Reliability of X-ray Photoelectron Spectroscopy for Investigating Schottky Barriers at the Metal–Semiconductor Interfaces

João Fonseca , Borja Caja-Muñoz , Archit Dhingra *

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Perspective

Reliability of X-ray Photoelectron Spectroscopy for Investigating Schottky Barriers at the Metal–Semiconductor Interfaces

João Fonseca [1], Borja Caja-Muñoz [2] and Archit Dhingra [1,3,*]

[1] Institut de Ciència dels Materials de la Universitat de València (ICMUV), University of Valencia, Carrer del Catedrátic José Beltrán Martinez, 2, 46980 Paterna, Valencia, Spain

[2] Materials Science Institute of Madrid (ICMM/CSIC), Cantoblanco, E-28049 Madrid, Spain

[3] Instituto Madrileño de Estudios Avanzados, IMDEA Nanociencia, Calle Faraday 9, 28049 Madrid, Spain

* Correspondence: archit.dhingra@imdea.org

Abstract: Owing to the global incentives targeted towards the advancement of semiconductor science and technology, the importance of a reliable method for the fundamental characterization of the interface between metals and low-dimensional semiconductors cannot be emphasized enough. For decades now, X-ray photoelectron spectroscopy (XPS) has been relied upon rather heavily when it comes down to investigating the band-bending, and hence the likelihood of a Schottky-barrier formation, at the resulting interfaces. However, the true extent to which the usually reported analyses of XPS measurements, attempting to unravel the true nature of metal–semiconductor interfaces, can be taken without a grain of salt is questionable at best. Therefore, in this article, a conceptual advance aiming to alter the status quo pertaining to the use of XPS for the aforementioned studies is presented.

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As is now well-understood, a solid understanding of the chemical and physical phenomena dictating the metal–semiconductor interfaces (MSIs) is imperative for an unerring realization of semiconductor devices [1,2]. Schottky–Mott rule, in its crude form, predicts that interfacing a high work function metal with a low work function n-type semiconductor will result in a Schottky barrier at the MSI [3,4]. Conversely, a Schottky barrier can also be expected at the interface formed between a low work function metal and a high work function p-type semiconductor [5,6]. While the existence of such barriers is a requirement for some device applications [7], it can be undesirable for others [1,8]. Therefore, selecting the right combination of metals and semiconductors for the desired application necessitates an unerring characterization of the MSI of interest. This is where X-ray photoelectron spectroscopy (XPS) comes in handy: it is often used for a systematic investigation of the MSI wherein a series of metal-thickness dependent core-level photoemission spectra are collected and analyzed [2,6,9–14], and based on the metal-coverage dependent changes in the core-level binding energies, or lack thereof, the presence (or absence) of Schottky-barrier at the MSI is deduced [2,6,11–15]. Besides such metal-thickness dependent spectroscopic measurements (see refs. [2,11–20] for specific examples of clear signatures of band bending in obtained photoemission spectra), examining the electrical transport characteristics of electronic devices comprising the same metal–semiconductor assembly is another viable way for experimentally deciphering the true nature of interfacial phenomena at the MSI.

However, as is well-established, the simple Schottky–Mott model is anything but correct as it usually fails to explain the experimentally observed phenomena at the MSI due to multiple reasons discussed elsewhere [2,9,21] and in the following paragraph. This should not come off as surprising since ideal theoretical models seldom help explain the experimental data entirely; nevertheless, this

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gives rise to a question of paramount importance, which now appears to be the elephant in the room. The all-important question is: can one always expect the results of XPS to show a clear correlation with the electrical transport measurements when studying a given MSI? Here, we intend to answer the above-mentioned question through a rigorous, multifactored, argument founded on the combination of fundamental interfacial physics and chemistry.

According to the simple Schottky–Mott model, when a high work function (Φ_M) metal is interfaced with a low work function n-type semiconductor (Φ_N) it leads to transfer of charges across the interface. This charge transfer, which is purely physical in nature, continues until the Fermi levels (E_F) match (top panel of Figure 1a), resulting in a Helmholtz double layer due to induction of charges at the interface. So, in an ideal world free from any interfacial chemical interactions and complete electrical isolation from the ambience, the height of the n-type Schottky barrier ($\Phi_{SBH\text{-}N}$) would be the difference between the work function of the metal and the electron affinity of the n-type semiconductor (χ_N), i.e., $\Phi_{SBH\text{-}N} = \Phi_M - \chi_N$ [21,22]. Likewise, the height of the p-type Schottky barrier ($\Phi_{SBH\text{-}P}$) occurring at the interface between a low work function metal and a high function p-type semiconductor (Φ_P), under the ideal conditions (bottom panel of Figure 1a), would be the difference between the work function of the metal and the ionization energy of the p-type semiconductor (IE_P), i.e., $\Phi_{SBH\text{-}P} = IE_P - \Phi_M$ [21,22]. In the real world, however, things are way far away from the Schottky–Mott limit and these watered-down, generic, expressions for calculating the Schottky barrier heights fail in more than aspect as metal-induced gap states [23–25], quasi-bonding-induced gap states [26] and interfacial dipole due to the difference between Φ_M and Φ_N (or Φ_P) weigh in [9,21]. It must also be noted that since the cause behind the formation of the obtained double layer at the MSI is purely physical, in principle, it can be undone by getting rid of the accumulated charge at the MSI.

The ideal Schottky–Mott limit considers the metals and semiconductors to be semi-infinite but in reality none of these systems are semi-infinite, and since the dielectric constant of any given metal is extremely high, the charges accumulated at the interface (on the side of the metal) will redistribute themselves and accumulate at the surface of the metal far from the MSI. And this would be true as long as the metal–semiconductor assembly is electrically isolated. However, this may not always be the case when the metal contacts are thermally evaporated on top the semiconducting material for in situ XPS analysis, as the evaporated contacts might form thin blankets that will eventually establish good electrical contacts with the spectrometer. This is an extremely important point to consider as the samples and the spectrometer are usually grounded, with their Fermi levels aligned (see Figure 1b), during a standard XPS measurement [27]. In other words, depending on the kind of metal being evaporated on the surface of the semiconductor, the surface energy of the evaporated metal, and the degree of the coalescence of its islands, the band-bending and the expected Schottky barrier may disappear completely as the deposited metal makes a proper contact with the sample plate (as can be inferred from the green curves in Figure 3 of ref. [14]). When the thickness of the Au contact in Figure 3 of ref. [14] is increased to 0.8 nm, the binding energy of the S 2p and Zr 3d core levels return to their original values (i.e., the values in the absence of thermally evaporated Au on top of ZrS_3). This phenomenon would imply that the Schottky-barrier has vanished, and thus expecting an Ohmic Au/ZrS_3 interface would be a reasonable expectation. Nonetheless, the device characteristics reveal that the Au/ZrS_3 is far from Ohmic [14]. Therefore, here, it is fair to say that had the device measurements in ref. [14] been absent, the chances of conveying the true character of the Au/ZrS_3 interface, in an unequivocal manner, would have been low.

Moreover, due to the size of nanomaterials, which are being extensively investigated for their promising applications, the probability of occurrence of such a phenomenon is amplified even for lower metal thicknesses than usual. Therefore, adding extra complexity to the analysis of the metal thickness-dependent XPS spectra taken to unravel the nature of the MSI formed between a given metal and the nanomaterial of interest. Another crucial factor that cannot be overlooked, and adds further ordeal to the analysis of the metal thickness-dependent XPS, is the uncompensated charge in the semiconductor lattice resulting as a direct consequence of charge transfer across the MSI. The presence of uncompensated charge in the semiconductor lattice, right at the MSI, will strongly alter

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χ (and *IE*) of the semiconductor at the MSI. Such an influence of Fermi-level alignment on the electronegativity and ionization energy of the semiconductor will, as one may expect, manifest itself as enhanced likelihood of interfacial chemical interactions at the MSI (as can be easily deciphered from [2,5,14,15,28]). Analysis of the metal-coverage dependent XPS spectra could be hindered further in case one or more core levels of any of the elements, comprising the material of interest, overlap with any of the core levels of the thermally evaporated metal contact [2,18]. This is not all, because when it comes to analyzing core-level XPS spectra of metals, the databases referred for charge referencing purposes can be highly misleading as is reflected by a sizeable spread of ~3 eV in the reported binding energy values of a given core-level [29]. Elaborately speaking, depending on the spatial and temporal coordinates of the conducted XPS experiments, the reported values of binding energy for a certain metallic core-level can vary by as much as 3 eV [29]. Thus, any attempt aimed towards extracting a complete fundamental understanding of the MSI solely through the analysis of the metal thickness-dependent XPS data is inadvisable owing to misleading XPS databases [29], and a myriad of cumbersome parameters whose knowledge prior to the data analysis is indispensable.

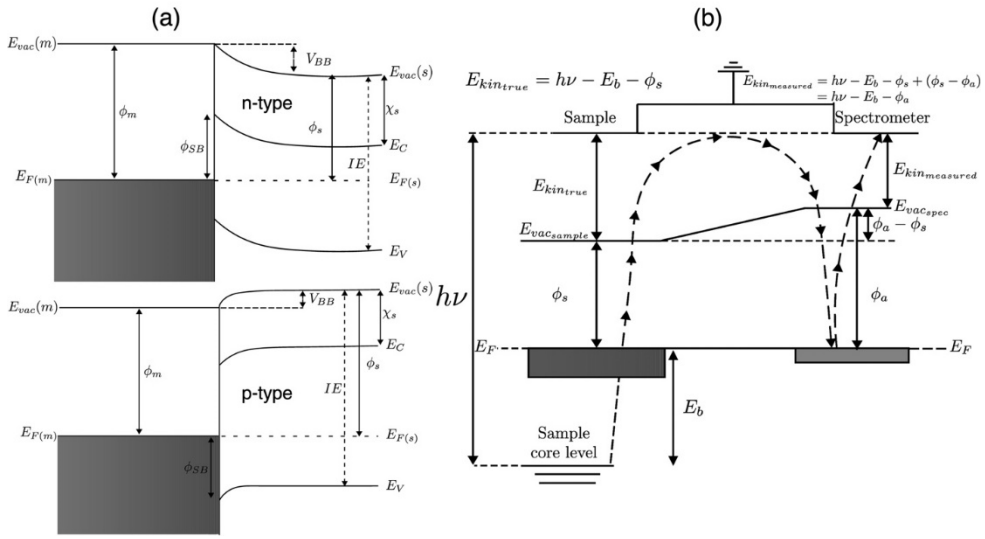

Figure 1. (a) Band diagrams illustrating Schottky-barrier formation at the metal/n-type semiconductor interface (top panel) and the metal/p-type semiconductor interface (bottom panel) within the Schottky–Mott limit. (b) General band diagrams showing energy level alignment for a sample in good electrical contact with the sample. All the important physical parameters depicted in these diagrams are self-explanatory.

Nonetheless, there does exist a viable route to outmaneuver this scenario in order to look at the Schottky barriers at the MSI. This route involves fabricating three-terminal field-effect transistors (FETs) with the semiconductor of interest as the channel material [2,11–16,18,30] (schematic shown in Figure 2) and measuring the current–voltage characteristics (I–V characteristics) at zero gate bias (i.e., $V_G = 0$ V). Maintaining $V_G = 0$ V, while the drain-to-source voltage (V_{DS}) is changed, ensures that no additional states are added to the E_F. Hence, the MSI can be studied and the interfacial phenomenon can be eventually analyzed with relative ease, without any external perturbation to the intrinsic states at the MSI (various elaborate examples demonstrating the characterization of MSIs via this approach are contained in [2,5,11–16,18,30,31]). For a purist, if a Schottky barrier does exist at the MSI it will manifest itself as a double Schottky barrier [32–35] in the I–V measurements of the FET based on the semiconductor of interest. Finally, for further clarification, we would like to add that the reason why XPS results may not always correlate with electrical transport measurements is because, sooner or later, the thermally evaporated contacts establish good electrical contacts with the spectrometer (as described in the preceding paragraph and can be reckoned from [2,14,31]). Therefore, during the XPS measurements the metal–semiconductor assembly is not electrically isolated from its surroundings anymore. However, in the case of FETs, the metal–semiconductor

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assembly on top of the dielectric oxide is, by definition, electrically isolated. Another noteworthy difference between the XPS-assisted characterization and electrical characterization of the MSI is that they are essentially two quite different worlds to begin with, as the first method of characterization would generate an immense number of charges unlike the latter. And if the surface of the semiconductor of interest is highly insulating then the eventual attempt of decoupling the effect of surface charging effects [29,36], which result in shifting of core-level photoemission spectra towards higher binding energies, from the actual band bending would be anything but trivial.

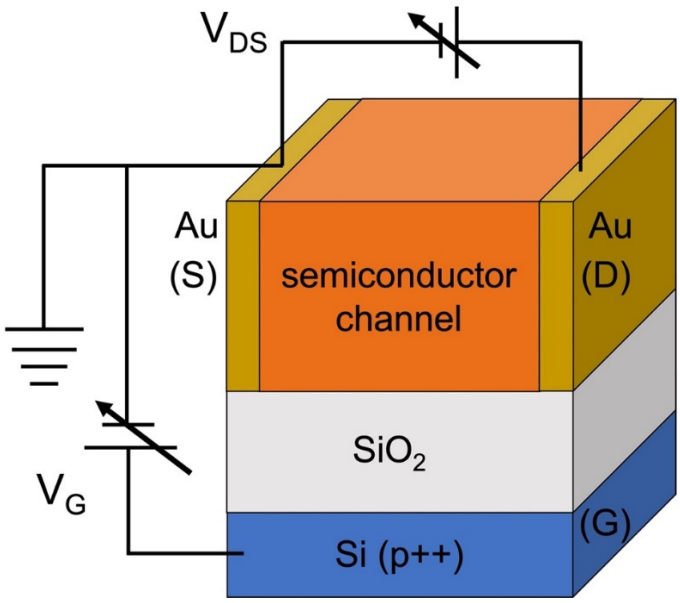

Figure 2. General schematic of a three-terminal FET with SiO_2 as the gate oxide, and Au contacts.

In conclusion, it is evident that, for decades, the photoemission community all across the globe has been exploiting the strengths of XPS in order to gather fundamental physical and chemical insights into the metal–semiconductor interfaces. But just because something is a longstanding tradition does not make it flawless. Therefore, since not all the parameters required for accurate analyses of the metal-thickness dependent XPS data (obtained for the MSI of interest) are known a priori, its standalone use for such studies is discouraged. To circumvent a plethora of complexities that one may encounter while using core-level photoemission spectroscopy to understand the MSI [14], characterization of the MSI via electrical transport measurements is recommended for extraction of unambiguous information about the same. Especially, if the eventual goal is to fabricate semiconductor-based electronics, there is all the more reason for the device transport measurements to take the center stage for the investigation of the MSI, relegating metal-thickness dependent XPS to a secondary position. Since the research in the area of semiconductors is currently transcending multiple science and engineering communities, the discussions presented herein are bound to alter the global status quo pertaining to semiconductor science and technology.

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