Supplementary Information

Volatile HRS Asymmetry and Subloops in Resistive Switching Oxides

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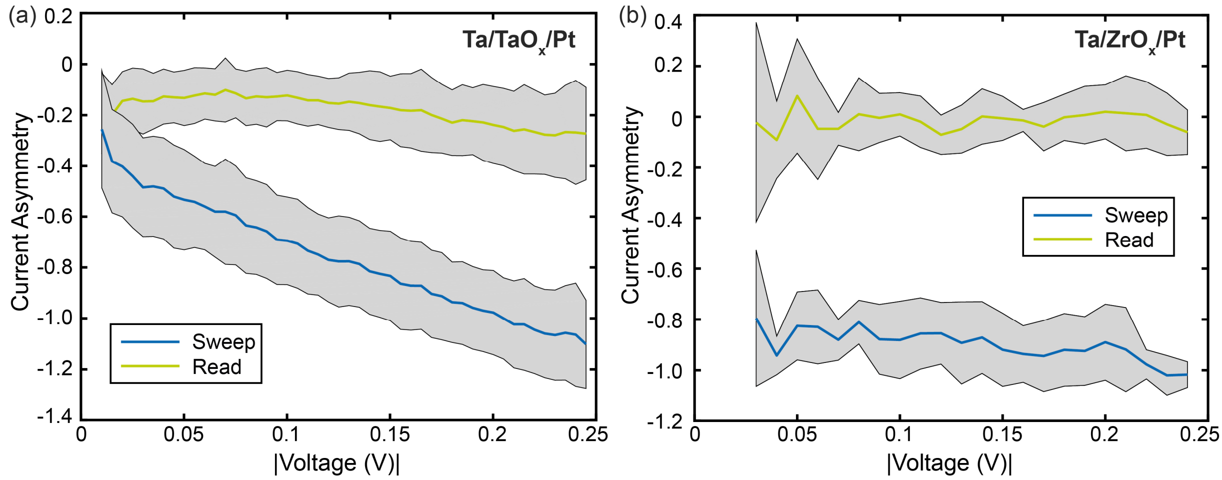

Fig. S1 Detailed analysis of the current asymmetry of switching sweep (blue) and read (green) depending on the voltage for the TaO_x and ZrO_x devices shown in Fig. 1a and 1c, respectively. The current asymmetry is defined as $\frac{I(+V)-|I(-V)|}{\text{mean}[I(+V),|I(-V)|]}$ [1]. For the asymmetry calculation of the switching sweep, the HRS from the RESET branch ($I(-V)$) and the HRS from the SET branch ($I(+V)$) of the following switching sweep are used. For the ZrO_x, the calculation of the read asymmetry is analog, using $I(+V)$ from the positive branch with decreasing voltage and $I(-V)$ from the negative branch with increasing (absolute) voltage. The asymmetry of 4 reads and switching sweeps was calculated. For the TaO_x sample, the HRS of the read ($I(-V)$) and the HRS from the SET branch ($I(+V)$) of the following switching sweep give the read asymmetry as no read with positive voltages was conducted. 30 reads and switching sweeps were analyzed.
The means for the TaOx and ZrOx devices are drawn in Fig. S1a and 1c, respectively. The gray areas describe the intervals of mean ± standard deviation. For both oxides, The HRS asymmetry in the switching sweeps is clearly larger than that of the read and increases with increasing voltage. The negative sign signifies that the current for negative voltages (RESET direction) is larger.

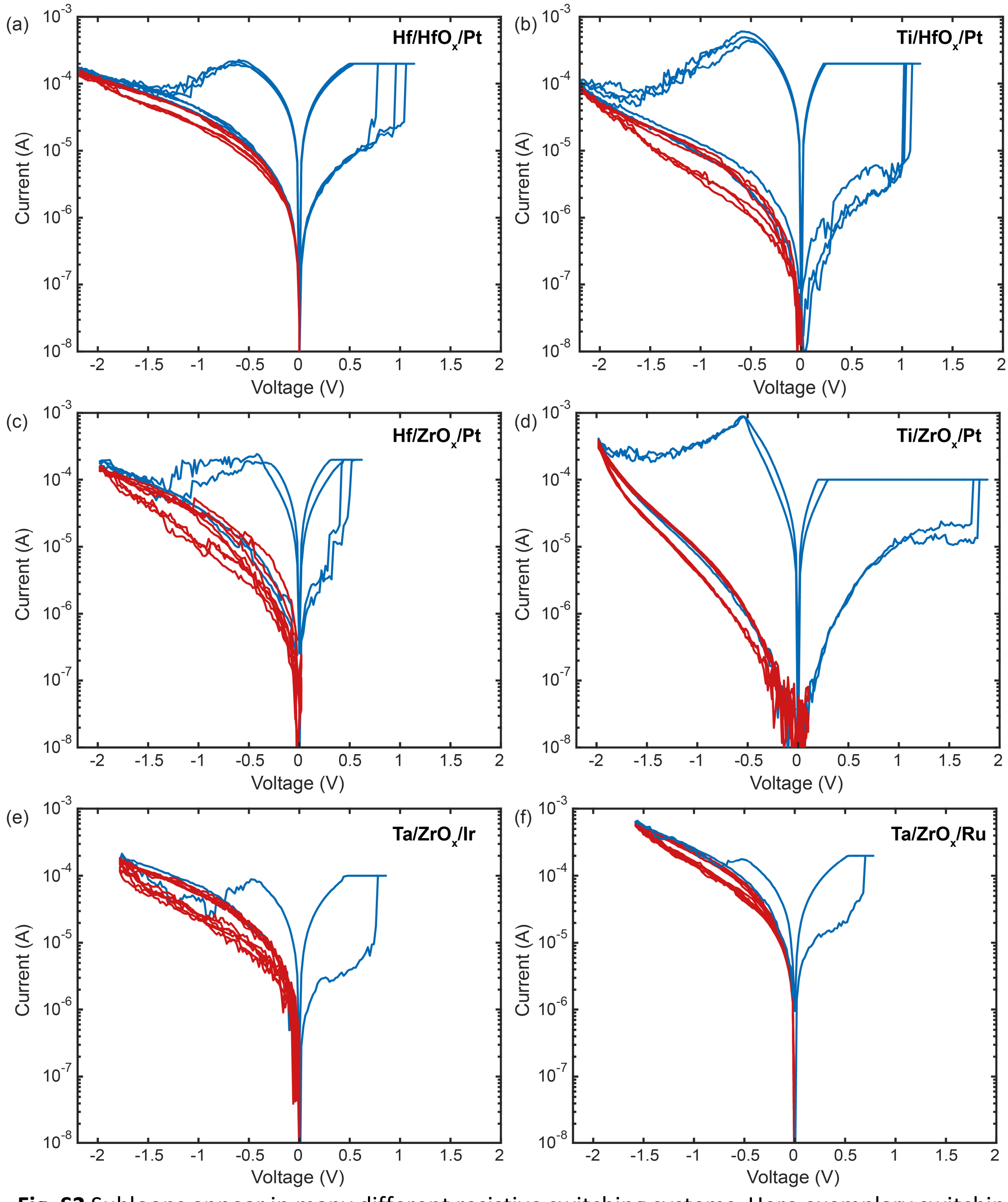

Fig. S2 Subloops appear in many different resistive switching systems. Here exemplary switching cycles, followed by subloops are shown for (a) 30 nm Pt/5 nm HfO_x/10 nm Hf/ 30nm Pt, (b) 30 nm Pt/5 nm HfO_x/10 nm Ti/ 30nm Pt, (c) 30 nm Pt/5 nm ZrO_x/15 nm Hf/ 30nm Pt, (d) Pt/5 nm ZrO_x/10 nm Ti/ 30nm Pt, (e) Ir/5 nm ZrOx/15 nm Ta /30 nm Pt and (f) 30 nm Ru /5 nm ZrOx/15 nm Ta /30 nm Pt

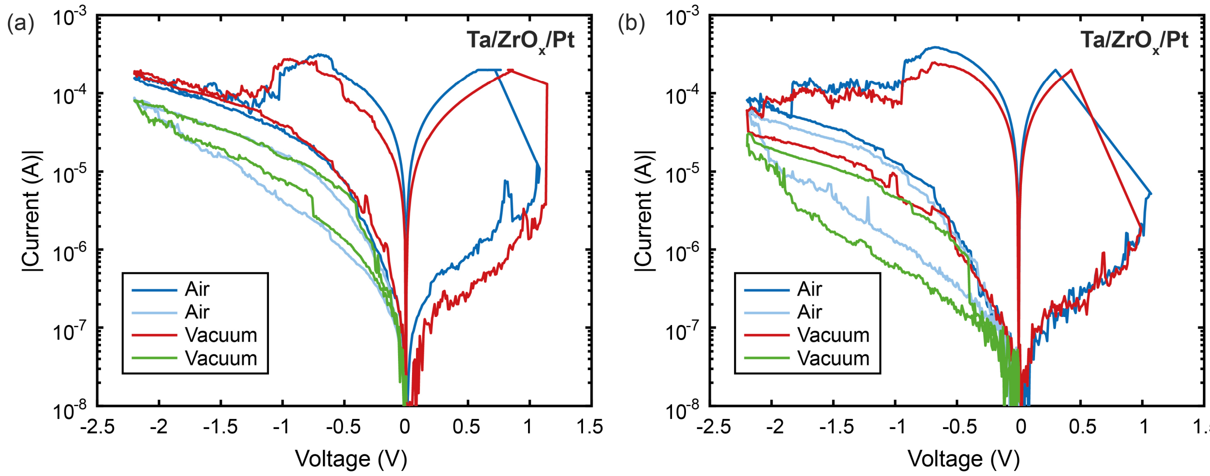

Fig. S3 Influence of moisture. Two examples of ZrO_x devices are shown (stack and cell geometry described in the main text) that were measured first in air and then in vacuum, after a bake out at 150 °C for 30 min. As subloops occur in air and vacuum, the presence of moisture cannot be mandatory for the appearance of subloops. The device in (a) is an example of cells whose excited subloop state and the HRS of the switching sweeps do not coincide except for small voltages. This behavior exists in air and vacuum. In (b), exemplary switching sweeps are shown that differ between air and vacuum but the difference lies in the order of the typical cycle-to-cycle variability of these cells.

UV light experiment

In order to study the influence of trap charges on subloops, experiments under UV light were performed. In the TaOx sample, the 80 nm Pt layer on top is too thick to allow a considerable amount of UV light to penetrate. In the ZrOx sample, the UV light has to pass through 30 nm Pt + 10 nm Ta + 3.5 nm ZrOx to reach the interface in question. Experiments were conducted on the ZrOx sample using a Heraeus UV lamp with high power density that heated the cell and increased the temperature to 325 K. Due to restrictions in the measurement setup, the immediate influence of turning on the UV light could not be measured. Assuming that a considerable amount of UV light reached the ZrOx/Pt interface, the cells show subloops under UV light and the variations between UV light on and off lie in the range of the usual cycle-to-cycle variability. Due to the high variability and the uncertainty in the experiment, the results can be seen neither as evidence for the trap theory nor as counter evidence.

References

1. Catherine E. Graves, Noraica Dávila, Emmanuelle J. Merced-Grafals, Sy-Ty Lam, John Paul Strachan and R. Stanley Williams, *Applied Physics Letters*, 2017, **110**, 123501.