Supplementary Information

On the role of the metal oxide / reactive electrode interface during the forming procedure of valence change ReRAM devices

Andreas Kindsmüller[a], Alexander Meledin[b,c], Joachim Mayer[b,c], Rainer Waser[a,d], and Dirk J. Wouters[a]

a. Institut für Werkstoffe der Elektrotechnik 2 & JARA-FIT,RWTH Aachen University, 52056 Aachen, Germany

b. Central Facility for Electron Microscopy & JARA-FIT, RWTH Aachen University, 52074 Aachen, Germany

c. Ernst Ruska-Centre for Microscopy and Spectroscopy with Electrons (ER-C)& JARA-FIT, Forschungszentrum Jülich GmbH, 52428 Jülich, Germany

d. Peter Gruenberg Institute & JARA-FIT, Forschungszentrum Jülich GmbH, 52425 Jülich, Germany

Table S1: Results of all fits for Fig 1. With the upper and lower 3σ boundary.

	ZrO_2	Ta_2O_5
lower 3σ Pt OE: best fit *Upper 3σ*	$0.430\frac{V}{nm}d_{ZrO_2} + 1.317\,V$ $0.448\frac{V}{nm}d_{ZrO_2} + 1.506\,V$ $0.466\frac{V}{nm}d_{ZrO_2} + 1.695\,V$	$0.328\frac{V}{nm}d_{Ta_2O_5} + 1.512\,V$ $0.357\frac{V}{nm}d_{Ta_2O_5} + 1.816\,V$ $0.386\frac{V}{nm}d_{Ta_2O_5} + 2.120\,V$
lower 3σ Ta OE: best fit Upper 3σ	$0.445\frac{V}{nm}d_{ZrO_2} + 0.056\,V$ $0.462\frac{V}{nm}d_{ZrO_2} + 0.209\,V$ $0.478\frac{V}{nm}d_{ZrO_2} + 0.362\,V$	$0.454\frac{V}{nm}d_{Ta_2O_5} - 0.115\,V$ $0.480\frac{V}{nm}d_{Ta_2O_5} + 0.140\,V$ $0.506\frac{V}{nm}d_{Ta_2O_5} + 0.394\,V$
lower 3σ Hf OE: best fit Upper 3σ	$0.458\frac{V}{nm}d_{ZrO_2} - 0.498\,V$ $0.476\frac{V}{nm}d_{ZrO_2} - 0.329\,V$	$0.482\frac{V}{nm}d_{Ta_2O_5} - 0.640\,V$ $0.515\frac{V}{nm}d_{Ta_2O_5} - 0.288\,V$

	$0.493\frac{V}{nm}d_{ZrO_2} - 0.159\,V$	$0.548\frac{V}{nm}d_{Ta_2O_5} + 0.064\,V$

Table S2: Precise results of all fits for Fig 2. With the upper and lower 3σ boundary.

	ZrO2	Ta2O5
lower 3σ	$3.199\frac{1}{nm \cdot nF}d_{ZrO_2} + 1.376\frac{1}{nF}$	$1.490\frac{1}{nm \cdot nF}d_{ZrO_2} + 4.774\frac{1}{nF}$
Pt OE: best fit	$3.235\frac{1}{nm \cdot nF}d_{ZrO_2} + 1.733\frac{1}{nF}$	$1.512\frac{1}{nm \cdot nF}d_{ZrO_2} + 5.016\frac{1}{nF}$
Upper 3σ	$3.272\frac{1}{nm \cdot nF}d_{ZrO_2} + 2.090\frac{1}{nF}$	$1.535\frac{1}{nm \cdot nF}d_{ZrO_2} + 5.257\frac{1}{nF}$
lower 3σ	$3.186\frac{1}{nm \cdot nF}d_{ZrO_2} + 1.024\frac{1}{nF}$	$2.190\frac{1}{nm \cdot nF}d_{ZrO_2} + 2.735\frac{1}{nF}$
Ta OE: best fit	$3.290\frac{1}{nm \cdot nF}d_{ZrO_2} + 1.889\frac{1}{nF}$	$2.256\frac{1}{nm \cdot nF}d_{ZrO_2} + 3.438\frac{1}{nF}$
Upper 3σ	$3.395\frac{1}{nm \cdot nF}d_{ZrO_2} + 2.753\frac{1}{nF}$	$2.322\frac{1}{nm \cdot nF}d_{ZrO_2} + 4.140\frac{1}{nF}$
lower 3σ	$3.268\frac{1}{nm \cdot nF}d_{ZrO_2} + 1.682\frac{1}{nF}$	$2.561\frac{1}{nm \cdot nF}d_{ZrO_2} + 2.887\frac{1}{nF}$
Hf OE: best fit	$3.289\frac{1}{nm \cdot nF}d_{ZrO_2} + 1.887\frac{1}{nF}$	$2.639\frac{1}{nm \cdot nF}d_{ZrO_2} + 3.723\frac{1}{nF}$
Upper 3σ	$3.310\frac{1}{nm \cdot nF}d_{ZrO_2} + 2.092\frac{1}{nF}$	$2.716\frac{1}{nm \cdot nF}d_{ZrO_2} + 4.560\frac{1}{nF}$

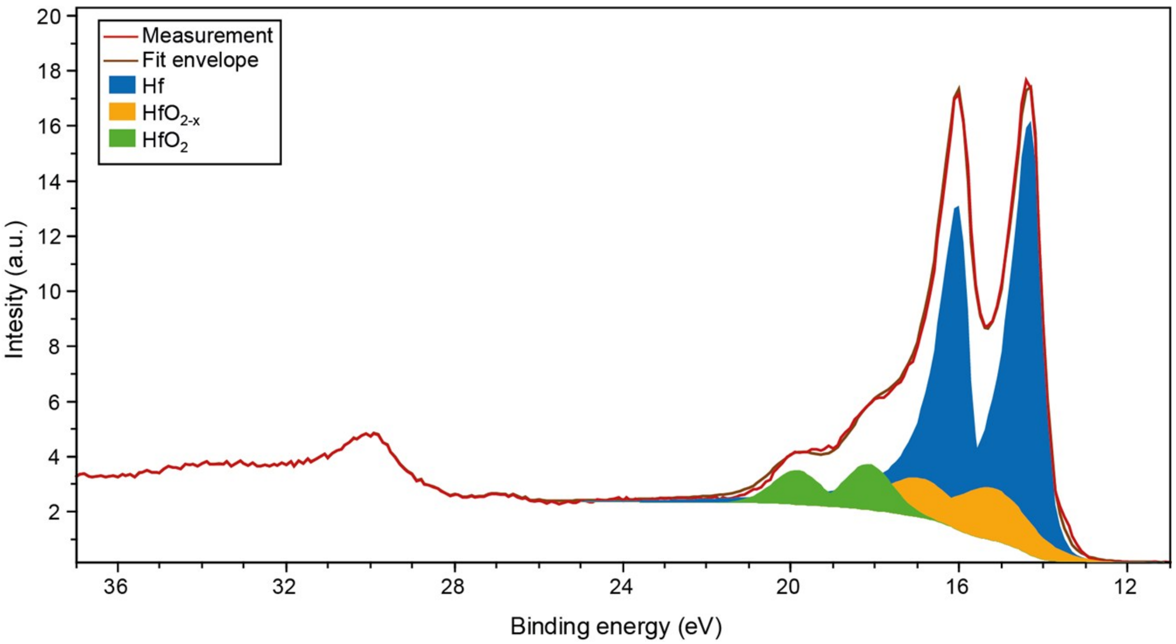

Fig. S1: A Hf XPS spectrum after 3510 s sputter time. At this point, Hf close to the Hf / Ta_2O_5 interface is investigated. Therefore we can also see a significant contribution of HfO_2. The exact parameters of the different Ta and Hf peaks and the details of the fitting procedure are given in Table S3.

Table S3: Allowed peak positions and FWHM of the peaks. During the fitting of each XPS spectrum the spin orbit spitting of the $4f_{7/2}$ and $4f_{5/2}$ is kept constant – for Hf a spin orbit splitting of 1.71 eV and for Ta a spin orbit splitting of 1.91 eV is assumed [1]. The area ratio between the $4f_{7/2}$ and the $4f_{7/2}$ peak is fixed to 4:3. Additionally, the FWHM for the $4f_{7/2}$ and $4f_{5/2}$ peak has to be the same for each component. The position and FWHM limits are set according to the table. Then, these fitting parameters are applied to all 119 Hf4f-Ta4f XPS spectra acquired. The Hf metallic and HfO_2 peak position fit well with literature values [2] and also our own previous measurements. Also the Ta peak position fit reasonably well with literature values [3].

	Position $4f_{7/2}$ (eV)	FWHM $4f_{7/2}$ (eV)	Position $4f_{5/2}$ (eV)	FWHM $4f_{5/2}$ (eV)
Hf	14.28 ± 0.1	0.6 ± 0.1	15.99 ± 0.1	0.6 ± 0.1
HfO_{1-x}	14.99 ± 0.1	0.62 ± 0.1	16.7 ± 0.1	0.62 ± 0.1
HfO_{2-x}	15.3 ± 0.1	2.03 ± 0.1	17.01 ± 0.1	2.03 ± 0.1
HfO_2	18.05 ± 0.1	1.45 ± 0.1	19.76 ± 0.1	1.45 ± 0.1
Ta	22.25 ± 0.1	0.9 ± 0.1	24.16 ± 0.1	0.9 ± 0.1
TaO_{1-x}	23.45 ± 0.1	0.86 ± 0.1	25.36 ± 0.1	0.86 ± 0.1
TaO_{2-x}	24.55 ± 0.1	2.94 ± 0.1	26.46 ± 0.1	2.94 ± 0.1
Ta_2O_5	26.85 ± 0.1	1.35 ± 0.15	28.76 ± 0.1	1.35 ± 0.15

For the calculation of the average oxidation state, the atomic percentage of each peak is multiplied with its energy position. The sum of all those multiplications gives the area related centre of weight.

$$E_{centre\ of\ weight} = \sum_i c_{Atomic,Peak\ i} \cdot E_{Peak\ i}$$

With i as index running through all peak parameters, $c_{\text{Atomic,Peak}\ i}$ the relative atomic concentration of peak i and $E_{\text{Peak}\ i}$ the energy position of peak i. For comparison, the area related centre of weight for the metallic and for the stoichiometric oxide has to be calculated:

$$E_{Centre\ of\ weight,\ \ metal} = c_{Atomic,Peak\ 1} \cdot E_{Peak\ 1} + c_{Atomic,Peak\ 1} \cdot E_{Peak\ 1}$$

With $c_{\text{Atomic,Peak}\ 1}$ is the concentration of the first metal peak (i.e. 4/7 or 0.571 for the $4f_{7/2}$ peak), $E_{\text{Peak 1}}$ the energy of the peak (e.g. the $4f_{7/2}$ peak), $c_{\text{Atomic,Peak 2}}$ the concentration of the second metal peak (i.e. 3/7 or 0.429 for the $4f_{5/2}$ peak), $E_{\text{Peak 2}}$ the energy of the second peak (e.g. the $4f_{5/2}$ peak). The centre of weight for the full oxide is calculated equivalently.

Then, the average oxidation state is approximated by a linear interpolation of centre of weight of the actual spectrum between the centre of weight of the metallic spectrum and the full oxide spectrum:

$$Average\ oxidation = max.\ oxidation \cdot \frac{E_{centre\ of\ weight} - E_{Centre\ of\ weight,\ \ metal}}{E_{centre\ of\ weight,\ Full\ oxide} - E_{Centre\ of\ weight,\ \ metal}}$$

With max. oxidation is the oxidation state of the metal cation in the full oxide configuration, i.e. 4+ for Hf and 5+ for Ta.

There are two advantages of this method in contrast to a direct comparison of the atomic concentration of the different peaks: Firstly it shows how much the material is oxidized in just one number and secondly, this number is nearly independent of the chosen peaks for fitting, as long as the line shape can be fitted reasonably well with those peaks.

References

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