

Physical Chemistry Chemical Physics

Electronic Supplementary Information

**Voltage-polarity dependent multi-mode resistive switching on sputtered
MgO nanostructures**

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Quantitative analysis of XPS data

A useful XPS analysis is the quantification of a single element through different peaks. Since the respective photoelectrons have different kinetic energies, they are differently attenuated when crossing the solid and therefore the ratio of the integrated intensities between different peaks is related to the stratification of the sample especially if their kinetic energies are quite different. Table S1 presents the atomic ratios that one would expect assuming the model and respective nominal thicknesses shown in Fig. S1, compared with the experimental atomic ratios computed from the areas of the different XPS peaks and considering the sensitivity factors mentioned in the experimental section.

Table S1. XPS ratios expected vs. experimental

	Expected	Experimental
Mg 2s/Mg 1s	72.0	1.2
Ta 4d/Ta 4p_{3/2}	1.0	0.9
Ru 3d/Ru 3p	0.9	0.9

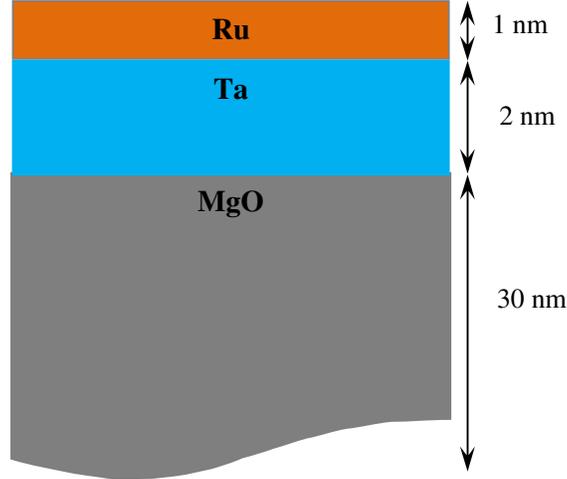


Fig. S1 Sample outermost layers.

For magnesium photoelectrons coming from the MgO layer, the expected intensities of Mg X photoelectrons, that is Mg 2s or Mg 1s, considering atomically flat layers and neglecting any shadow effects, should be given by expression (1) that accounts for the attenuation of the photoelectrons when crossing the different layers. Tantalum and ruthenium X photoelectrons (*i.e.* Ta 4d, Ta 4p_{3/2}, Ru 3d and Ru 3p) intensities are described by expressions (2) and (3).

$$I_{\text{Mg } X} \propto \left[1 - \exp\left(-\frac{\ell_{\text{MgO}}}{\lambda_{\text{Mg } X(\text{MgO})}}\right) \right] \times \exp\left(-\frac{\ell_{\text{Ta}}}{\lambda_{\text{Mg } X(\text{Ta})}}\right) \times \exp\left(-\frac{\ell_{\text{Ru}}}{\lambda_{\text{Mg } X(\text{Ru})}}\right) \quad (1)$$

$$I_{\text{Ta } X} \propto \left[1 - \exp\left(-\frac{\ell_{\text{Ta}}}{\lambda_{\text{Ta } X(\text{Ta})}}\right) \right] \times \exp\left(-\frac{\ell_{\text{Ru}}}{\lambda_{\text{Ta } X(\text{Ru})}}\right) \quad (2)$$

$$I_{\text{Ru } X} \propto \left[1 - \exp\left(-\frac{\ell_{\text{Ru}}}{\lambda_{\text{Ru } X(\text{Ru})}}\right) \right] \quad (3)$$

where ℓ_{MgO} , ℓ_{Ta} and ℓ_{Ru} are the nominal thicknesses of the MgO, Ta and Ru layers, respectively, and $\lambda_{\text{Mg } X(\text{MgO})}$, $\lambda_{\text{Mg } X(\text{Ta})}$, $\lambda_{\text{Mg } X(\text{Ru})}$, $\lambda_{\text{Ta } X(\text{Ta})}$, $\lambda_{\text{Ta } X(\text{Ru})}$ and $\lambda_{\text{Ru } X(\text{Ru})}$ are the Inelastic Mean Free Paths (IMFP) of Mg 2s or Mg 1s, Ta 4d or Ta 4p_{3/2}, Ru 3d or Ru 3p photoelectrons in the different materials. IMFP of photoelectrons crossing MgO, Ta and Ru were interpolated from the IMFP (calculated from TPP-2M equation or from optical data) reported in [1, 2].

Considering the nominal thicknesses ℓ_{Ta} and ℓ_{Ru} equal to 2 and 1 nm, respectively, the calculated “expected” ratios Ta 4d/Ta 4p_{3/2} and Ru 3d/Ru 3p are quite close to the experimental XPS ratios. However, since the couples of chosen photoelectrons have close kinetic energies (1257 eV and 1082 eV for Ta 4d and Ta 4p and 1207 eV and 1025 eV for Ru 3d and Ru 3p, respectively) they are not very sensitive to the ℓ_Y values, Y being the material of the different layers. For the Mg 2s and Mg 1s regions (kinetic energies are 1397 eV and 184 eV, respectively) a striking difference between the expected and the experimental Mg 2s/Mg 1s ratios exists. The most plausible explanation is the existence of some intermixing between Mg and the “external” layers or, alternatively, the existence of holes in those layers. Taking into consideration that some MgO diffusion through the metallic overlayers may occur, expression (1) should be as follows:

$$I_{\text{Mg}X} \propto \left[1 - \exp\left(-\frac{\ell_{\text{MgO}}}{\lambda_{\text{Mg}X(\text{MgO})}}\right) \right] \times \exp\left(-\frac{\ell_{\text{Ta}}}{\lambda_{\text{Mg}X(\text{Ta})}}\right) \times \exp\left(-\frac{\ell_{\text{Ru}}}{\lambda_{\text{Mg}X(\text{Ru})}}\right) \\ + f_i \left[1 - \exp\left(-\frac{\ell_{\text{MgO}_i}}{\lambda_{\text{Mg}X(\text{MgO})}}\right) \right] \times \exp\left(-\frac{(\ell_{\text{Ta}} + \ell_{\text{Ru}}) - \ell_{\text{MgO}_i}}{\bar{\lambda}_{\text{Mg}X(\text{Ta}, \text{Ru})}}\right) \quad (1')$$

Being f_i ratio between the intermixed magnesium and the layered one, ℓ_{MgO_i} the intermixing extent and $\bar{\lambda}_{\text{Mg}X(\text{Ta}, \text{Ru})}$ a weighted average IMFP value of magnesium X photoelectrons crossing Ta and Ru. The experimental Mg 2s/Mg 1s ratio is found for $f_i = 0.375$ and considering a maximum length of intermixing $\ell_{\text{MgO}_i} = 3$ nm.

Since the MgO layer thickness is very high compared to the Mg 1s IMFP, even when compared to the one for Mg 2s, the expected decrease of its value when the intermixing occurs has no impact on the estimated values.

Regarding the fraction of oxidized tantalum, the XPS spectrum shows that most of tantalum is Ta⁵⁺. In fact the experimental atomic ratios Ta/Ru, computed, from different XPS regions (Ta 4d or 4p_{3/2} and Ru 3d or 3p) and considering the atomic densities (d) 0.123, 0.092 and 0.037 mol/cm³ for Ru, Ta and Ta₂O₅, respectively, shows that 72 ± 5 % of tantalum is in the Ta⁵⁺ oxidation state. The value obtained is the average of the 4 fitted values for 4 atomic ratios (Ta 4d/Ru 3d, Ta 4d/Ru 3p, Ta 4p_{3/2}/Ru 3d and Ta 4d/Ru 3p). Equation (4) was used to estimate the fraction of oxidized

tantalum, f_{ox} , neglecting the impact that the oxidation has on $\frac{\ell_{Ta}}{\lambda_{Ta} X(Ta)}$. The nominal thicknesses of Ru and Ta (oxidized and not oxidized) layers', described above, were considered.

$$\frac{Ta}{Ru} = \frac{(1 - f_{ox}) \times d_{Ta} + f_{ox} \times d_{Ta_{ox}}}{d_{Ru}} \times \frac{\left[1 - \exp\left(-\frac{\ell_{Ta}}{\lambda_{Ta} X(Ta)}\right) \right] \times \exp\left(-\frac{\ell_{Ru}}{\lambda_{Ta} X(Ru)}\right)}{\left[1 - \exp\left(-\frac{\ell_{Ru}}{\lambda_{Ru} X(Ru)}\right) \right]} \quad (4)$$

References

- [1] S. Gurban, G. Gergely, J. Toth, D. Varga, A. Jablonski and M. Menyhard, "Experimental determination of the inelastic mean free path (IMFP) of electrons in selected oxide films applying surface excitation correction." *Surface and Interface Analysis* **38**, 624–627 (2006).
- [2] S. Tanuma, C. J. Powell and D. R. Penn, "Calculations of Electron Inelastic Mean Free Paths, III. Data for 15 Inorganic Compounds over the 50-2000 eV Range", *Surface and Interface Analysis* **17**, 927-939 (1991).

Electrical Characterization for Negative Forming Voltage

Additional measurements for positive and negative formings were performed in order to confirm that the polarity of the forming has no influence on the resistive switching behavior. Figure 2S shows the cumulative probabilities of Set and Reset voltages with formings at both positive and negative voltages for the (+,-) [Fig. S2(a)] and (-,-) [Fig. S2(b)] modes. A good repeatability was obtained for both cases, showing that there is no influence from the forming polarity on the resistive switching behavior. Figure 3S despite the same study for (+,+) and (-,-) [Fig. S3(a)] and (+,-) with (-,+) [Fig. S3(b)]. If the filament growth direction changed with the forming polarity, the results for the modes would just be reversed as: (+,+) \Leftrightarrow (-,-) and (+,-) \Leftrightarrow (-,+). As can be seen, this does not occur, as the modes behave equally between then for different forming polarities and differently from the other modes.

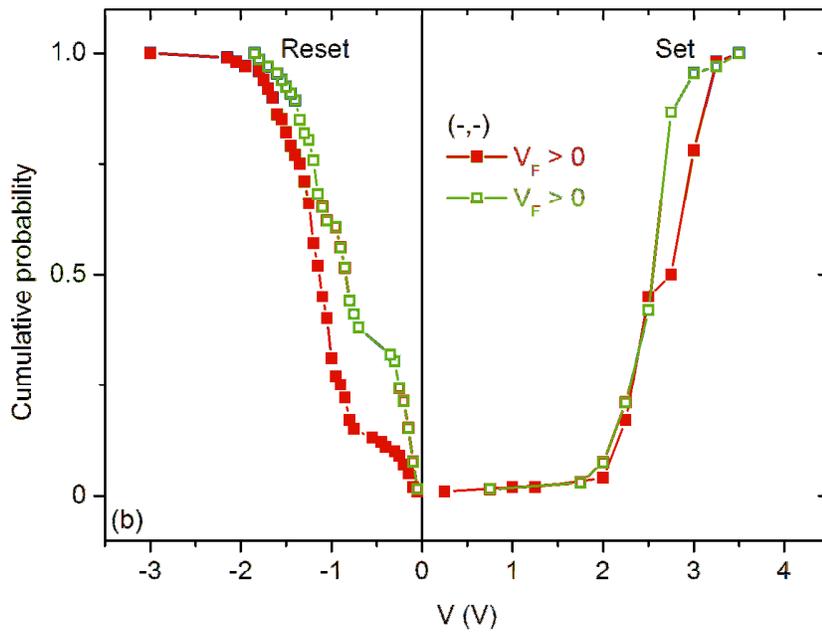
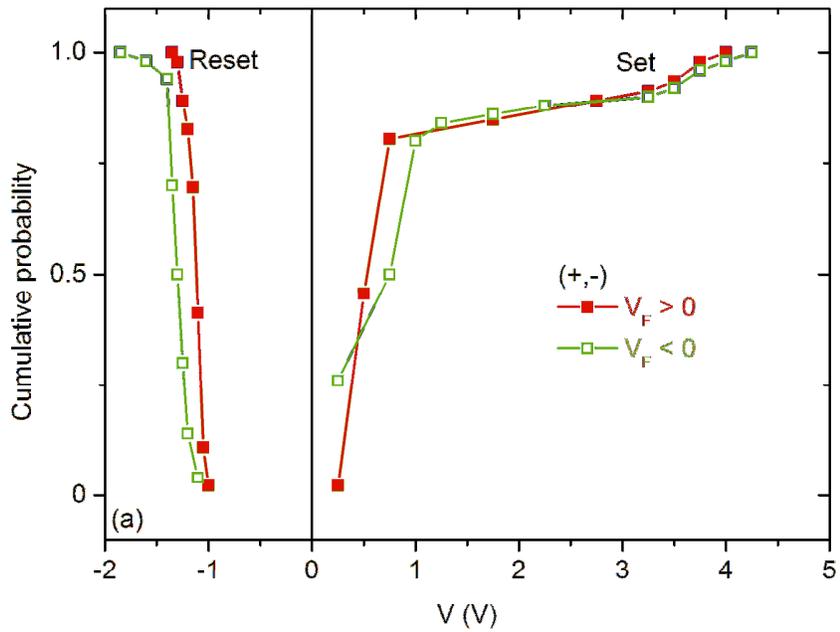


Fig. S2 Cumulative probability of the Set and Reset voltages for the (a) (+,-) and (b) (-,-) mode with forming at positive and negative voltages.

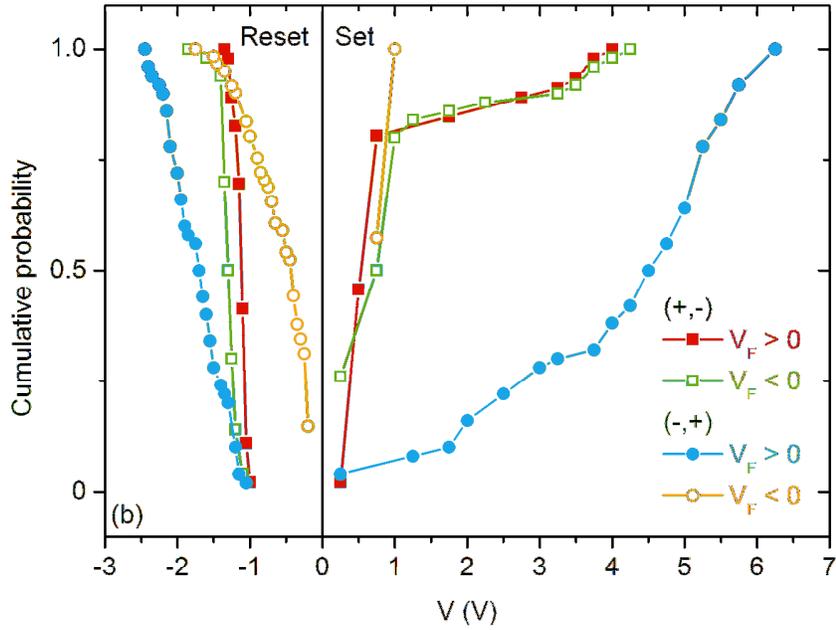
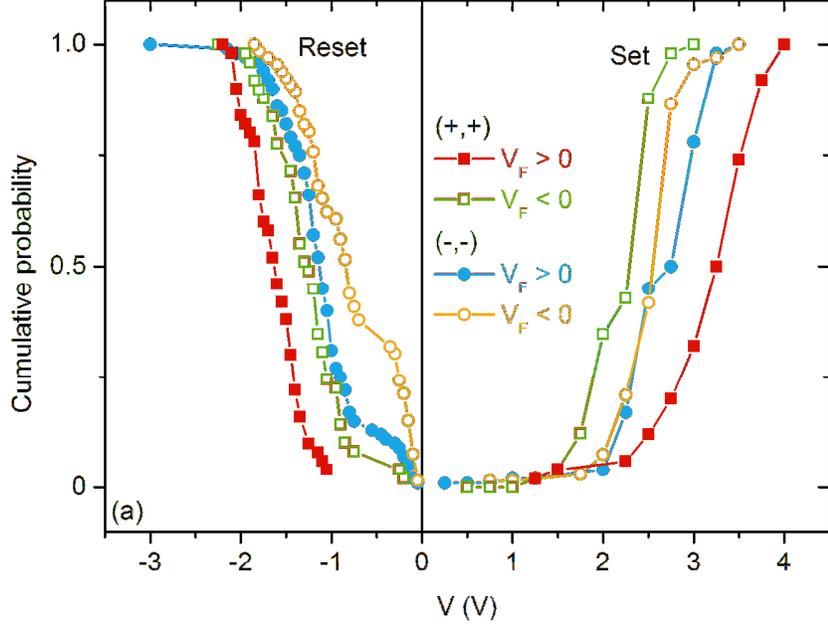


Fig. S3 Cumulative probability of the Set and Reset voltages for the (a) (+,+) and (-,-), and (b) (+,-) and (-,+) at positive and negative forming voltages.