**Electrical characteristics of interfacial barriers at Metal – TiO2 contacts**

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**Abstract:** The electrical properties of thin TiO2 films have recently been extensively exploited towards enabling a variety of metal-oxide electron devices: unipolar/bipolar semiconductor devices and/or memristors. In such efforts, investigations on the role of TiO2 as active material have been the main focus, however, electrode materials are equally important. In this work, we address this need by presenting a systematic quantitative electrical characterization study on the interface characteristics of Metal-TiO2-Metal structures. Our study employs typical contact materials that are used both as top and bottom electrodes in a Metal-TiO2-Metal setting. This allows investigating the characteristics of the interfaces as well as holistically studying an electrode’s influence to the opposite interface, referred to in this work as top/bottom electrodes interrelationship. Our methodology comprises the recording of current-voltage (I-V) characteristics from a variety of solid-state prototypes in the temperature range of 300-350 K and by analysing them through appropriate modelling. Clear field and temperature dependent signature plots were also obtained towards shinning more light on the role of each material as top/bottom electrodes in Metal-TiO2-Metal configurations. Our results highlight that these are not conventional metal-semiconductor contacts and several parameters such as the electrodes position (atop or below the film), the electronegativity, the interface states and even the opposite interface electrode material are involved on the formation of the interfacial barriers. Overall our study provides a useful database for selecting appropriate electrode materials in TiO2 based devices, offering new insights on the role of electrodes on metal-oxide electronics applications.

**Keywords:** TiO2, Metal Electrodes, Schottky Barrier, RRAM, TFT, Selectors

1. **Introduction**

Metal-oxides (MOs) combine a unique ensemble of properties presenting great potential to meet the diverse requirements of modern electronics. Specifically they offer low temperature (<100oC) manufacturability[1], thus compliance with large-scale uniformity and deployment on alternative materials (paper, flexible); adequate device level mobility[2] that can be further optimized by engineering appropriate gate dielectrics; high transparency due to their wide band gap; capacity for post fabrication tuneable resistance (memristive effects)[3],[4] and good chemical stability. These features enabled the use of MOs in a variety of applications ranging from Resistive Random Access Memories (RRAMs)[5],[6] and Thin Film Transistors (TFTs)[7],[8] to oxide-based photovoltaics[9] and sensors[10], introducing a new era for large area transparent/stretchable electronics[11],[12] and neuromorphic systems[13],[14].It is worth also mentioning two very recently published perspective articles[15],[16] discussing this envisioned new era. To this end, a variety of materials have been scrutinised over the recent years with distinct MO and thus properties being exploited according to the application needs, i.e neuromorphic applications favour MO devices that show large memory capacity[4].

TiO2 is without a doubt one of the most celebrated materials through practical implementations of memristors[17], TFTs,[18],[19], sensors[20] and corollary applications of these. The ability of TiO2 to obtain different microstructures (i.e. amorphous, micro/nano crystalline, rutile, anatase etc.) and thus a plethora of electronic properties that can be determined/controlled by the fabrication and/or biasing conditions augmented its use in practical applications. This is further enhanced by the incorporation of foreign metal elements (doping) in TiO2 thin films that were shown to improve RRAM switching characteristics[21] but also enable both n- and p-type functionalities[22],[23]. The latter area is still in its infancy, yet, offers substantial prospects for low-temperature manufacturable electronic systems. Research efforts are thus targeted on addressing outstanding challenges[24], with first proof-of-concept results on the development of bipolar components entirely based on TiO2 p-n homo-junctions[25],[26] showcasing the exciting technological potential.

Notwithstanding the importance of the oxide active layer, identifying appropriate metal contacts and deciphering their interfacial role is now of paramount importance to a device’s electrical behaviour. This role becomes even more important in highly scalable thin-film structures where their properties strongly rely on interfacial effects. Considering the up to date studies, metal contacts on oxide materials appear to attract important and continuously increasing research attention. Various metals on different oxide materials have been assessed and focused methods have been introduced aiming to the development of reliable contacts[27] as well as on understanding the formation mechanism [28][29]. Moreover, important advances on understanding the nature of metal/oxide (electrolyte) contacts is also made in the field of RRAM cells revealing the interesting nano-battery effect[30] and highlighting the role redox processes[31], of interfacial layers[32] and moisture[33].These aspects were recently summarized in a topical review[34]. All these suggest that these are not conventional Metal-Semiconductor contacts where the metal work function dominates the process. In addition, fabrication details[27][35],environmental conditions[36] and electrochemical interactions[37] have significant contribution as well.

More specifically regarding the metal-TiO2 contacts, it was reported that recording the rectification ratio measured at read out-voltage of ± 1V for a variety of top electrodes (deposited by RF magnetron sputtering on Metal-TiO2-(non-rectifying-Pt) configuration) can reveal the role of a metal’s electronegativity on the formation of the interface barrier[38]. In the same study, barriers evaluated by the forward diode current, suggested partial Fermi level pinning. In addition, the role of the top electrode (evaporated through shadow mask) on a Metal-TiO2-(non-rectifying-Pt) memory cell, evaluated with a read-out voltage of ± 1V, was correlated to the formation free energy for top metal electrode oxide[39]. Moreover, the symmetry/asymmetry of Metal-TiO2-(non-rectifying-Al) current-voltage characteristics attributed also to the top metal fabrication details such as the thermal annealing[40]. More recently, the source and drain electrodes of TiO2 based TFTs were found to play a major role on performance parameters such as the ON/OFF ratio and the field effect mobility[19]. All the above assessments are restricted to room temperature semi-quantitative approaches, focusing only in studying electrodes formed atop of TiO2 films.

In this paper, we present a detailed quantitative electrical characterization study of Metal-TiO2 interface characteristics. The work involves the commonly utilized contact metals acting both as top and bottom contacts in Metal-TiO2-Metal configuration, whilst it also reports the influence of the top electrode (TE) material to the bottom electrode (BE) interface. This is performed by recording the current-voltage (I-V) characteristics at different temperatures and through appropriate modelling and analysis that includes field and temperature dependent signature plots. Considering also the potential applications, the design and fabrication of all prototyped samples, on which this study was based, remained aligned to standard low temperature microelectronic processes, while the electrodes have been patterned through optical lithography and deposited via electron-beam evaporation.

1. **Experimental**

The tested devices were fabricated on two separate 6-inch Si wafers having a 200 nm thick SiO2 layer that was grown by dry oxidation at 1000°C with 5 slm of O2 flow. All electrodes and active areas where patterned via standard optical lithography and lift-off processes[41]. The first fabricated wafer was prepared to study the influence of TE metal variations on devices’ performances, therefore, a common BE metal was utilized, Au, that has a thickness of 20 nm preceded by 5 nm Ti adhesive layer. The TiO2-x core film was deposited on top of Au BE by Lambda controlled plasma assisted reactive magnetron sputtering (Helios Pro XL, Leybold optics) using a Ti target, with 8 sccm O2, 35 sccm Ar flows and 2 kW at the cathode, and 15 sccm O2 flow and 2 kW at an additional plasma source. This industrial tool allows having high quality films with low thickness variations across the wafer. Using “Woolham MD2000D Ellipsometer” TiO2-x thickness across 6-inch wafer was found to be of 24.09 ± 0.16 nm (see the Ellipsometry measurements shown in Figure 1 (c)).



Figure 1: Two separate were wafers fabricated. The first one (a) was dedicated to the study of different TE materials (Al, Ti, Ni, Au, Pt shown in grey in (a)) having common Au BE. The second wafer (b) was dedicated for the study of different BE with identical TiN TE (Au, Ti, Ni, Pt shown in grey in (b)). In Both cases highly uniform (24.09 ± 0.16 nm) amorphous TiO2-x films (c) were deposited as active area.

Films deposited by the above recipe exhibit an amorphous and almost stoichiometric nature of TiO2-x, with x in the range of 0.05-0.10, as previously demonstrated in the X-ray absorption spectroscopy study[42]. For the TEs, five separate areas were defined to deposit different TE metals: Al, Ti, Ni, Pt and Au, with thicknesses of 15 nm deposited by electron beam evaporation at a low rate of 0.5 Ås−1, for better uniformity, comparable to deposition rate of the BE.

Similar fabrication flow was adopted to fabricate the second wafer that was dedicated to study the BE metal variations influence on the performances of TiO2-based (24 nm) devices. In this wafer, four different BE metals were chosen; Ti, Ni, Pt and Au, with thicknesses of 15 nm. 5 nm Ti was also used for adhesive purposes. After TiO2 active film deposition and patterning, the same metal (15nm TiN) was sputtered across the wafer, serving as TE for all the four combinations.

The current vs voltage (I-V) characteristics were obtained on 30 x 30 μm2 devices using our in-house memristor characterization platform ArC ONETM [43]. The voltage sweeping was carried out in staircase mode towards positive biases, while both positive and negative polarities were always applied to the top electrode (TE) with respect to the bottom electrode (BE) that was continuously kept grounded. All experiments were performed on a Cascade SUMMIT 12000B semi-automatic probe station that incorporates a thermal chuck, whose temperature can be controlled by an ESPEC ETC-200L unit. Measurements were performed in the temperature range of 300 K to 350 K. The discontinuity appearing at V=0 V in some I-V curves is a result of our data acquisition system that does not acquire this point. This effect is negligible in most of the cases but not when measuring more conductive samples and for higher temperatures (340K-350K) when the conductivity/current further increases. However this has no effect on the measured data. Finally it is worth mentioning the role of moisture which was reported to affect both the transport and switching properties[36][37][44] of devices based on sputtered oxide films due to their porous structure. Despite this effect hasn’t shown significant influence in case of TiO2 layers[44] our experimental procedure was performed on environment where humidity and temperature were carefully controlled in order to minimize their influence on the measurements.

1. **Results and Discussion**

**3.1 Device Modelling and Parameters Extraction:** The studied Metal-TiO2-Metal devices are presented in Fig. 2(a). In order to obtain quantitative results the tested devices have been modelled by the equivalent circuit presented in Fig. 2(b). This consists of two series resistances accounting for the top (RTE) and the bottom (RBE) access electrodes and the device under test (DUT). As TiO2 exhibits an intrinsic n-type character[23], the DUT can be considered as two inverse polarized Schottky diodes, both emulating the TE and BE contacts, connected through a resistance that corresponds to the TiO2 core. This equivalent circuit was further used for calculating the effective applied bias (Veff)/electric field across the DUT, with respect to the bias applied through the voltage source (V) and as a function of the measured current (I), summarised by Eq.1

(1)

In the absence of an interface barrier, the Schottky diodes (TE/BE) can be considered as short-circuit. In this case the I-V characteristic should be symmetric with respect to the applied bias polarity and the dominant transport mechanism is purely determined by the properties of the active layer film. For the wide-band gap materials various mechanisms may dominate the transport. Most of them are critically affected by the density and the energy distribution of the band gap states and spatially by the film microstructure, e.g. conduction paths across the grain boundaries commonly exist in nanocrystalline films[45]. Depending on the applied electric field intensity and the operation temperature, transport may be dominated by hopping, space charge limited currents, Frenkel-Poole or even by free carriers in the bands[46]. Contribution of internal point defect related ionic motions [47][48] and/or those originating from the electrodes should also be taken into consideration. In particular for TiO2 films, the Ti/TiO2/Ti stack appears to be very useful for these studies as it allowed for a detailed assessment of core material controlled conduction mechanism[49][50]. The latter is supported by our results as Ti was found to form ohmic/non-rectifying contact when utilized both as top as well as bottom electrode.

For the interface-controlled transport is typically identified by an asymmetric I-V characteristic with respect to the applied bias polarity. The transport is then dominated by either tunnelling through the barrier formed at the interface or by thermionic emission over it. The two mechanisms can be distinguished via the temperature dependence of the I-V[46].

Tunnelling currents obey the following Eq. 2:

(2)



Figure 2: The studied Metal-TiO2-Metal devices (a). The equivalent circuit utilized to model the devices and the electrodes for our quantitative analysis.

with “b” being just a constant. Consequently, an asymmetric, temperature independent I-V, supporting also a linear relation on a ln(I/V*eff*2) vs 1/V*eff* signature plot serves as a strong indication of tunnelling dominated transport.

On the contrary thermionic emission over the interface barrier is the most commonly thermally activated mechanism for interface controlled transport. For those Schottky type contacts the current flow depends on whether the contact is forward or reverse biased. The forward current-voltage characteristic is given by Eq. 3:

(3)

whilst for the reverse biased case can be described by Eq. 4:

(4)

where K is the Boltzmann constant, T is the absolute temperature, ΦΒ0 is the zero bias potential barrier height at Metal/MO interface, A=(Area x A\*), with A\* being the Richardson constant, n the ideality factor, “α” the barrier lowering factor, q the electron charge and R stands for any series resistance.

For the cases where an interface barrier is formed, which is the main focus of this work, any positive bias applied to the TE, will result in a forward biased TE/TiO2 and reversed biased TiO2/BE contact. This is a system of the two back to back Schottky contacts that have been described in details in ref [51]. In our case, we emphasize our analysis in the regime where the current flow is determined by the reverse biased BE, given that this constitutes the most resistive element in this series configuration and thus as first approximation we may assume that V*eff*≈V. The situation is the opposite when a negative bias is applied to the TE; then the TE will determine the current flow.

For this regime, a straight line on a ln(I/T2) vs 1000/T plot for any applied electric field serves as strong evidence of thermionic emission. The slope of this line corresponds to the apparent interface barrier (Φ*App*) and should decrease by increasing the applied electric field/bias as:

(5)

If this Φ*App* vs V*eff*1/2 signature plot is also supported by the extracted results, then the intercept extrapolated to V*eff* =0 Volts, provides an experimental determination of ΦΒ0, whilst the slope corresponds to “α”. By following the aforementioned methodology we can obtain clear signature plots that allow deciphering the transport mechanism and provide quantitative measures of interfaces in Metal-TiO2-Metal structures. Moreover this analysis does not require the accurate knowledge of the Richardson constant for the amorphous metal-oxide, as this might differs by orders of magnitudes with respect to its commonly adopted value for silicon. This further highlight the necessity for implementing temperature dependent characterization.

**3.2The Top Electrode:** The TE/TiO2 contacts have been assessed to date mainly through evaluating the DUT’s resistance at a specific read-out voltage, typically of 1V. Here we are aiming to present an approach focusing more on quantitative extraction of parameters with physical meaning i.e. the zero bias potential barrier at the interface, ΦΒ0. For this, several configurations having different TE have been fabricated on the same wafer, with the TiO2 active layer films deposited on top of Au BE during the same process step. Therefore, with the exception to the TE interface, identical characteristics are expected. On the contrary, the results depicted in Fig. 3 provide evidence that the TE deposition plays indeed a major role on the device characteristics. For the I-Vs, the discrepancy appearing at V = 0V, as earlier mentioned, arises from our data acquisition system. However also I-Vs non-crossing the zero voltage point are expected in our case due to the change in the dominant Schottky contact at the point where the bias polarity change[51]. Moreover, it is worth mentioning particularly for the metal/electrolyte systems, that this behaviour has been also correlated with the nanobaterry effect[30]. More detailed study of this aspect requires precise measurements around zero.



Figure 3: Al and Ti as TE result in symmetric I-V denoting no formation of interface barrier (a). Asymmetric I-Vs obtained in cases of Au, Pt and Ni suggesting interface controlled conduction mechanism (b).

Ti and Al as TE, result in no rectifying barrier formation, and thus core material controlled conductivity, depicted by the symmetric I-V curves (Fig. 3(a)). Despite the identical (by fabrication) core-films, differences in the conductivity are obtained. A possible mechanism for the role of metal electrodes on the device resistivity proposed in Ref. 39 based on the Ellingham diagram, where the argument is that electrode metals interact with TiO2 generating oxygen vacancies. Oxygen vacancies act as n-type dopants, providing free electrons in the MO conduction band and thus determined the device resistance. The relation is not necessary straightforward however as in wide band gap materials the conductivity is also determined by the properties of the gap states through mechanisms such as hopping and Poole-Frenkel. Nevertheless the thorough investigation of the conduction mechanism through the film was not our main intent in this work.



Figure 4: I-V curves vs temperature for Ni (a), Pt (b) and Au (c), TE

When Au, Pt and Ni (Fig. 3(b)) are utilized asTE, interface barriers are formed as denoted by the asymmetric I-V curves (Fig. 3(b)). For these materials, detailed temperature characterization (Fig. 4) was performed and clear signature plots were extracted (Fig. 5). This led to the calculation of the zero bias potential barrier ΦΒ0 and of the barrier lowering factor “α” (Fig. 6(a)) that are summarized in Table 1.For these TE materials the conductivity is controlled by thermionic emission over the interface barriers, as confirmed by the clear signature plots (Figures 5, 6(a)).

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| **TE material** | **W*f* (eV)** | **Xm** | **Interface Barrier at TE** | **Additional Information** |
| **Al** | 4.28 | 1.61 | Non Rectifying Contact | |
| **Ti** | 4.1 | 1.54 | Non Rectifying Contact | |
| **Pt** | 5.65 | 2.28 | 0.61 eV | α = 0.265 eV1/2 |
| **Ni** | 5.15 | 1.91 | 0.50 eV | α = 0.208 eV1/2 |
| **Au** | 5.1 | 2.54 | 0.70 eV | α = 0.203 eV1/2 |

Table 1: Quantitative results extracted from the experimental data regarding the TE/TiO2interface



Figure 5: Signature plots (I-Vs at Fig. 3)Ni (a), Pt (b) and Au (c), TE respectively, confirming Schottky emission as the dominant transport mechanism.

Considering our pristine (not electroformed) and almost stoichiometric TiO2-x films, low concentration of mobile ions is expected and the interface barrier should in principle be proportional to the metal work function[46] (W*f* [52]). In cases however where large amount of defect states are present at the interface, the total trapped charge has also an important role[46]. Fermi level pinning resulting in barrier heights independent of or weakly dependent on the metal work function are commonly obtained, as in the case for example of III-V materials[53]. Nonetheless, this does not apply to our work as although the barrier formed is not proportional to the metal work function; significant variations exist for distinct electrode materials. In order to better understand the formation of the interfacial barrier we have to bear also in mind that intermediate thin oxide layers of a few nanometres may be formed at metal/oxide interfaces[37] especially on samples exposed to environmental conditions [36]. Further to this, electrode/electrolyte interfaces maybe degraded due to electrode reactions[34] whilst some induction of oxygen vacancies, acting as equivalent to doping, is also expected[38]. These processes result in the formation of an effective barrier with height that deviates from the expected theoretical predictions. For ionic materials the formed barriers have been correlated to the metal electronegativity[46] (Xm [54]). The strength of the correlation is typically assessed by the index S:

(6)

A strong correlation to electronegativity is considered as the S index approaches 1. For example, Silicon results in S=0.05 while SiO2 to S=1[46]. A clear linear relation is supported by our results depicted in Fig. 6(b). The calculated index is S= 0.32. Similar trends, extracted in a completely different way, are presented in Ref. 38 that resulted to S= 0.55 including materials, such as Al and Ti, which in our case appear not to form interface barrier. This is referred to as partial Fermi pinning that showcases the important role of interface states.

At this point it is worth noting an issue that has not been pointed out to date. This is the obtained interrelationship between the two interfaces. Throughout this study, we employ this term for highlighting that the TE material also results in modifications to the BE interfaces (positive biases in the I-V). Considering that the BE and the TiO2 should be identical due to common fabrication, we consider this an interesting finding and therefore it is discussed in more detail in the following section.



Figure 6: Experimental verification for the conduction mechanism and extraction of the zero bias potential barrier at the top interface (a). The barrier is found to increase linearly with the electronegativity of the TE material (b).

**3.3Top/Bottom Electrode interrelationship:** The TE material is found to affect the bottom Au/TiO2 contacts (Fig. 3, positive biases) that are nominally identical for all employed prototype devices. In cases of Al and Ti, no barrier is formed and therefore the conductivity is mainly determined by the film properties. In contrast, depositing Ni, Pt or Au as TE, appears to also instigate the formation of a barrier at the bottom interface, offering the opportunity to perform a quantitative study regarding the role of the TE to the BE interface.

Before proceeding to this analysis however, it is essential to confirm that the diffrences obtained in the postitive part of the I-Vs are not the effect of the forward biased TE schottky contact. For this we initialy assumed that the BE is indeed ohmic and the current flow is then desrcribed by Eq. (3) resulting in forward biased Schottky contact. In this case by diffrentiating (and for V>3KT/q) we obtain

(7)

Therefore a plot of dV/d(LnI) versus I should give a straight line with a slope corresponding to series resistance R and the intecept to the ideality factor n[55]. The plots for Ni, Pt and Au TEs are shown in figure 7 where clearly no linearity was observed.



Figure 7: dV/d(LnI) plots for (a) Ni, (b) Pt and (c) Au TE. In case of an ohmic bottom contact a straight line is expected which is clearly not the case for any of the utilized TE materials.

Another potential conduction mechanism, in case of an ohmic BE, is the space charge limited currents (SCLC). SCLCs are commonly obtained in wide band gap materials and insulators when electrons are injected from the electrodes and no compensation charge exist. Typically SCLC present an ohmic dependence for low biases, followed by a regime where the traps dominate the process and I∼Vm  with m>2 [56]. For higher biases/ injection conditions, the SCLC density, J is given by Eq. 8 [46]

(8)

where ε is the dielectric permittivity, μ the electrons mobility and d the film thickness.

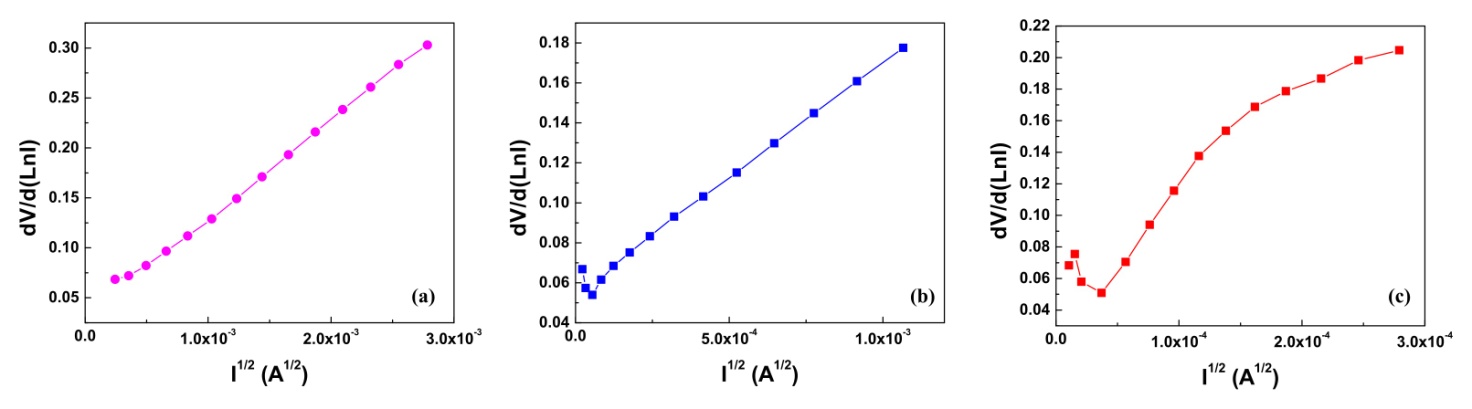
In this case, where the series resistance is not constant, we can then write from Eq. (8)

(9)

By subtracting R in Eq. (3) with Eq. (9) and by differentiating, Eq. (7) modifies to Eq. (10)

(10)

Thus a linear realtion in a plot of dV/d(LnI) versus I1/2 is expected. The results for the TE metals are presented in figure 8.

Figure 8: dV/d(LnI) plots for (a) Ni, (b) Pt and (c) Au TE, as modified for variable series resistance due to SCLC (Eq. 10).

In addition to this, for high biases where any interface barrier (forward or reverse biased, Eq (4)) is diminished, SCLC should obey Eq. 8 by showing V2 dependence and very weak (or negligible for a narrow temperature range) temperature variation possible due to changes in the electrons mobility.

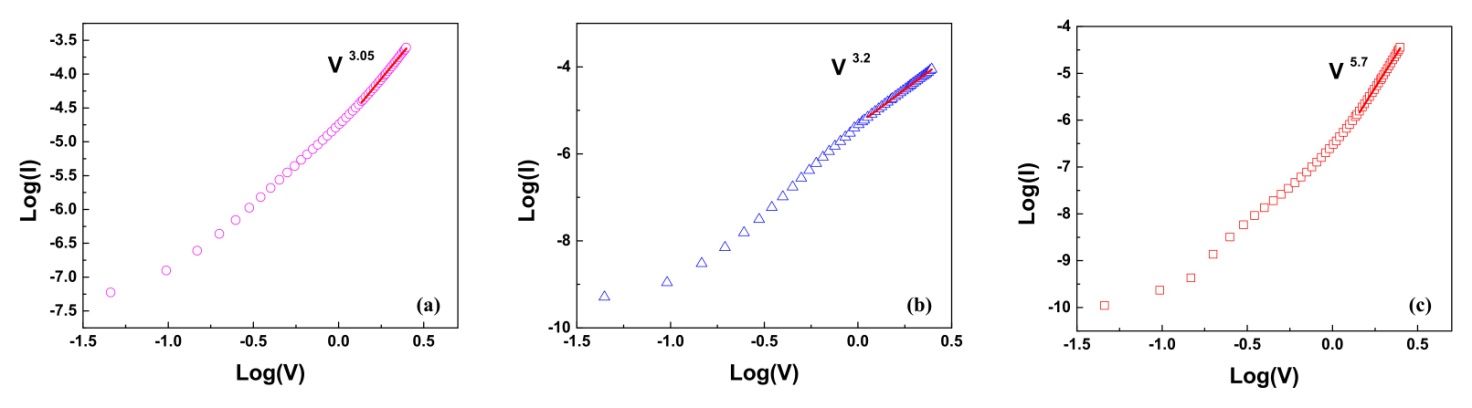


Figure 9: Log - Log plots for (a) Ni, (b) Pt and (c) Au TE, showing potential SCLC signature.

Although the results presented in figure 8 may be considered as supportive to Eq. 10 in case of Pt (Fig. 8(b)) (fitting the linear regimes for Ni (Fig. 8(a)) and Au (Fig. 8(c)) TE result in ideality factor n<1), the current-voltage dependence do not obey Eq. (8) as presented in figure 9, while a strong temperature effect also presented in figure 4. Such a bias dependence (m>2) obtained above V=2V along with the temperature variation may be attributed to traps-controlled SCLC. This indicates that devices have not reached the high injection regime (Eq. (8)) and thus for lower biases (V< 2V) an ohmic dependence is expected rather than the one indicated by Eq. 8. The latter is however not supported by figure 7 (Eq. 7) neither by figure 9.

Considering all these aspects, the Au(BE)/TiO2 interfaces have been further assessed in detail following the previously employed temperature dependent methodology. The obtained results for the Au/TiO2 BE with respect to the TE material are summarized in table 2, while the corresponding signature plots are presented in Fig. 10. The fitting results (signatures) strongly support this analysis. A linear relation to the electronegativity of the TE material was also obtained for the BE interface barriers. In this case, the barriers formed are lower than the TE ones but the same trend is followed. The data presented in Fig. 11 lead to S= 0.48. This clearly depicts the influence of the TE material throughout the TiO2 all the way to the BE, but also signifies the major role of the interface states.

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| **TE material** | **W*f* (eV)** | **Xm** | **Interface Barrier at BE** | **Additional Information** |
| **Al** | 4.28 | 1.61 | Non Rectifying Contact | |
| **Ti** | 4.1 | 1.54 | Non Rectifying Contact | |
| **Pt** | 5.65 | 2.28 | 0.54 eV | α = 0.279 eV1/2 |
| **Ni** | 5.15 | 1.91 | 0.37 eV | α = 0.161 eV1/2 |
| **Au** | 5.1 | 2.54 | 0.67 eV | α = 0.236 eV1/2 |

Table 2: Quantitative results extracted from the experimental data regarding the bottom interface with respect to the TE materials



Figure 10: Signature plots (I-Vs at Fig. 3) correspond to the bottom interface, for Ni (a), Pt (b) and Au (c) TE, confirming Schottky emission as the dominant transport mechanism.

It is worth noting that while this feature was identified for the TE, it is not the case for the BE, highlighting the differences in the formation mechanism for the two interfaces.



Figure 11: Further experimental verification for the conduction mechanism and extraction of the zero bias potential barrier at the interface for the bottom interface (a). The barrier is found to increase linearly with the electronegativity of the TE material (b).

**3.4The Bottom Electrode:** It is quite possible for the bottom electrode-TiO2 interface to show a distinct behaviour to an identical interface, in terms of electrode material, lying at the top of a device, due to processing induced effects. The up to date published works have typically utilized non-rectifying junctions for the bottom electrode, solely targeting the influence on the top interface characteristics and therefore assuming similar signatures for both interfaces due to symmetry. Nonetheless, we recently demonstrated that even symmetric structures may overall render an asymmetric performance[57].

The I-V characteristics of structures having Au, Ti, Ni and Pt as BE are presented in Fig. 12(a). The study was performed on a separate wafer targeted fabricated for this study (Fig. 1b). In all cases the TE is TiN deposited by sputtering. By observation to the acquired symmetric I-Vs, it follows that no interface barrier is formed in the cases where Au and Ti were utilized as bottom electrodes, denoting that the overall conductivity is controlled by the TiO2 thin-film. Besides, the two structures exhibit different conductivity, suggesting that the BE material plays also major role on the deposited film electrical properties. In cases where Pt and Ni were utilized as BE, strongly asymmetric I-V characteristics where obtained, denoting an interface controlled transport. In these cases, the I-V characteristics have been further assessed in the temperature range of 300 K to 350 K in order to obtain the corresponding signature plots. The applied biases have been limited up to 1.5 V and 1 V respectively to avoid the devices undergoing either a soft or irreversible (hard) breakdown. For the sample with Pt BE (Fig. 12(b)), the part of I-V plot corresponding to the BE (positive biases) presents a temperature independent behaviour (highlighted in the red square). This along with the signature plot presented in Fig. 12(c), supports that tunnelling is the major mechanism responsible for the conductivity, indicating the presence of a quite high barrier at this interface that is however immeasurable via Eq. 2.



Figure 12: Devices having identical TiN TE and different BE were assessed (a). Tunnelling identified in case of Pt BE signature plots (b),(c) and Schottky emission when Ni is the BE (e), (f).

On the contrary for the device formed atop of Ni BE (Fig. 12(d)), clear signature plots have been obtained that confirm thermionic emission over the interface barrier as the dominant transport mechanism. The data analysis allowed by the clear signature plots, led to the estimation of the zero bias potential barrier at the interface as ΦΒ0 = 0.69 eV (Fig. 12(e),(f)). The results for the BE study are summarized in table 3 along with the metal work function and electronegativity as those parameters may determine the interface barrier.

The differences obtained between the same metals utilised as top or bottom electrode could be assigned to both differences in the two interfaces as well as the core area of the film. It has been reported that BE materials may affect the concentration of the ions in the film[58], whilst local imperfections e.g. roughness could have a major role on the film microstructures[59] and thus both parameters can in turn modify the device electrical response. These two parameters are also heavily involved on the formation of the interface barrier. This however is a much more complicated issue. The BE is the first layer that is deposited and thus this interface is more exposed during the sequential fabrication steps and the environmental influences with respect to the top one, which is typically the last step before the characterization[58]. Moreover during the oxide film deposition high energetic particles are coming into contact with the BE material making the local formation of the interfacial layer sensitive to this process step[34]. On the contrary, for the upper layers of the film, the new deposited particles are hosted on a well formed oxide film, rendering the formation of the top interface completely different to the BE one. Therefore identical metals form quite different barriers when utilized as top or bottom electrodes [57].We note however that no straightforward quantitative correlation can be obtained at this stage for the BE, nor for its influence on the top interface. Therefore our results should raise the attention for the necessity of more thorough and targeted studies towards understanding and control of the BE/TiO2 interface. Ni as BE results in a clear Schottky behaviour for the TiN TE, whilst in case of Pt, the important hysteresis presented in fig 10(b) denotes notable contribution of ions that do not allow for accurate extraction of parameters for the TiN TE (in the presence of sufficient number of mobile ions the conventional Schottky analysis is not valid), although its strong rectifying character is clear.

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| **BE material** | **W*f* (eV)** | **Xm** | **Interface Barrier** | **Additional Information** |
| **Au** | 5.1 | 2.54 | Non Rectifying Contact | |
| **Ti** | 4.1 | 1.54 | Non Rectifying Contact | |
| **Ni** | 5.15 | 1.91 | 0.69 eV | α = 0.511 eV1/2 |
| **Pt** | 5.65 | 2.28 | Very high | Tunnelling |

Table: 3: Quantitative results extracted from the experimental data regarding the BE materials

**3.5Discussion:** This study has provided several new insights into the electrical properties of Metal-TiO2 interfaces. Evidently, these cannot be considered as conventional Metal-Semiconductor contacts, where the formation of the interface barrier is determined by the metal work function. Our quantitative results suggest that there are many parameters involved in the formation of these barriers not in a straightforward manner and therefore drawing concluding remarks should be based on carefully selected experimental comparisons and observations. Considering these and for the devices fabricated on the same wafer having nominally identical Au BE and TiO2 active layers deposited during the same process, we can reliably demonstrate the following.

Regarding the top contacts two major regimes obtained. Al and Ti, TE do not form a rectifying barrier. In this case the conductivity of the structure is determined by the TiO2 film. This is found to be affected by the TE material, possibly due to interactions lead to increase of oxygen vacancies. On the contrary, in cases of Ni, Pt and Au TE, an interface barrier is formed and we can present some clear conclusions. The barrier height at the top interface is found to be proportional to the metal electrode electronegativity highlighting the important role of the interface reactions on the formation of these barriers. The proportionality factor (S index) is far from 1, thus denoting the major contribution of the interface states (partial pinning). This study also came across an unexpected observation (interface interrelationship), where the common Au BE interface barrier, is not identical but it was found to be determined by the TE material. Non-rectifying and electronegativity depended barriers obtained respectively. This requires that the metal electrodes are selected in pairs, as the TE defines the properties of the bottom interface as well. Considering this interesting finding not reported before, thickness dependence study will be a natural progression to further verify our results. Therefore comparisons performed on different stacks should be carefully considered as they may lead to serious misinterpretations.

Regarding the BE, the same trend, i.e. the BE barrier determined by the electronegativity is not however true. It is therefore concluded that different mechanism are responsible for the formation of the interfaces in cases of BE, where the TiO2 film is deposited on the metal, in contrast to the TE interfaces where the metal is deposited atop the TiO2 film. This comply with our previous study where asymmetric barrier obtained on purely symmetric contacts[57]. BE however seems also to affect the top interfaces as presented by our results on devices having identical films and TiN TE, not with a straightforward quantitative relation however. This further support our argument that electrode materials should always be selected in pairs. Moreover, each material should be carefully considered with respect to its utilization as TE or BE; although in some case like Ti, no rectifying barrier is formed for either configuration rendering the Ti/TiO2/Ti system as the most suitable to study the film controlled transport[50].

Considering the growth and the perspectives[15],[16] for the oxide based applications including Internet of Things, wearable electronics, reconfigurable and/or bio-inspired systems, the major role of TiO2-based electronic devices, as well as the necessity for metal electrodes on top or below their active area, we proceed by sharing some thoughts on the usefulness of our results across the diverse MO applications. In the field of RRAM, where typically the devices are utilized after an electroforming step, Schottky barriers at the TE are considered essential for supporting resistive switching[60]. It was also reported that high barriers at TE support both Unipolar and Bipolar resistive switching, in contrast to lower barriers that typically favour bipolar operation[61]. Moreover metal-oxide interfaces are critically determine the operation of both Valence Change Memories (VCM) and Electrochemical Metallization Cells (ECM) through formation of barriers and electrochemical reactions[34]. The proper selection of metal electrodes can be utilized for engineering the electroforming process, in terms of polarity and applied field intensity, and perhaps even developing forming-free RRAM technologies. The electrodes’ characteristics are also of major importance to semiconductor devices. For example, when considering TiO2-based bipolar devices it is essential to avoid any rectification stemming from the metal electrodes. Moreover, in the case of TFTs, different configurations may require the Source and Drain electrodes atop or below the deposited MO films defining the TFTs’ active area and thus should be accordingly selected. Finally, several applications require the monolithic integration of such technologies. A prominent example is the use of diodes/transistors as selecting elements[62] for RRAM, rendering 1D1R and/or 1T1R configurations. Such cases typically exploit common metal electrodes acting both as BE and TE for different devices and thus should be accordingly considered, bearing also in mind the TE/BE interrelationship issues.

1. **Conclusions**

A quantitative electrical characterization study of the interfacial barriers at Metal-TiO2 contacts presented. This involved targeted fabrication of Metal-TiO2-Metal prototypes, recording of the I-V curves at different temperatures and analysis through appropriate modelling. Distinct characteristics identified for contacts formed atop and below the active area films. For Ni, Pt and Au that forms rectifying contacts at the top interface, the barriers were found to be proportional to their electronegativity, showing partial pinning. For those devices the top metal electronegativity was also appeared to determine the nominally identical Au/TiO2 bottom interfaces in a similar manner. For the bottom electrode however the same trend is not obvious. Despite that, the different bottom electrodes were also found affecting the nominally identical top interfaces but in this case a quantitative correlation is presently not straightforward, suggesting the need for more targeted studies. Overall we may conclude that the electrode materials in TiO2 devices should be selected in pairs, bearing always in mind their position with respect to the active film (top/below) and the metal electronegativity in particular for the top ones. Our results act as a very useful background for the wide range of TiO2 based applications covering RRAMs, TFTs, bipolar semiconductor devices and monolithic integration including 1T1R structures.

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**Data Availability**

All data supporting this study are openly available from the University of Southampton repository at: <https://doi.org/10.5258/SOTON/D0630>

**References**

[1] Yu X, Marks T J and Facchetti A 2016 Metal oxides for optoelectronic applications *Nat. Mater.***15** 383–96

[2] Brox-Nilsen C, Jidong J, Yi L, Peng B and Song A M 2013 Sputtered ZnO Thin-Film Transistors With Carrier Mobility Over 50 cm2/ Vs *Electron Devices, IEEE Trans.***60** 3424–9

[3] Kim W, Chattopadhyay A, Siemon A, Linn E, Waser R and Rana V 2016 Multistate Memristive Tantalum Oxide Devices for Ternary Arithmetic *Sci. Rep.***6** 36652

[4] Stathopoulos S, Khiat A, Trapatseli M, Cortese S, Serb A, Valov I and Prodromakis T 2017 Multibit memory operation of metal-oxide Bi-layer memristors *Sci. Rep.***7** 17532

[5] Ielmini D 2016 Resistive switching memories based on metal oxides: mechanisms, reliability and scaling *Semicond. Sci. Technol.***31** 063002

[6] Sawa A 2008 Resistive switching in transition metal oxides *Mater. Today***11** 28–36

[7] Park J S, Maeng W J, Kim H S and Park J S 2012 Review of recent developments in amorphous oxide semiconductor thin-film transistor devices *Thin Solid Films***520** 1679–93

[8] Kamiya T, Nomura K and Hosono H 2009 Origins of High Mobility and Low Operation Voltage of Amorphous Oxide TFTs: Electronic Structure, Electron Transport, Defects and Doping*J. Disp. Technol.***5** 273–88

[9] Rühle S, Anderson A Y, Barad H N, Kupfer B, Bouhadana Y, Rosh-Hodesh E and Zaban A 2012 All-oxide photovoltaics *J. Phys. Chem. Lett.***3** 3755–64

[10] Fine G F, Cavanagh L M, Afonja A and Binions R 2010 Metal oxide semi-conductor gas sensors in environmental monitoring *Sensors***10** 5469–502

[11] Petti L, Münzenrieder N, Vogt C, Faber H, Büthe L, Cantarella G, Bottacchi F, Anthopoulos T D and Tröster G 2016 Metal oxide semiconductor thin-film transistors for flexible electronics *Appl. Phys. Rev.***3**

[12] Liu Y, Pharr M and Salvatore G A 2017 A Lab-on-Skin: A Review of Flexible and Stretchable Electronics for Wearable Health Monitoring *ACS Nano* acsnano.7b04898

[13] Serb A, Bill J, Khiat A, Berdan R, Legenstein R and Prodromakis T 2016 Unsupervised learning in probabilistic neural networks with multi-state metal-oxide memristive synapses *Nat. Commun.***7** 12611

[14] Mehonic A and Kenyon A J 2016 Emulating the electrical activity of the neuron using a silicon oxide RRAM cell *Front. Neurosci.***10**

[15] Myny K 2018 The development of flexible integrated circuits based on thin-film transistors *Nat. Electron.***1** 30–9

[16] Zidan M A, Strachan J P and Lu W D 2018 The future of electronics based on memristive systems *Nat. Electron.***1** 22–9

[17] Strukov D B, Snider G S, Stewart D R and Williams R S 2009 The missing memristor found *Nature***459** 1154–1154

[18] Shih W S, Young S J, Ji L W, Water W and Shiu H W 2011 TiO2-Based Thin Film Transistors with Amorphous and Anatase Channel Layer *J. Electrochem. Soc.***158** H609

[19] Choi H, Shin J and Shin C 2017 Impact of Source/Drain Metal Work Function on the Electrical Characteristics of Anatase TiO2 -Based Thin Film Transistors *ECS J. Solid State Sci. Technol.***6** 379–82

[20] Bai J and Zhou B 2014 Titanium dioxide nanomaterials for sensor applications *Chem. Rev.***114** 10131–76

[21] Trapatseli M, Khiat A, Cortese S, Serb A, Carta D and Prodromakis T 2016 Engineering the switching dynamics of TiOx-based RRAM with Al doping *J. Appl. Phys.***120**

[22] Zhao L, Park S G, Magyari-Köpe B and Nishi Y 2013 Dopant selection rules for desired electronic structure and vacancy formation characteristics of TiO2 resistive memory *Appl. Phys. Lett.***102**

[23] Anitha V C, Banerjee A N and Joo S W 2015 Recent developments in TiO2 as n- and p-type transparent semiconductors: synthesis, modification, properties, and energy-related applications *J. Mater. Sci.***50** 7495–536

[24] Wang Z, Nayak P K, Caraveo-Frescas J A and Alshareef H N 2016 Recent Developments in p-Type Oxide Semiconductor Materials and Devices *Adv. Mater.***28** 3831–92

[25] Hazra A, Chattopadhyay P P and Bhattacharyya P 2015 Hybrid Fabrication of Highly Rectifying p - n Homojunction Based on Nanostructured TiO2*IEEE Electron Device Lett.***36** 505–7

[26] Vasu K, Sreedhara M B, Ghatak J and Rao C N R 2016 Atomic Layer Deposition of p-Type Epitaxial Thin Films of Undoped and N-Doped Anatase TiO2*ACS Appl. Mater. Interfaces***8** 7897–901

[27] Hossein-Babaei F, Gharesi M and Moalaghi M 2017 Diffusion Bonding of Metal Wires Directly to the Functional Metal Oxide Semiconductors for Forming Reliable Electrical Contacts *ACS Appl. Mater. Interfaces* **9** 26637–41

[28] Hossein-Babaei F, Moghadam S and Masoumi S 2015 Forming ohmic Ag/SnO2contacts *Mater. Lett.***141** 141–4

[29] Ashworth D G, Oven R and Page M C 2017 Field-assisted diffusion of silver in SnO2 thin films *J. Phys. Conf Series* 939 012007

[30] Valov I, Linn E, Tappertzhofen S, Schmelzer S, Van Den Hurk J, Lentz F and Waser R 2013 Nanobatteries in redox-based resistive switches require extension of memristor theory *Nat. Commun.***4** 1771–9

[31] Tappertzhofen S, Waser R and Valov I 2014 Impact of the Counter-Electrode Material on Redox Processes in Resistive Switching Memories *ChemElectroChem***1** 1287–92

[32] Lubben M, Karakolis P, Ioannou-Sougleridis V, Normand P, Dimitrakis P and Valov I 2015 Graphene-Modified Interface Controls Transition from VCM to ECM Switching Modes in Ta/TaOx Based Memristive Devices *Adv. Mater.***27** 6202–7

[33] Tappertzhofen S, Valov I, Tsuruoka T, Hasegawa T, Waser R and Aono M 2013 Generic relevance of counter charges for cation-based nanoscale resistive switching memories *ACS Nano***7** 6396–402

[34] Valov I 2017 Interfacial interactions and their impact on redox-based resistive switching memories (ReRAMs) *Semicond. Sci. Technol.***32** 093006

[35] F.Hossein-Babaei, Navid Alae-Sheini M M L 2016 Oxygen adsorption at noble metal/TiO2 junctions *IOP Conf. Ser. Mater. Sci. Eng.* 1–6

[36] Lübben M, Wiefels S, Waser R and Valov I 2017 Processes and Effects of Oxygen and Moisture in Resistively Switching TaO*x* and HfO*xAdv. Electron. Mater.***1700458** 1700458

[37] Cho D Y, Luebben M, Wiefels S, Lee K S and Valov I 2017 Interfacial Metal-Oxide Interactions in Resistive Switching Memories *ACS Appl. Mater. Interfaces***9** 19287–95

[38] Zhong N, Shima H and Akinaga H 2010 Rectifying characteristic of Pt/TiOx/metal/Pt controlled by electronegativity *Appl. Phys. Lett.***96**

[39] Yang J J, Strachan J P, Miao F, Zhang M X, Pickett M D, Yi W, Ohlberg D A A, Medeiros-Ribeiro G and Williams R S 2011 Metal/TiO2 interfaces for memristive switches *Appl. Phys. A Mater. Sci. Process.***102** 785–9

[40] Hossein-Babaei F, Lajvardi M M and Alaei-Sheini N 2015 The energy barrier at noble metal/TiO2 junctions *Appl. Phys. Lett.***106**

[41] Serb A, Khiat A and Prodromakis T 2018 Seamlessly fused digital-analogue reconfigurable computing using memristors *Nat. Commun.***9** 2170

[42] Carta D, Mountjoy G, Regoutz A, Khiat A, Serb A and Prodromakis T 2015 X-ray absorption spectroscopy study of TiO2-x thin films for memory applications *J. Phys. Chem. C***119** 4362–70

[43] Berdan R, Serb A, Khiat A, Regoutz A, Papavassiliou C and Prodromakis T 2015 A μ-Controller-Based System for Interfacing Selectorless RRAM Crossbar Arrays *IEEE Trans. Electron Devices***62** 2190–6

[44] Tsuruoka T, Terabe K, Hasegawa T, Valov I, Waser R and Aono M 2012 Effects of moisture on the switching characteristics of oxide-based, gapless-type atomic switches *Adv. Funct. Mater.***22** 70–7

[45] Michalas L, Koutsoureli M, Saada S, Mer-Calfati C, Leuliet A, Martins P, Bansropun S, Papaioannou G, Bergonzo P and Ziaei A 2014 Electrical assessment of diamond MIM capacitors and modeling of MEMS capacitive switch discharging *J. Micromechanics Microengineering***24** 0–8

[46] S.M. S and K.K. N 2006 *Physics of Semiconductor Devices* (John Wiley & Sons)

[47] Schaub R, Wahlstro E, Rønnau A, Lægsgaard E, Stensgaard I and Besenbacher F 2006 Oxygen-Mediated Diffusion of TiO2 ( 110 ) Surface **299**

[48] Wedig A, Luebben M, Cho D Y, Moors M, Skaja K, Rana V, Hasegawa T, Adepalli K K, Yildiz B, Waser R and Valov I 2016 Nanoscale cation motion in TaOx, HfOxand TiOxmemristive systems *Nat. Nanotechnol.***11** 67–74

[49] Hossein-Babaei F and Alaei-Sheini N 2017 A model for the electric conduction in metal/poly-TiO2metal structure *J. Phys. Conf. Ser.***939** 0–7

[50] Hossein-Babaei F and Alaei-Sheini N 2016 Electronic Conduction in Ti/Poly-TiO2/Ti Structures *Sci. Rep.***6**29624

[51] Fu J, Hua M, Ding S, Chen X, Wu R, Liu S, Han J, Wang C, Du H, Yang Y and Yang J 2016 Stability and its mechanism in Ag/CoOx/Ag interface-type resistive switching device *Sci. Rep.***6** 35630

[52] http://www.kayelaby.npl.co.uk/atomic\_and\_nuclear\_physics/4\_3/4\_3.html

[53] Search H, Journals C, Contact A, Iopscience M and Address I P 1999 Fermi Level Pinning and Schottky Barrier Height Control at Metal-Semiconductor Interfaces of InP and Related Materials *Jap. J. Appl. Phys.***1098** 1098–102

[54] Allred A L 1961 Electronegativity values from thermochemical data *J. Inorg. Nucl. Chem*. **17** 215-21

[55] Cheung S K and Cheung N W 1986 Extraction of Schottky diode parameters from forward current-voltage characteristics *Appl. Phys. Lett.***49** 85–7

[56] Lampert M A 1956 Simplified theory of Space-Charge-Limited Currents in an insulator with traps *Phys. Rev*. **103** 1648-56

[57] Michalas L, Trapatseli M, Stathopoulos S, Cortese S, Khiat A and Prodromakis T 2017 Interface Asymmetry Induced by Symmetric Electrodes on Metal-Al:TiOx -Metal Structures *IEEE Trans. Nanotechnol.* in press

[58] Lübben M, Menzel S, Park S G, Yang M, Waser R and Valov I 2017 SET kinetics of electrochemical metallization cells : in fl uence of counter-electrodes in SiO2/ Ag based systems *Nanotechnology* **28** 135205

[59] Munde M S, Mehonic A, Ng W H, Buckwell M, Montesi L, Bosman M, Shluger A L and Kenyon A J 2017 Intrinsic Resistance Switching in Amorphous Silicon Suboxides: The Role of Columnar Microstructure *Sci. Rep.***7** 1–7

[60] Hernández-Rodríguez E, Márquez-Herrera A, Zaleta-Alejandre E, Meléndez-Lira M, Cruz W D La and Zapata-Torres M 2013 Effect of electrode type in the resistive switching behaviour of TiO2 thin films *J. Phys. D. Appl. Phys.***46**

[61] Kim W-G and Rhee S-W 2010 Effect of the top electrode material on the resistive switching of TiO2 thin film *Microelectron. Eng.***87** 98–103

[62] Cortese S, Khiat A, Carta D, Light M E and Prodromakis T 2016 An amorphous titanium dioxide metal insulator metal selector device for resistive random access memory crossbar arrays with tunable voltage margin *Appl. Phys. Lett.***108**