#### Supplementary Information

# Resistive switching and role of interfaces in memristive devices based on amorphous NbO<sub>x</sub> by anodic oxidation

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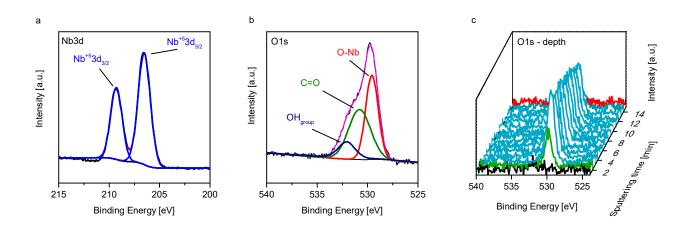


Figure S1 a) A particular of the HR-spectrum of Nb3d at the surface of the as-grown NbO<sub>x</sub>, definitively only the doublet related to Nb<sub>2</sub>O<sub>5</sub> is present, meaning the oxidation state of Nb is +5 at the surface after the oxidation process. b) HR-spectrum of O1s at the surface. Three main bonding are identified, at lower energy (red line) the peak related to the Nb bonding, at medium energy (green line) the double bonding with C=O, at the highest energy (blue line) the peak related to OH group. c) Cumulative HR-spectra of O1s during depth profile analysis. The black line represents the HR spectrum acquired in the Au top electrode, the green line, 2 min sputtering time is acquired at the interface Au/NbO<sub>x</sub>, the cyan peaks are acquired in the NbO<sub>x</sub> bulky region and the red one (15 min sputtering time) is acquired in the Nb bottom electrode. No concentration of oxygen is detectable in the two electrodes and definitively only one peak is present in the region in between them meaning oxygen is bonded only with Nb and no other elements bonded with it are present.

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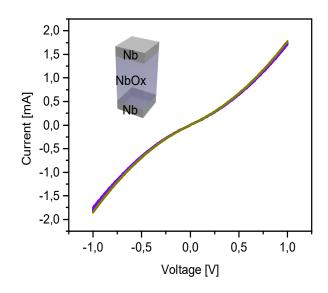


Figure S2 Pristine state of the Nb/NbO<sub>x</sub>/Nb cells. In comparison with the Au/NbO<sub>x</sub>/Nb cell, these are more conductive. This is a direct consequence of the barriers at the interface with the oxide layer. As explained in the electrical characterization section, the insulating properties of the cell are not due to the lonely oxide layer, but also from the electrodes. In this case, a symmetric cell with Nb on both sides reduces very a lot the barriers at the interfaces with NbO<sub>x</sub> making the cell one thousand times more conductive than the one with Au on top. On the top-left a scheme of the symmetric cell. On the bottom-right a scheme of the back-to-back diode equivalent circuit of the cell: in this case the two diodes are represented with the same dimension meaning the barriers at the interfaces with the oxide are of the same entity.

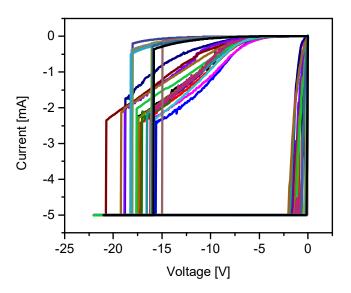


Figure S3 Electroforming process curves related to different Au/NbO<sub>x</sub>/Nb cells. The Forming voltage is around -17 V. The forming process is carried out using a compliance current of -5 mA, but some devices suggest the electroforming can occur using lower compliance. Nevertheless, the electroforming condition used for these devices leads to reliable resistive switching properties of endurance.

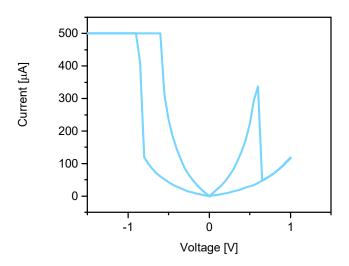


Figure S4 Example of a *I-V* characteristic with CC of 500 µA: the linearity is lost in the LRS when the CC used to program the device is too small.

## Supplementary Information

Table S1. Comparative analysis of anodic NbOx-based devices with the literature

Cell	Oxide thickness	Туре	V <sub>SET</sub> /V <sub>RESET</sub>	Endurance	Retention	R <sub>ON</sub>	R <sub>OFF</sub>	Reference
Au/NbOx/Nb	60 nm	Bipolar	-0.6 V/0.6 V	>10 <sup>3</sup>	>104	10 <sup>2</sup> - 10 <sup>3</sup> Ω	8 kΩ- 10 <sup>5</sup> Ω	Present work
Pt/NbOx/Nb	20 nm	Bipolar	n.a.	>10 <sup>6</sup>	>105	10 <sup>2</sup> - 10 <sup>3</sup> Ω	10 <sup>4</sup> - 10 <sup>7</sup> Ω	Zrinski et al. 1
Nb/Nb2O5/Pt	31 nm	Bipolar	1.2-1.5 V/- 0.8—0.9 V	n.a.	n.a.	n.a.	n.a.	Zaffora et al. <sup>2</sup>
Au/Nb2O5/Nb	90 nm	unipolar	1.3-2.9 V/ 0.4- 0.9 V	<10 <sup>2</sup>	n.a.	<100 Ω	10 <sup>4</sup> - 10 <sup>5</sup> Ω	Kundozerova et al. <sup>3</sup>

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### Supplementary Information

#### **Notes and references**

1. Zrinski, I. et al. Impact of Electrolyte Incorporation in Anodized Niobium on Its Resistive Switching. Nanomaterials 12, 813 (2022).

2. Zaffora, A., Macaluso, R., Habazaki, H., Valov, I. & Santamaria, M. Electrochemically prepared oxides for resistive switching devices. Electrochim Acta 274, 103–111 (2018).

3. Kundozerova, T. v., Stefanovich, G. B. & Grishin, A. M. Binary anodic oxides for memristor-type nonvolatile memory. Physica Status Solidi (C) Current Topics in Solid State Physics 9, 1699–1701 (2012).