Band offsets in transition-metal oxide heterostructures
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Abstract
We measured valence band offsets in Ta$_2$O$_5$–WO$_3$, Ta$_2$O$_5$–Nb$_2$O$_5$ and WO$_3$–Nb$_2$O$_5$ heterostructure couples by in situ x-ray photoelectron spectroscopy, immediately following the bi-layer growth in ultra-high vacuum. Conduction band offsets were estimated using the measured valence band offsets in conjunction with the literature values for the respective band gaps. The offsets between Ta$_2$O$_5$ and WO$_3$ and between Ta$_2$O$_5$ and Nb$_2$O$_5$ layers were strongly asymmetric, with 0.8–1.1 eV (0.1–0.2 eV) barriers for the conduction (valence) bands, depending on the particular couple and the stacking sequence. Such asymmetry can be very useful in switching devices.

Online supplementary data available from stacks.iop.org/JPhysD/46/295303/mmedia

(Some figures may appear in colour only in the online journal)

1. Introduction
Band offsets have been a critical issue in many types of electronic, optoelectronic and sensing devices, be it in the field of metal-oxide-semiconductor (MOS) technology [1–8], photovoltaics and solar cells [9–17], photochromism [18], photochemistry and catalysis [19–22], gas sensing [23], etc. Recently, significant performance improvements of resistive memory switches, based on transition-metal oxides (TMOs), have been reported in devices fabricated as stacked metal/oxide [24] and oxide/oxide heterostructures [25–27]. In particular, stacking tantalum pentoxide (Ta$_2$O$_5$), which had already demonstrated many desirable resistive switching properties [28–32], with other tantalum oxide phases has reduced switching current, increased endurance (up to 10$^{12}$ cycles) [26], and stabilized the switching mode to bipolar operation [25]. Stacking heterogeneous oxides of two different metals, for example Ta and Ti, has dramatically increased the nonlinearity of the current–voltage ($I$–$V$) characteristics of tantalum oxide memristors in the low resistance state (LRS), which is important for limiting half-select current in a passive crossbar memory application [27]. Thus, understanding the electronic properties of TMO heterojunctions is becoming important for a complete picture of the device physics of an oxide-based memristor. Present models are based on simple Ohmic and Schottky contacts, with the oxide heterostructure stack represented as resistors in series [26, 27]. A first step in improving the understanding of electronic transport in TMO heterostructures is to measure the valence and conduction band (CB) offsets at the interfaces between two oxides.

Here we present valence band offsets measured using photoemission between pairs of TMO materials that are commonly used for resistive switches, namely sputtered layers of amorphous Ta$_2$O$_5$, WO$_3$ and Nb$_2$O$_5$. We have found highly asymmetric offsets, with the barriers for electrons markedly higher than those for the holes, both in WO$_3$/Ta$_2$O$_5$ and Nb$_2$O$_5$/Ta$_2$O$_5$ heterostructures. Slight variations of these values were measured in the inversely ordered, i.e. Ta$_2$O$_5$/WO$_3$ and Ta$_2$O$_5$/Nb$_2$O$_5$, stacks.

2. Experimental
The band offsets were measured by photoemission using the method developed by Kraut et al [33, 34], and widely adopted as a standard ever since [10–14, 35]. The method is based on
Figure 1. Precise determination of the valence band maxima (VBM) for the thick individual Ta$_2$O$_5$, Nb$_2$O$_5$ and WO$_3$ films.

x-ray photoelectron spectra (XPS) acquired from a bi-layer, grown with a thick bottom layer, and the top layer just thick enough to produce a sufficiently intense signal, yet thinner than the photoelectron escape depth of 2–4 nm, so that the both top and bottom layers are sampled by XPS. First, the binding energy (BE) of the valence band maximum (VBM) of each material was precisely determined from the intersection of the extrapolated VBM leading edge with the base line (figure 1) in spectra from thick films. Second, the BE difference between each VBM and the shallowest core level (CL) was measured ($\Delta E_{CL-VBM}$), as shown in figure 2, and finally the band bending upon contact at a bi-layer heterostructure, as expressed through the BE difference between the respective CL peaks of the top and bottom layers ($\Delta E_{CL}$) (figure 3) was determined.

The Ta$_2$O$_5$, WO$_3$ and Nb$_2$O$_5$ films were RF-sputtered in an AJA International, Inc magnetron sputtering system from elemental Ta, W and Nb targets, respectively, onto commercially available 110 nm SiO$_2$/p-Si(0 0 1) substrates, with 150 W. The chamber pressure was dynamically controlled to $\sim 8 \times 10^{-8}$ mbar. All the stacked bi-layers were deposited at room temperature. Immediately after the deposition, the films were transferred under UHV into the analysis chamber, an Omicron Nanotechnology, GmbH system ($6 \times 10^{-10}$ mbar base pressure) with XPS and Auger electron spectroscopy (AES). XPS analysis employed monochromated x-rays from an Al anode (1486.7 eV). The absolute BE scale of the spectrometer was calibrated by adjusting the spectrometer work function on Au 4f$_{7/2}$ (BE = 83.98 eV) and Ag 3d$_{5/2}$ (BE = 368.26 eV) spectral lines. The spectral resolution was determined by measuring the full-width at half-maximum (FWHM) of the same lines to yield $\sim 0.6$ eV at a 15 eV pass energy and $\sim 1.0$ eV at 50 eV.

The spectra were normalized to eliminate inherent sample-to-sample intensity variations and some, particularly for the more resistive samples, were also adjusted in BE to compensate for charging-induced shifts, by fixing the O 1s peak at 530.9 eV.
and Lorentzian (GL) functions (combination of a tail modifier function with a GL peak shape was necessary to fit Nb–O samples to correct for the Shirley asymmetry), to obtain precise BE values of the core peaks.

3. Results and discussion

The VBM determination for the three individual oxide layers is shown in figure 1, where the entire VB for each is shown in figures 1(a), (c) and (e), and the high-resolution extrapolation of the linear portion of the leading edge to the baseline in figures 1(b), (d) and (f). The so measured VBM values were 3.0 ± 0.1 eV for Ta2O5 and Nb2O5, and 2.7 ± 0.1 eV for WO3. The CL peak maxima were precisely determined by fitting, and yielded 26.4 eV for Ta5+ 4f7/2 (figure 2(a)), 35.6 eV for W6+ 4f7/2 (figure 2(c)) and 207.6 eV for Nb5+ 3d5/2 (figure 2(e)). Thus the resulting $\Delta E_{\text{CL-VBM}}$ was accordingly 23.4 eV (figure 2(b)), 32.9 eV (figure 2(d)) and 204.6 eV (figure 2(f)). $\Delta E_{\text{CL}}$ in a Ta2O5/WO3 heterostructure was measured to be 9.4 eV (figure 2(a)), and 9.6 eV in WO3/Ta2O5 (figure 3(b)). Similarly, $\Delta E_{\text{CL}}$ in a Ta2O5/Nb2O5 heterostructure was 181.0 eV (figure 3(c)), and 181.3 eV in Nb2O5/Ta2O5 (figure 3(d)), and 171.6 and 171.8 eV in WO3/Nb2O5 and Nb2O5/WO3, respectively (figures 3(e) and (f)). Comparing, for example, heterostructure BEs in figures 3(a) and (b) to those of the individual oxides in figures 2(a) and (c), we see that upon contact in a Ta2O5/WO3 stack, the WO3 bands bent downwards by 1.1 eV, and those of Ta2O5 by 0.9 eV, whereas in the WO3/Ta2O5 configuration (figure 3(b)) the WO3 bands did not change at all, while those of Ta2O5 bent upwards by 0.4 eV. Using these data, the VB offset in a WO3/Ta2O3 heterostructure is

$$\Delta E_V (\text{WO}_3/\text{Ta}_2\text{O}_3) = [\Delta E_{\text{CL-VBM}} (\text{Ta}_2\text{O}_3) + \Delta E_{\text{CL}}] - \Delta E_{\text{CL-VBM}} (\text{WO}_3)$$

$$= [(26.4 \text{ eV} - 3.0 \text{ eV}) + (35.6 \text{ eV} - 26.0 \text{ eV})]$$

$$- (35.6 \text{ eV} - 2.7 \text{ eV}) = [23.4 \text{ eV} + 9.6 \text{ eV}]$$

$$- 32.9 \text{ eV} = 0.1 \text{ eV}$$

CB offsets, $\Delta E_C$, are best obtained using inverse photoemission, but are often estimated with the aid of the measured $\Delta E_V$ and the literature values for the relevant band gaps ($E_g$) [10, 35]. The most frequently quoted values are, $E_g (\text{Ta}_2\text{O}_5) = 4.2 \text{ eV}$ [36–38], $E_g (\text{WO}_3) = 3.3 \text{ eV}$ [18, 21, 23], $E_g (\text{Nb}_2\text{O}_5) = 3.2 \text{ eV}$ [19, 39, 40], although they may vary as a function of the preparation method and the resulting oxide’s state and structure (bulk versus thin film, amorphous versus crystalline, etc). Our recent spectrophotometric band gap measurements in the ultraviolet–near infra-red range (UV-Vis-NIR, see supplementary information stacks.iop.org/JPhysD/46/295303/mmedia), on the oxide layers identical to those shown in this work, are in excellent agreement with the above quoted figures. Therefore, in the WO3/Ta2O3 example,

$$\Delta E_C (\text{WO}_3/\text{Ta}_2\text{O}_3) = [E_g (\text{Ta}_2\text{O}_3) + \Delta E_V] - E_g (\text{WO}_3)$$

$$= [4.2 \text{ eV} + 0.1 \text{ eV}] - 3.3 \text{ eV} = 1.0 \text{ eV}.$$ The derived flat-band heterostructure diagrams are shown in figure 4 (with all offsets marked as positive, for the sake of simplicity). In both cases, $\Delta E_C$ and hence the barrier for electrons are about 10 times larger ($\sim 1.0 \text{ eV}$) than the $\Delta E_V$ barrier for holes. Although the actual asymmetry may be smaller, if the lowest known $E_g$ values are used rather than the canonical ones, it will still be considerable. While such asymmetry is undesirable in, for example, MOS devices, where leakage of both electrons and holes should be avoided, it can be a feature for resistive switching devices, where such asymmetry may have different effects on the low- and high-resistance states and induce an appropriate non-linearity. The barrier directions were identical in both cases, i.e. blocking electron tunneling from WO3 or Nb2O5 into Ta2O5. The offsets slightly vary when the stacking order is reversed, e.g. in a WO3/Ta2O3 stack $\Delta E_C = 1.0 \text{ eV}$ and $\Delta E_V = 0.1 \text{ eV}$, whereas in a Ta2O3/WO3 stack $\Delta E_C = 0.8 \text{ eV}$ and $\Delta E_V = 0.1 \text{ eV}$. In addition, while the $\Delta E_C$ direction in Ta2O5/WO3 and Ta2O3/Nb2O5 is no different from that in the WO3/Ta2O3 and Nb2O5/Ta2O3 stacks, the $\Delta E_V$ direction is reversed, because upon deposition sequence reversal the heterojunctions change their character from type I (straddling) to type II (staggered) gap.

The small observed VB offsets are straightforwardly understood in the framework of a simple ‘common anion’
Since all three oxides share the same anion (oxygen), and since the VB is predominantly related to anionic states (O 2p band in this case), their heterostructures are expected to exhibit very small VB offsets. However, a more quantitative evaluation of the band offsets using oversimplified models, such as the Anderson rule based on a textbook definition of a heterojunction between two ideal semiconductors (SC/SC) in terms of the difference in electron affinities (Δχ) and band gaps (ΔE\text{g}), fails to predict the observed values. For example, since it postulates ΔE_C = Δχ, and the electron affinities of the three oxides are almost identical, 3.2–3.3 eV (though, just like the band gaps, may vary depending on the preparation method and the resulting state and structure [41–49]), it predicts negligible CB offsets. Consequently, the VB offsets should be practically equal to the band gap differences (ΔE_V = ΔE_g - Δχ = ΔE_g - ΔE_C ≈ ΔE_g), namely ~1 eV at least in Ta_2O_5 and WO_3 (ΔE_g = 0.9 eV) and Ta_2O_5 and Nb_2O_5 (ΔE_g = 1.0 eV) couples, contrary to the observed here. For the same reason, discrepancies arise when comparing the band bending values from figure 4 to those calculated from the built-in potential, defined as the work function difference between the two SC, which, in the framework of the same ideal model of intrinsic SCs with the Fermi levels lying in the respective mid-gaps, amounts to V_{bi} = (E_{g,A} + 1/2 + χ_A) - (E_{g,B} + 1/2 + χ_B).

Anderson rule can only work in an ideal coherent heterojunction, with a perfect lattice match between the two SCs. Once such match is lacking, the presence of defects, such as dislocations and dangling bonds, and/or strains at the interface may introduce states in the band gap, even if there are not any in the individual SCs. As was pointed out by Tersoff, such surface or interface states are analogous to metal-induced gap-states (MIGS), in the sense that they generate an interface dipole, which tends to affect the band lineup [50]. Thus the so-called ‘branching point’, E_B, lying closer to CB or VB, becomes the dominant parameter [50, 51], rather than the canonical mid-gap Fermi energy, E_F, which
will be now pinned to $E_B$. In our case, not only there are no epitaxial or even commensurate relationships between two crystals, but the interface is between two amorphous oxides, which implies complete disorder and vast amount of defects bound to create states in the gap of a heterojunction (see the effect of copper concentration at the CdS/Cu(In,Ga)S$_2$ interface on the junction band offsets [11, 12]). Moreover, the situation is likely to be further exacerbated by a plausible reduction of one oxide member of a bi-layer by the other (with a higher affinity to oxygen, e.g. WO$_3$ by Ta$_2$O$_5$), which may promote the formation of Schottky-like barrier and affect the band lineup yet again. The latter may have a dramatic effect on resistive switching, because application of a forward bias would promote transition to a LRS, whereas reverse bias would do the opposite. Finally, the XPS-based method of band offset determination used in this work, based on the original work of Kraut et al [33, 34], does not take into account possible band bending due to charging, which may affect to some extent the core-level energy difference, $\Delta E_{CL}$.

4. Conclusions

In summary, we measured band offsets between three important binary transition-metal oxides. The offsets are very asymmetrical, with $\sim 10:1$ ratio of conduction to valence band offset ratio. These results are well corroborated by the common anion rule, though quantitative derivation of the band offsets is complicated by the likely surface and interface states, and may have important implications in many technological areas, in particular in the field of resistive-switching memory devices.

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