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Probing energy landscapes in multilayer heterostructures: Challenges and opportunities

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ABSTRACT
Quantitative characterization of energy landscapes at buried interfaces is essential for assessing their functionality. This perspective highlights recent developments in reconstructing internal potential profiles based on hard x-ray photoemission experiments that have proved to be a rich source of information. We show that band-edge profiles can be reconstructed from core-level photoelectron spectra by performing a comprehensive search for the best-fit set of associated layer-resolved spectra. The use of hard x-rays allows heterostructures to be probed over length scales comparable to relevant electronic screening lengths. Significantly, this information takes our understanding of such systems to a new level that is not currently achievable using any other experimental technique.

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INTRODUCTION
Heterojunctions are active ingredients in many important devices that constitute much of our current electronics, photonics, and energy harvesting technologies. Complex layered structures consisting of metals, semiconductors, and insulators enable functionality in field-effect transistors, solar cells, light emitting diodes, solid-state lasers, and photoelectrochemical electrodes.

Knowledge of band-edge depth profiles \( E(z) \), where \( z \) is a coordinate in the off-plane direction, for these structures is of utmost importance in understanding the associated properties as these profiles determine how charges move and interact. Certain features of energy landscapes, such as band offsets and Schottky barriers, can often be determined from I-V and C-V data. However, I-V and C-V measurements do not generate detailed \( E(z) \) profiles. If a heterojunction is composed of well-understood materials, such as Group IV or Group III-V semiconductors, and the interface structures and compositions are at least qualitatively understood, then Poisson-Schrodinger (PS) modeling can be done to calculate \( E(z) \). In this simulation, a heterostructure is treated as a one-dimensional quantum well and the Poisson and Schrodinger equations are solved iteratively. However, for other functional materials of current interest, such as complex oxides and 2D materials, there are many unknowns about the pure phases and their interfaces. These unknowns include spatial distributions and properties of defects carrying nonzero electric multipoles. Without this information, PS simulations can result in irrelevant or misleading results. Thus, there is strong motivation to develop a method that will allow the energy landscape to be experimentally determined in a straightforward way.

Any viable candidate method to accomplish this purpose should (i) yield orbital energies relative to a well-defined reference, such as the Fermi level, (ii) be sensitive to all phases and functional regions in the system, and (iii) produce information-rich data from which a unique solution to the energy landscape can be reliably extracted. We propose that hard x-ray photoelectron spectroscopy (HAXPES) satisfies these conditions and, if properly interpreted, uniquely uncovers band-energy profiles for multilayer functional materials.

HOW IT WORKS
In HAXPES, hard x-rays incident on the solid of interest are absorbed by valence and core electrons as they penetrate over a scale of micrometers. The attenuation lengths (\( \lambda \)) of the resulting photoelectrons are a few to several nanometers, depending on the x-ray energy, resulting in total probe depths (defined as \( \sim 4.6\lambda \), over which 99% of the signal is generated) of several to several tens of nanometers. The advantage of HAXPES over conventional XPS is that the achievable probe depths are sufficiently large that...
In semiconductor heterostructures, there are typically discontinuous changes in the band edge energies at the buried interfaces (band offsets), and band bending can occur within the individual semiconductors, depending on the extent of charge transfer across interfaces. The measured HAXPES binding energies and line shapes for core-level photoelectrons are affected by these electronic properties, as depicted in Fig. 1. Inasmuch as core-level spectra originate at specific atoms, their binding energies and line shapes contain information about the electrostatic potential at the depth of those atoms within the heterostructure. This method enables the extraction of a set of layer-resolved spectra from the raw data which when summed reproduce the measured heterojunction spectra. The valence-band (VB) edge energy profile is then obtained by subtracting from the core-level binding energy profile the energy difference between the top of the VB and the core orbital for each material, as measured using a pure reference specimen. Finally, the conduction-band (CB) edge energy profile is obtained by subtracting the bandgap from the VB edge profile.

Now consider a specific heterostructure consisting of three materials of the form R₄B₄G₂, as shown on the left side of Fig. 2, where R (red), B (blue), and G (green) represent the different component materials, and the subscripts are the respective numbers of unit cells (u.c.). The x-ray energy is chosen to be sufficiently high that all three materials are effectively probed, the limiting factor being the resulting photoelectron attenuation lengths. If potential gradients are present (center), they can be extracted from the spectra taken from the three materials, provided the core levels do not overlap in energy. For example, the four u.c. of the blue material produce peaks of increasing binding energy and decreasing intensity in going from layers one to four (numbered 1–4 in lower right and color coded to the diagrams in the middle and on the left). The actual spectrum will be the sum of the four. The measured binding energy and peak width will be larger than what would result if all four u.c. were at the same potential, such as that of the top u.c. (upper right). As a result, the composite spectrum contains convoluted information about the core-level binding energy and thus the band-edge energy for each u.c. In order to extract the energy profiles, we developed an algorithm that performs a comprehensive search over all binding energies for each u.c. and finds the set of energies resulting in the best fit to the measured spectrum. The algorithm is based on two assumptions that are consistent with the physics of built-in potentials in semiconductors: (i) the binding energies are continuous functions of depth and (ii) they change monotonically with depth except for possible discontinuities at internal
interfaces. The process starts by assigning a reference spectrum, measured for the corresponding phase-pure material in its flat-band state, to each u.c. which is in turn assigned a randomly generated binding energy shift relative to the flat-band value. The resulting binding energies are then sorted, in either increasing or decreasing order, and reassigned to individual layers to simulate a potential that varies monotonically with depth. After attenuating the intensity of each spectrum to an extent based on the depth of its layer, the simulated layer-resolved spectra are summed and a cost function that assesses the goodness of the fit between the simulated and experimental spectra is calculated. Next, the binding energies are incrementally changed, and the process is repeated iteratively until the best fit is found. The goodness of the solution is quantified by the cost function that includes a term that ensures the continuity of the extracted built-in potential and its derivatives, in addition to the one that maximizes the goodness of the spectral fit. The search is carried out with both signs of the binding energy gradient in each phase. As a result, all conceivable binding energies for each layer are tested subject to the constraint of a monotonic dependence on depth and the uniquely best-fit set of layer-resolved spectra is found. Details of the method, sensitivity of the solution to fitting parameters, and uniqueness of the solution are discussed elsewhere.

AN EXAMPLE

The power of this method is illustrated using results for epitaxial heterojunctions of $n$-$\text{SrNb}_x\text{Ti}_{1-x}\text{O}_{3-\delta}$ (SNTO) on Si(001) grown by molecular beam epitaxy (MBE). $\text{STO}/\text{Si}$ is a prototypical oxide/semiconductor system of significant and ongoing technological and scientific interest. For example, two decades ago, $\text{SrTiO}_3$ (STO) was under consideration as a candidate high-$k$ gate replacement oxide for $\text{SiO}_2$ in Si-based MOSFETs. It was demonstrated using conventional XPS with soft x-rays that for thinner (\~{}2–3 nm) epitaxial films of STO on $n$- and $p$-$\text{Si}(001)$ that the conduction band offset is near zero, resulting in extensive electron leakage in $n$-channel devices.\cite{10,11} The spectral line shapes indicated that the bands were flat on both sides of the interface. More recently, other complex oxide systems, such as $\text{SrTiO}_3/\text{LaAlO}_3$ interfaces, have been integrated with doped Si to realize new functionalities.\cite{18}

Here, transport measurements for thicker (12 nm) films of $\text{STO}$ and SNTO on undoped Si(001) with $x$ up to 0.2 reveal the presence of a high-mobility hole gas at and above room temperature. Films with greater thickness or higher $x$ value either do not exhibit a hole gas or exhibit a hole gas with a much weaker signature in transport. Conventional XPS cannot probe such a deeply buried interface because the probe depth is less than the film thickness. Interestingly, HAXPES data reveal complex core orbital line shapes in both the SNTO and the Si that are normally associated with extensive secondary phase formation.\cite{19} However, three other analytical techniques [reflection high-energy electron diffraction, x-ray diffraction, and high-resolution scanning transmission electron microscopy (STEM)] indicate that these films are phase pure and well ordered and that the interface is very well ordered, with no evidence of secondary interface phases. Rather than indicating poorly ordered, multiphase materials, these unusual HAXPES line shapes reveal charge distributions caused by large electric fields.

![FIG. 3. Fitting of HAXPES spectra for a 12 nm $n$-$\text{SrTiO}_3$/$\text{Si}(001)$ heterojunction: best-fit layer-resolved Si 2p and Ti $^{4+}2p_{3/2}$ spectra (left and upper right), composite best-fit spectra overlaid with measured heterojunction spectra (center), and resulting band-edge profiles (lower right). Adapted from Ref. 15.](https://scitation.aip.org/content/aip/journal/aplm/7/11/10.1063/1.5129155)
at the interface and across the film not seen for thinner films in doped Si.

We came to this conclusion after the band-edge profiles in the SNTO and Si obtained using the Ti$^{4+}$ 2p$_{3/2}$ and Si 2p HAXPES peaks, respectively. The results for $x = 0$ are summarized in Fig. 3. The best-fit families of spectra are shown topographically on the left and in 3D in the upper right. When summed, these composite spectra yield excellent fits to the heterojunction spectra, as seen in the center. The band edge profiles are plotted in the lower right. The band offsets were determined by taking differences in band-edge energies directly at the interface. The sharp decrease in band energy with the valence band maximum (VBM) cutting across the Fermi level on the Si side near the interface explains and locates the hole gas. The large built-in potential in the SNTO near the interface is enhanced by electron transfer from ionized O donors in the Si which diffused from the bulk of the Czochralski-grown Si and diffused from the STO during MBE growth. Significantly, the Poison-modeling of the potential in the Si near the interface based on the oxygen atom distribution measured using $^{18}$O time-of-flight secondary ion mass spectrometry yields the same results as the Si 2p modeling. Likewise, the Poison-Schrodinger modeling of the potential in the STO based on the carrier concentrations measured by the Hall effect produces results very similar to those from the Ti$^{4+}$ 2p$_{3/2}$ modeling, including a maximum in the itinerant electron concentration of $\sim 1.6 \times 10^{22}$ cm$^{-3}$ (one electron per u.c.) directly at the interface, consistent with the apparent presence of reduced species in the Ti 2p$_{3/2}$ and Nb 3d spectra. The HAXPES results are thus fully consistent with the transport data. A similar investigation has been carried out for the n-STO/p-Ge(001) heterojunction, yielding valuable insights into the photoelectrochemical properties of this system.

PATH FORWARD

This method can be used to probe the energy landscape for any structurally and compositionally well-defined heterostructure for which the conductivity is sufficiently high that HAXPES can be carried out without deleterious charging-induced binding energy shifts. Such measurements would be very useful for systems comprising materials and interfaces with incompletely characterized defect densities for which the Poison–Schrodinger modeling is insufficient as the sole means of determining the band-energy profiles. Examples include ferroelectric materials in which internal electric fields are present when the material is poled, modulation doped structures in which the spatial separation of carriers from their source atoms creates notched potentials that confine the carriers, and photoactive materials in which light-generated electrons and holes are thought to be responsible for defect formation that affects performance. In all cases, knowledge of the depth dependence of the built-in potential(s) and the associated time evolution would be invaluable in gaining detailed understanding of the electronic structure.

This method can also be used to probe more complex systems. For example, if the interface undergoes atomic mixing, the interfacial region becomes a new phase with a composition that is distinct from that on either side, as well as being compositionally graded in the direction normal to the interface plane. Decomposition of HAXPES data over atomic planes may yield information on the energy landscape within such phases provided the effects of potential gradient and changing chemical environment can be separated. Likewise, if multiple buried interfaces are present, HAXPES should be a rich source of information on built-in potentials and band offsets at each interface. We note that for the special case of superlattices, the closely related techniques of standing-wave XPS and HAXPES are powerful for determining these electronic quantities.

There are at present no other experimental methods that yield the kind of detailed, quantitative information about heterostructure energy landscapes that can be extracted from HAXPES in a non-destructive way. This attribute makes this technique highly complementary to standard p vs T, Hall effect, and I-V transport measurements. TEM holographic tomography has been used to generate three-dimensional maps of electrostatic potentials at the nanoscale as well as potential profiles along specific probe beam trajectories across Si p-n junctions.$^{22,23}$ Additionally, differential phase contrast scanning transmission electron microscopy (STEM) has been shown to be sensitive to electric fields at specific atoms.$^{24}$ However, in all cases, destructive techniques must be used to prepare samples for imaging. HAXPES uniquely yields accurate lateral-area-averaged $E(z)$ profiles without sample damage that can be used to assess the charge-transfer properties of epitaxial heterostructures. Any combination of materials can be probed provided the multi-layer system is sufficiently conductive to measure HAXPES without charging. The presence of defects, even in significant concentrations, does not preclude the use of this method. In fact, the effects of defects, which are often difficult to ascertain using other methods, can be understood from the electronic properties of the system as determined by HAXPES, precisely because of the high degree of sensitivity of the HAXPES probe to all parts of the heterostructure. HAXPES spectra and the corresponding reconstructed band-edge profiles can then be linked to the synthesis and processing conditions in order to enable predictive synthesis of functional multilayered structures.

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