Electronic Supporting Information

Physical mechanism for the synapse behaviour of WTiO_x-

based memristors

Hengjie Zhang,^{ab} Chuantong Cheng,^{*ab} Huan Zhang,^{ab} Run Chen,^{ab} Beiju Huang,^{*abc} Hongda Chen^{abc} and Weihua Pei^{ab}

^aState Key Laboratory on Integrated Optoelectronics, Institute of Semiconductors, Chinese Academy of Sciences, Beijing 100083, People's Republic of China

^bCollege of Materials Science and Opto-Electronic Technology, University of Chinese Academy of Sciences, Beijing 100049, People's Republic of China

^cBeijing Key Laboratory on Inorganic Stretchable and Flexible Information Technology, Beijing 100083, People's Republic of China

E-mail: chengchuantong@semi.ac.cn, bjhuang@semi.ac.cn



Figure S1. I-V curves of unannealed material. (a) The I-V curve of the Au/WTiO_x/Au device. (b) The I-V curve of the Ti/WTiO_x/Au device.



Figure S2. photograph of the device under an optical microscope. (a) Photograph of the device of $WTiO_x$ in 6 sccm O_2 samples. (b) Photograph of the device of $WTiO_x$ in 10 sccm O_2 samples.



Figure S3. XPS data. (a) XPS spectra of $WTiO_x$ films at -10 to 30 eV. (b) XPS spectra without background of $WTiO_x$ in 6 sccm O_2 samples of Figure 1d of the main text.



Figure S4. EDX data of $WTiO_x$ films sputterring on SiO₂. (a) EDX spectroscopy of $WTiO_x$ in 6 sccm O₂ flux. (b) EDX spectroscopy of $WTiO_x$ in 10 sccm O₂ flux.

Experimental Details

Post-annealing is carried out under pure 4sccm N_2 and standard pressure for better crystallization (In order to avoid secondary oxidation, oxygen flow is not introduced). The temperature and time are 300 °C and 30 min, respectively. Due to the lower temperature and non-vacuum annealing, the contribution of post-annealing to oxygen vacancies is negligible, and oxygen vacancies are primarily caused by oxygen-deficient atmosphere during sputtering. Post-annealing treatment can improve the switching properties of the materials as conductive filaments are more easily formed in the grain boundary gap of crystal material than in amorphous materials.

Actually, without post-annealing treatment the I-V curves of the fabricated devices fluctuate greatly. Although Au/WTiOx/Au devices have resistive properties, their I-V features are unstable as shown in Figure S1(a). There are no switching properties observed for $Ti/WTiO_x/Au$ devices, as shown in Figure S1(b).

The optical micrographs of Au/TiWO_x/Au and Ti/TiWO_x/Au devices are shown in Figure S2(a) and Figure S2(b), respectively. It can be found that the light transmittance of TiWO_x layers in Ti/TiWO_x/Au devices is better than that in Au/TiWO_x/Au devices, which means the oxygen vacancy concentration in pristine Au/TiWO_x/Au device is higher.

In Figure S3(a), two main peaks at about 22 eV (O2s) and 3–10 eV (W5d and O2p) can be seen, and the valence band spectra of 6 sccm O_2 samples showed a small bump very close to the Fermi level (indicated by the black arrow), which is attributed to W5d states.^{1, 2} It is well known that there is no electronic state near the Fermi level in a WO₃ stoichiometric insulator.³ The W5d states near the Fermi level indicate the presence of the low-valence and metallic states. The presence of a small bump at a low binding energy (~34 eV, indicated by the red arrow) in the W4f spectra (6 sccm O_2 samples in Figure 1(d)) is the evidence of the low-valence and metallic states, too. This bump is due to the high V_0 concentration in the 6 sccm O_2 samples. Figure S3b shows a partial-peak fit of the 6 sccm O_2 sample with a low-valence area ratio of about 5.1%, which roughly determinates the oxygen vacancy concentration.⁴ There is almost no V_0 concentration as no low-valence and metallic states was found in the 10 sccm O_2 samples. Hence, both the XPS data and the optical micrograph data present the same results.

Energy Dispersive X-Ray Spectroscopy (EDX) data of $WTiO_x$ films sputterring on SiO_2 in 6 sccm and 10 sccm O_2 atmospheres is shown in Figure S4a and S4b, respectively, and the W:Ti

atomic ratio is close to 1:1.

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