Supplementary Information (SI) for Physical Chemistry Chemical Physics.

Supplementary Information

Spectroscopic Investigation of the Structural and Electronic Properties of Oxygen-deficient Tantalum Oxide Thin Films

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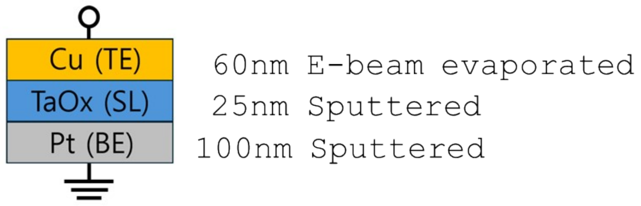
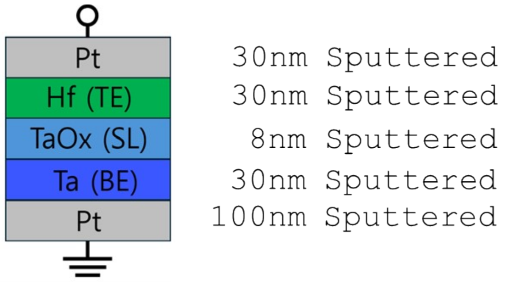
Details in the I-V characteristics used for Figure 1 in the main text

a. Sample preparation

All the layers in both samples (Cu/TaO$_x$/Pt and Pt/Hf/TaO$_x$/Ta/Pt) are prepared by magnetron sputtering except for the top Cu (prepared by e-beam evaporation). The thicknesses are as written in the schematics below. The top electrodes (TE) are patterned in square shapes and the sizes of the Cu TE and Pt/Hf TE were $25\ \mu m \times 25\ \mu m$ and $50\ \mu m \times 50\ \mu m$, respectively.





b. I-V characterization

The cyclic voltametry data were collected by using Keithley 6430 under an air ambiance at room temperature. Figure 1 in the main text displays the I-V curves of Cu/TaO$_x$/Pt and Pt/Hf/TaO$_x$/Ta/Pt for the first 10 cycles. The sweep rates were 0.15 V/s for Cu/TaO$_x$/Pt and 0.60 V/s for Pt/Hf/TaO$_x$/Ta/Pt. The I-V curves were obtained for 10 cycles with a current compliance of +1 mA for Cu/TaO$_x$/Pt (Fig. 1(a)) or -1 mA for Pt/Hf/TaO$_x$/Ta/Pt (Fig. 1(b)). The voltage sweep ranges were -1.1 V to +1 V for Fig. 1(a) and -2 V to +2 V for Fig. 1(b), respectively.

In the case of Cu/TaO$_x$/Pt (Fig. 1(a) in the main text), the SET process (to complete formation of Cu-based filaments in the TaO$_x$ matrix) was done by a positive bias, which is typical for ECM-type switching, whereas the RESET process done by a negative bias with large area of the closed I-V loop in the negative I (and V) region, which is for VCM-type switching. Thereby we judged that the Cu/TaO$_x$/Pt sample showed a combinational VCM + ECM-type switching (8-wise; a counter-clockwise loop under positive bias and a clockwise loop under negative bias).

In contrast, Pt/Hf/TaO$_x$/Ta/Pt, in which TaO$_x$ is sandwiched by Hf and Ta metals show a counter-8-wise switching (that is, a clockwise loop under positive bias and a counter-clockwise loop under negative bias) with much narrower I-V loop than the case of ECM or VCM. This can be interpreted by bi- (or multi-)stable resistances in the TaO$_x$ matrix. In a previous report by Chen *et al.*,[3] it was demonstrated that (Hf or Ta)/TaO$_x$ interface forms an Ohmic contact and the multi-level resistance of filament can be stabilized in Hf/TaO$_x$/Ta structure so that its conduction mechanism is categorized by FCM. The oxidation state and the local structure in the TaO$_x$ matrix and particularly near the interfaces toward the two electrodes (TE and BE) will be crucial to determine the type of the memristive switching, and this is the motivation of this study in the main text.

XPS O 1s Peak Fitting

Figure S1 shows the results of O 1s XPS peak fitting for TaO$_{1.0}$ and Ta$_2$O$_5$ reference. For a fair comparison, both spectra are taken after the surface etching. Here, the model for the fit comprises two major peaks (Peak 1 at BE = 530.8 eV and Peak 2 at BE = 532.1 eV) and the Shirley-type background. Most plausibly, Peak 1 originates from the lattice oxygen. Meanwhile, the origin of Peak 2 is unclear; it may be due in part to oxygen ions chemically affected by the oxygen vacancy and in part to surface contamination. Nevertheless, the area ratio of Peak 2 / Peak 1 can be used to roughly estimate the overall significance of oxygen vacancies in the Ta-oxide films, since both spectra are obtained after the same etching process.

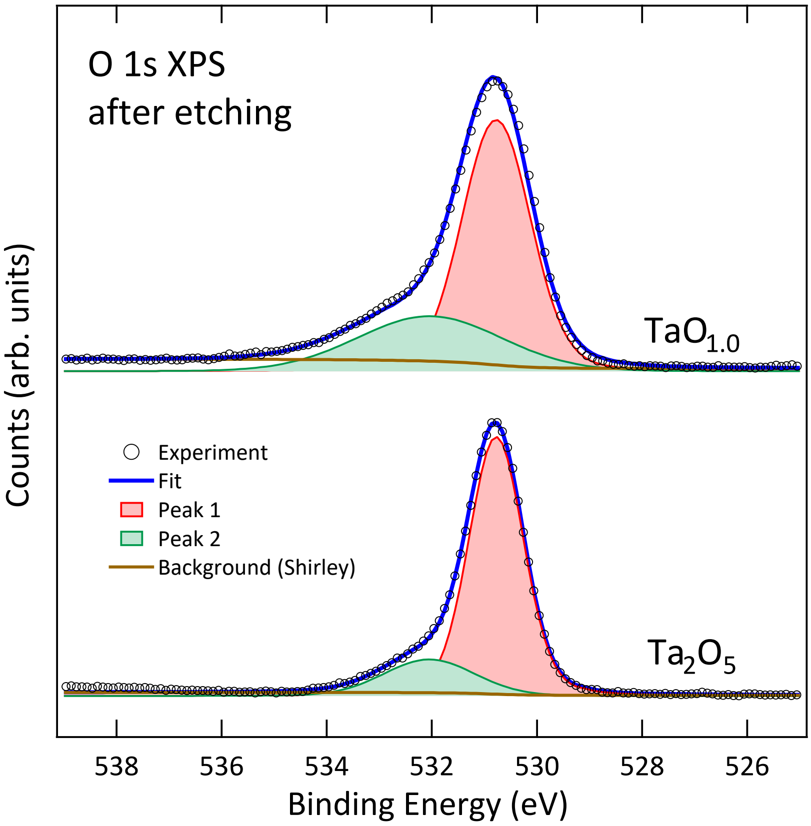


Fig. S1. O 1s XPS peak fitting (after surface etching)

It is observed that the Peaks 1 and 2 for $TaO_{1.0}$ are overall broader than their counterparts for the Ta_2O_5 reference. This suggests that the valence states of oxygen ions in $TaO_{1.0}$ are less deterministic than those in the stoichiometric oxide (Ta_2O_5). The estimated area ratios of Peak 2 / Peak 1 were 22.8% for the Ta_2O_5 film and 44.1% for the $TaO_{1.0}$ film. Given the large difference between the values, the increased area ratio for $TaO_{1.0}$ indeed reflects the strong influence of oxygen vacancies in the extremely oxygen-deficient composition.