambiguously determined a mechanism, and in fact finds contradictory results in some instances demonstrating some of the limitations of HAXPES, it has still made significant contributions to the understanding of the LAO/STO system.

Angle-resolved HAXPES [104] was used to study the spatial distribution of the conductive layer and to estimate the carrier density from the $\text{Ti}^{3+}:\text{Ti}^{4+}$ ratio, using the Ti^{3+} as a proxy for the conductive layer. Comparing samples with different thicknesses of LAO that were prepared under different conditions, the thickness of the conductive layer was estimated to be between one and ten STO unit cells. The carrier density showed a clear increasing trend from $2.1 \times 10^{13} \text{ cm}^{-2}$ at 2 unit cells of LAO to $11.1 \times 10^{13} \text{ cm}^{-2}$ at 6 unit cells. The results were considered to be consistent with the electronic reconstruction model due to the confinement of the conductivity to within perhaps one unit cell of the interface, albeit with a lower than expected carrier density. Grazing incidence/total external reflection HAXPES [105] was also used to measure the distribution of charge carriers (below a critical angle the incident x-rays form evanescent waves along the sample surface and do not propagate into the bulk). This technique permits a highly interface-sensitive measurement. Here the Ti^{3+} distribution was determined to extend to about 12 unit cells into the STO, and a higher carrier density was found, $1.4 \times 10^{14} \text{ cm}^{-2}$. Again the results were considered to be in agreement with the electronic reconstruction model, with the consideration of both localized and non-localized Ti 3*d* electrons, which had been previously discussed in theoretical works [106,107]. Neither study, however, explicitly considered the possibility of oxygen defects, which could potentially account for the observed differences in the depth distribution of Ti^{3+} which may arise due to subtle differences in the sample processing.

HAXPES has also measured the band alignment between STO and LAO films between 4 and 20 unit cells thick [108]. A valence-band offset of $0.35 \pm 0.10 \text{ eV}$ was found for all film thicknesses. Importantly, the LAO bands were found to be flat; i.e. no electric field was observed in the LAO film, contradicting the expectation of the electronic reconstruction model. However, the results were again discussed only in relation to this model, with added considerations for photo-induced charge carriers and defects which may offset the electric field. In contrast, a small but measurable electric field exists in Al-rich LAO deposited on STO as shown in Figure 19 [109]; such a field had also been observed in cross

sectional STM [110] and electrical measurements [111]. The electric field was observed in the valence band region only. Due to the probing depth and natural resolution limits of XPS, such a small field could not be observed in the core levels, which may explain the contrast with prior measurements. No electric field was found by the authors for stoichiometric and La-rich LAO. The distributions of La, Al, and Sr with depth were also probed for the stoichiometric and off-stoichiometric films. In the stoichiometric and La-rich films, La and Al enrichment were observed at the interface and surface respectively. The Al-rich film showed a more consistent La:Al ratio throughout the LAO film. These results were found to be consistent with the off-stoichiometry defect-driven electronic reconstruction [98].

Figure 19: (Color online) Valence band of 10 unit cell LAO on STO. Theoretical valence bands reconstructed from the cross section weighted and broadened partial density of states shows the Al-rich valence band to be narrower than the stoichiometric and La-rich valence bands, while the experiment shows a broader feature, suggestive of a small electric field in the Al-rich film. Figure from [109].

While the HAXPES results described above do not definitively settle on a mechanism for the nature of the conductivity at LAO/STO interfaces, it is important to emphasize the commonalities of the measurements. First, HAXPES finds that the conductive layer is confined to the interface. Second, the built-in electric field is considerably smaller than the 0.4 eV per unit cell predicted by the simple electronic-reconstruction model [108].

D. Non-destructive depth profiling

The enhanced bulk sensitivity of HAXPES combined with the tunable photon energy of a synchrotron source provides the opportunity for non-destructive depth-dependent measurements through variable kinetic energy XPS (VKE-XPS). VKE-XPS extracts depth-dependent information from HAXPES spectra collected at different photon energies. The information depth in HAXPES with photon energies between 1500 and 15000 eV range from less than 10 nm to more than 50 nm [14]. VKE-XPS is also suitable for depth profiling of materials with non-planar geometries, as compared with angle-resolved XPS, where changes in analysis geometry can lead to shadowing or other effects not typically accounted for [112].

The VKE-XPS measurement is elegantly illustrated in the study of a buried SiO_2 layer between HfO_2 and Si [113], as displayed in Figure 20. Here the Si 1s core level was probed with photon energies ranging from 2140 eV to 3500 eV. At 2140 eV, the most surface-sensitive photon energy for this core level, the spectrum is dominated by a single peak from the oxidized interlayer. By $h\nu = 2500$ eV, bulk Si from the substrate is also observed. As $h\nu$ increases further, the signal from the substrate increases dramatically with respect to the interfacial oxide showing the increasing probe depth. From the subtle shift in the Si-oxide seen at the most surface-sensitive photon energies, the authors [113] determined that a sub-stoichiometric oxide exists at the $\text{HfO}_2/\text{SiO}_2$ interface, due to the HfO_2 layer gettering oxygen from the SiO_2 interlayer.

Figure 20: Si 1s VKE-XPS spectra of a Si/2nm SiO₂/3nm HfO₂ heterostructure. Figure from [113].

Similar VKE-XPS measurements were applied to the study of the thermal stability of InGaAs/Al₂O₃ interfaces [114]. High-mobility semiconductors such as InGaAs and high dielectric-constant oxides such as Al₂O₃ are important component materials for current and next generation metal-oxide-semiconductor field-effect transistors (MOSFETs) that power modern computers. MOSFETs built from these materials must have excellent thermal stability under expected processing conditions to avoid degradation of ultimate device behavior during processing. To study the thermal stability of high-mobility semiconductor/high-dielectric constant oxides, identical Al₂O₃ blanket films were deposited on InGaAs and annealed at various temperatures under N₂ atmosphere and studied by VKE-XPS. The use of a non-destructive depth-profiling technique such as VKE-XPS is essential in these measurements as the energetic ions in other profiling techniques may cause changes in the chemical structure of the analyzed films. HAXPES core levels were recorded for each constituent species at both surface-sensitive (2200 eV) and bulk-sensitive (4000 eV) photon energies. With the exception of the Ga 2p_{3/2} core level, peak shapes showed little variation after annealing suggesting that no chemical changes occurred. However, the Ga 2p_{3/2} core level showed increasing oxidation with increasing annealing temperature, especially at the surface-sensitive photon energy, demonstrating the interfacial oxidation of Ga.

The elemental distribution was probed by comparing the surface-sensitive and bulk-sensitive core-level intensities. Core-level intensity ratios, corrected for photoionization cross sections [3,25] and IMFPs and referenced to the intensity of either the Al or O 1s core level from the Al₂O₃ layer, are shown in Figure 21. The Ga 2p_{3/2} intensity ratio shows a clear increase with increasing anneal temperature, demonstrating the up-diffusion of Ga into the Al₂O₃ layer. A smaller increase is observed for the As 2p_{3/2}, while a hint of a decrease is observed for In 3d_{5/2}. From these trends, a model structure was developed: with deposition, a thin interlayer primarily of Ga and As oxide forms. As the film is annealed, this interlayer thickness increases, leading to the subtle attenuation of the In signal. At the highest temperatures, Ga up-diffuses further into the Al₂O₃ layer.

Figure 21: (Color online) Core-level intensity ratios ($h\nu = 2200$ eV / $h\nu = 4000$ eV). For each core level, this intensity ratio reflects the depth-distributions of the element. Figure from [114].

Quantitative depth analysis

The above analysis demonstrates the use of VKE-XPS for *qualitative* depth profiling; for *quantitative* depth profiles, modeling and statistical methods can be used. The Simulation of Electron Spectra for Surface Analysis (SESSA) software [115,116] offered by the National Institute of Standards and Technology is a powerful package for modeling of photoelectron spectra in the HAXPES energy range. SESSA contains numerous databases of relevant parameters for the simulation of HAXPES data, including IMFP's, attenuation lengths, and photoionization cross sections. SESSA simulates the trajectories of electrons considering both inelastic and elastic scattering effects and from these trajectories constructs the intensity and peak shapes for photoemission and Auger. SESSA is capable of simulating spectra for numerous sample morphologies and has been found to provide results in excellent agreement with experiment [117].

Another modeling approach [118,119] involves the consideration of the ratio of experimental peaks integrated over a sample volume (see Equation 2). This approach allows for the consideration of sample structures, such as spheres or cylinders, from the integration coordinates. For example, this approach was used to determine the structures of 3nm diameter spherical CdS/CdSe and CdSeS core/shell nanocrystals [118]. Here, the Se 3*p* to S 2*p* intensity ratio was tracked over a broad range of photon energies. A 3-layer nanocrystal model was constructed, with an inner core from $r = 0$ to r_1 , a second-alloy layer between r_1 and r_2 , and finally a surface layer between r_2 and r_3 . By fitting the model to the measured intensity ratios, it was determined that the nanostructures contained a core and single shell; i.e. $r_2 = r_3$. A similar approach, but considering two dimensional film layers, was used to determine the role of B-diffusion in CoFeB/MgO magnetic tunnel junctions [119]. B diffusion was found to be controlled by the capping Ta layer.

SESSA and other simulations can determine quantitative depth distributions from HAXPES and VKE-XPS data; however, such techniques require user input. Such user input may inadvertently lead to operator bias in model selection, especially where multiple models may produce similar simulated spectra. By applying statistical methods for selection of a depth profile model, the user input can be minimized, thereby reducing the risk of operator bias. It is important to note, however, that statistical methods do not provide the “correct” depth profile, but instead the *most likely* depth profile *given the input assumptions about the data*. The maximum entropy method (MEM) is one such statistical method which has been applied to angle-resolved XPS (see, e.g. [120–123]); it has also recently been adapted for VKE-XPS [124]. MEM works by maximizing a functional, Q , defined as:

$$Q = \alpha S - \chi^2/2. \quad (14)$$

Here χ^2 is the weighted difference between the measured and simulated data squared, and α is a regularization parameter. The entropy functional, S , is used to minimize the amount of ‘additional’ information introduced above input values, though other S functions may also be used (see for example [125]).

VKE-XPS data from 2.5 nm and 25 nm atomic layer deposited TiO₂ films on Si is shown in Figure 22. Film thicknesses were measured by spectroscopic ellipsometry prior to the VKE-XPS measurements. HAXPES spectra for Ti 2p, O 1s, C 1s, and Si 1s were collected at 2500, 3000, 3500, 4000, and 4500 eV photon energy. The core-level intensities were measured after background subtraction, and referenced to the IMFPs and photoionization cross sections. Data were collected in a ‘multiplex’ mode, so that any drifts in beam intensity were averaged across all core levels. For the 2.5 nm film, a clear increase in the Si substrate signal is observed with increasing $h\nu$ while the O signal decreases. For the 25 nm film, only subtle changes are observed with $h\nu$, due to the fact that even at the highest photon energies the TiO₂ film makes up the bulk of the analysis depth. However, a small Si signal is observed at the highest photon energies, allowing for the calculation of the depth profile. For MEM regularization, an initial model was used that consists of a homogeneous mixed C, Ti, O, and Si-O film of the thickness measured by ellipsometry on top of a Si substrate. The resulting depth profile for the 25 nm film shows the C to mainly exist at the surface, while the Si-O is fixed at the interface, as expected because the deposition was performed on un-etched Si wafers. For the 2.5 nm film, a mainly mixed film is observed, although the mixing may be due to limited depth resolution or non-planar morphology and cannot be determined from these measurements alone.

Figure 22: (Color online): VKE-XPS data for 2.5 nm and 25 nm TiO_2 films deposited on Si (top). Error bars were estimated from the signal-to-noise ratios. A maximum-entropy method algorithm was applied to the VKE-XPS data to reconstruct the concentration vs depth profiles (bottom). The dashed lines show the initial model. Figure from [124].

E. Resonant Photoemission

Resonant photoelectron spectroscopy (ResPES), the tracking of changes in photoemission or Auger peaks as the photon energy is scanned through an absorption edge, has been used to study a variety of material systems. By applying hard x-rays, deeper core levels can be analyzed; some examples can be found in Ref. [126]. Recently, ResPES has been used to study dynamical processes, and these measurements have been referred to as “core-hole clock spectroscopy” [127–129]. In this technique, the core-hole lifetime is used as an internal reference clock to study electron dynamics. The charge-transfer time scale can be studied by probing the electron resonantly excited to unoccupied state from a localized core level. The accompanying autoionization due to the core-hole decay has two channels: Raman autoionization and charge transfer. The ratio of the two channels is a measure of the charge-transfer time through a simple exponential model, and we note that the dispersive energy shift observed in resonant Auger has been used to study electron dynamics in adsorbed systems [127].

ResPES can also be used to study the fundamental physics of photoionization, such as inter-channel coupling [130]. The photoionization cross section is typically considered to be dominated by single-electron transitions, especially for deep core levels [131]; consequently, a single-particle approximation is typically used to model the photoemission processes (see e.g. [22]). However, the single-particle approximation breaks down due to electron correlations and inter-channel coupling. Changes in the photoionization cross sections above threshold have been noted [132], but the overall

“shape” of the cross sections were not tracked. Recent use of ResPES to track the Ag 3d core levels at excitation energies near the L thresholds has exposed the inter-channel coupling effects on the photoionization cross section well above threshold [130].

Accurate Ag $3d_{5/2}$ and $3d_{3/2}$ intensities from a Ag foil were measured as a function of photon energy between $h\nu = 3000$ and 4000 eV. To account for changes in x-ray flux, the intensities were normalized to a Cu $2p_{3/2}$ core line collected immediately before and after each Ag spectrum. Ag spectra collected at the L_3 and L_2 edges (3351 eV and 3524 eV respectively) and at 3450 eV are shown in Figure 23. Changes are observed in both the absolute and relative core-level intensities, and these changes are especially evident by following the intensity trends of the two spin-orbit split components: The Ag $3d_{3/2}$ intensity increases with increasing $h\nu$, while the Ag $3d_{5/2}$ first shows an increase between 3351 and 3450 eV, but then decreases between 3450 and 3524 eV. The Ag intensities were further tracked across a 1000 eV range of photon energies and compared to calculated intensities from the relativistic random-phase approximation (RRGA) that included different coupling channels. The significant structures in the cross sections were only observed when coupling with the $2p$ and $2s$ photoionization channels were included, successfully demonstrating inter-channel coupling.

Figure 23: (Color online) Ag 3d spectra collected with photon energy at the L_2 edge, between the L_2 and L_3 edges, and at the L_3 edge. Figure from [130].

Energy-loss satellite structure can also be studied by ResPES [16,133]. Photoemission satellites are typically small features that occur on the high binding-energy side of the main photoelectron transition and are a measure of the electron correlations present. The Ti satellite structure in tetravalent STO and TiO_2 has been well studied [134–140], but characterization of the satellite features has relied to a

large extent on fitting parameters from *ad hoc* theoretical models to experimental data. The fact that new theoretical approaches [140] are being developed for the characterization of these satellites demonstrates that the problem has not been satisfactorily solved.

The Ti 2*p* spectrum from STO shows two dominant spin-orbit split components that are accompanied by smaller intensity satellites each located approximately 13 eV below the main features, as seen in Figure 24. An additional satellite at approximately 5 eV binding energy relative to the main lines has been suggested, but not directly observed [136] in either the Ti 2*p* spectrum due to its overlap with the Ti 2*p* spin-orbit split component or in the Ti 2*s* spectrum due to the anomalously large Coster-Kronig width of the Ti 2*s* peak [141]. However, by using HAXPES, the Ti 1*s* transition can be measured unhindered by spin-orbit splitting, and the 5 eV satellite is clearly observed in the spectrum (Figure 24) [16].

Figure 24: (Color online) Ti 1*s* and 2*p* core levels for STO showing 5 eV and 13 eV satellite features. Figure from [16].

Measuring the Ti *K-L₂L₃* Auger line with photon energies around and above the Ti *K* edge gives direct insight into the nature of the two satellites. Figure 25 shows the primary contribution to the Auger decay collected with photon energy set to the 1*s* to 4*p* resonance and with excess energies above it. The peak is narrowest at resonance as expected [142]; at 5 eV above resonance, a high-kinetic-energy shoulder “turns on.” The position and relative intensity of this shoulder remain constant until the excess photon energy reaches the binding energy of the second satellite upon whence its intensity again increases. Above this energy, however, its intensity remains constant. The difference spectrum, shown in the inset of Figure 25, indicates that the new feature is located 2 eV higher kinetic energy relative to the main Auger line; this energy is equivalent to that measured for the Auger decay when the photon energy is set to either the 1*s* to *t_{2g}* or 1*s* to *e_g* 3*d* resonances, i.e. when the core hole is screened by a spectator electron in a Ti 3*d* orbital [16]. These observations demonstrate that the high-energy Auger feature arises from the additional screening of the core hole due to charge transfer from the oxygen ligand. Analysis of

the positions and intensities of the two satellites suggests that the 5 eV satellite is due to O $2p\ t_{2g}$ to Ti $3d\ t_{2g}$ charge transfer, while the 13 eV satellite is due to O $2p\ e_g$ to Ti $3d\ e_g$ charge transfer [16].

Figure 25: (Color online) Ti KLL Auger spectra from STO recorded with photon energy set to the Ti $1s$ to $4p$ resonance and with excess photon energies above it as indicated. Figure from [16].

IV. Future Directions

While HAXPES has emerged as a powerful tool that has general applicability to the study the true bulk and buried interface properties of complex materials systems, further advances in instrumentation are leading it into new research areas. Two examples of new HAXPES-based capabilities, time-resolved HAXPES and hard x-ray photoemission electron microscopy (HAXPEEM), increase the depth of analysis by adding new dimensions to HAXPES.

A. Time resolved HAXPES

The progress in the development of x-ray free electron lasers (FEL) is playing a significant role in the ongoing development of HAXPES. The Linac Coherent Light Source (LCLS) at the Stanford Linear Accelerator Center and the Spring-8 Angstrom Compact Free Electron Laser (SACLA) at Spring-8, amongst other FEL's, now have active experimental programs. The high-intensity, ultra-fast x-ray pulses of FEL's provide direct information in real time on the dynamics of the electronic structure of materials. As mentioned above, dynamical information such as charge transfer and ultra-fast electron delocalization has been studied by core-hole clock methods [127–129,143,144], but these measurements are limited to

the time range set by the lifetime of the core-excited states. Attempts to study dynamics of electronic structure in a laboratory environment have led to the development of the pump-probe technique known as 2-photon photoemission spectroscopy (2PPE) [145,146]. In this technique, a first laser pulse excites an electron into an intermediate state and a second pulse photo-emits the excited electron from that state. By controlling the temporal delay between the pulses, decay times have been reliably measured to a few femtoseconds. This technique, however, limits the wavelength available to the harmonics of the laser used.

The use of ultra-fast, tunable-energy FELs can overcome this limitation. However, a significant problem facing all FEL-based time-resolved XPS measurements is vacuum space-charge effects; i.e., the multi-electron emission due to the pump and probe pulses can cause both shifts and peak broadening. Significant progress, however, has been made in theoretical understanding of space charges [147,148] as recently demonstrated by time-resolved HAXPES measurement at SACLA [149]. In these measurements, an 8000 eV FEL was used to probe the vacuum space-charge effects on V 1s spectra from VO₂ and the Ti 1s spectra from SrTiO₃. Figure 26 shows a schematic illustration of the experimental design, and Figure 27 shows the extracted peak shifts and broadening of the V 1s and the Ti 1s core levels as a function of pulse energy. The peaks were fit with Voigt functions and the experimental data was compared with numerical simulations. It was observed that broadening due to space charge was less than the intrinsic core-level widths. Additionally, the possibility of modelling the space-charge effects offers the advantage of isolating these effects from intrinsic dynamics in the electronic structure.

Figure 26: (Color online) Experimental setup for time resolved HAXPES at SACLA. Figure from [149].

Figure 27: (Color online) (a) Spectral shift (b) spectral broadening of Ti 1s and V 1s as a function of FEL pulse energy. Figure from [149].

B. HAXPEEM

Photoemission-electron microscopy (PEEM) using hard x rays (HAXPEEM) is an emerging experimental technique that combines the benefits of sub-micron imaging resolution with greater depth sensitivity than available using traditional PEEM. The combination of HAXPEEM with the non-destructive depth profiling techniques discussed above should also provide semi-quantitative three-dimensional chemical- and electronic-structure maps of materials. Considering the current trends in device miniaturization and nanoscale engineering, HAXPEEM should become an integral research tool for such study.

PEEM can be operated under various spectral modes. For example, in a fixed electron-detection energy mode, the photon energy is scanned to provide chemical contrast (i.e. NEXAFS imaging). In a fixed photon-energy mode, the detector energy is scanned for chemical contrast (XPS imaging). These two modes provide different but complimentary chemical information; e.g., occupied vs unoccupied state densities, due to the different underlying spectral techniques (i.e. XPS vs NEXAFS); and indeed most PEEM systems can operate in either mode. However, in HAXPEEM it is the fixed photon-energy mode that takes full advantage of the increased bulk sensitivity of HAXPES.

Initial work in HAXPEEM has focused on the NEXAFS imaging mode [150,151]. Images were recorded of SbTe amorphous/crystalline patterned samples from recordable digital video discs (DVDs),

and the ability to distinguish the amorphous vs crystalline regions in a $200 \times 200 \text{ nm}^2$ area was demonstrated [150]. Later, using a Cr-patterned Au film, the probe depth of HAXPEEM was determined to be about ten times longer than with soft x-rays, with better than 106 nm resolution in the HAXPEEM measurement [151]. The increased depth sensitivity of HAXPEEM is due to the higher kinetic energies of the Auger transitions associated with the NEXAFS absorption as well as the measurement of the inelastically scattered electrons that have travelled farther within the sample.

The probe depth of NEXAFS-mode HAXPEEM depends on the core-level energies of the materials studied; lighter elements such as carbon and oxygen, for example, will always be more surface sensitive as their deepest Auger levels lie at lower kinetic energy. However, in XPS imaging mode, where the kinetic energy of the analyzed photoelectrons can be tuned by the incident photon energy, this limitation is not present. This mode has been developed using an electrostatic immersion lens and a double-hemisphere analyzer design [152–155]. For the imaging of high-kinetic-energy electrons, the electron optical design was modified, and a sample bias was used to define the imaged electron energy [155], as shown in Figure 28. With this design, sub- μm level imaging resolutions can be achieved.

Figure 28: (Color online) Analyzer design modified for HAXPEEM measurements. Figure from [155].

The probing of buried films was demonstrated through the analysis of a film stack consisting of 7 nm pads of Au deposited on 20 nm Fe-doped SrTiO_3 on Nb-doped SrTiO_3 [152]. Data is shown in Figure 29. The upper right inset shows a $\text{Sr } 2p_{3/2}$ image; the Au pads (lower Sr intensity) show up as dark squares. Two regions of interest are highlighted in the image: one on the Au pad and the other on the film itself. The extracted HAXPES spectra from these two regions are shown in the main portion of the figure. There is a clear difference in $\text{Sr } 2p_{3/2}$ intensity between the two regions, with the bare-film region showing significantly more intensity than that under the pad – as expected due to the attenuation from the Au overlayer. However, the Sr signal is still visible even underneath 7 nm of Au, demonstrating the applicability of this HAXPEEM method for the imaging of buried films.

Figure 29: (Color online) Extracted spectra from HAXPEEM image of Au pad deposited on SrTiO_3 and bare SrTiO_3 film. Regions of interest are shown in the top right. Sample structure shown in left inset. Figure from [152].

V. Summary

HAXPES has emerged as a technique that permits the chemical and electronic characterization of a full range of materials systems previously inaccessible to low-energy XPS. While the underlying physics of HAXPES and traditional XPS are the same, the higher photon energies used for HAXPES measurements lead to longer photoelectron IMFPs. Some care, however, must be taken in the interpretation of HAXPES spectra as non-dipole effects in the photoionization cross sections and electron-recoil effects become more important. The greater penetration depth achievable with HAXPES permits the measurement of a range of materials with length scales relevant to modern science and engineering, including the measurement of “real” samples taken directly from air with no prior surface or ultra-high vacuum preparation in addition to *in-situ* measurements of liquid/solid interfaces and of samples with capping electrodes for measurements under electrical bias. Also extremely practical is the measurement of buried interfaces and “true” bulk electronic structure. Additionally, HAXPES can be made *site* and *depth* specific through the use of x-ray standing-wave excitation. While the technique has been extensively used in these and other applications, it is still being developed into a multi-dimensional technique via time-resolved measurements and photoelectron microscopy.

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