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**Supplementary Information**

# Probing electrochemically induced resistive switching of $TiO_2$ by SPM techniques

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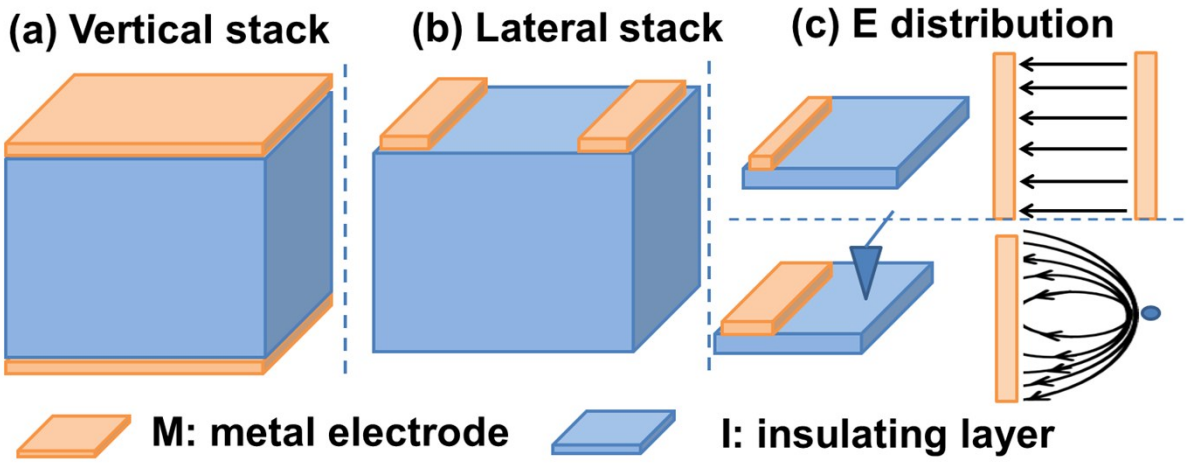
## Comparison of the Resistive Switching Cell structure

The resistive switching cell in practical use possesses the MIM structure and there are mainly two approaches to assembly this MIM structure, including 1) vertical stack; and 2) lateral stack.[1] The following figure schematically shows the geometries of these two resistive switching cells, both of which are widely adopted to configure the resistive switching cells with numerous examples being reported in the literature.[2-6]




In this study, a resistive switching cell was configured by laterally depositing two metal electrodes (M) on the surface of the prepared $TiO_2$ thin film (I), schematically showing in Figure 1 of the main text, which resembles the lateral MIM stack, with the major difference being one of the metal electrodes is the Pt-coated SPM tip in the work presented here. In addition, the electrical field distribution of between these two different lateral stacks may be different considering the area of the Pt tip electrode is much less than the pad electrode. The electrical field between two pad electrodes would be more evenly distributed than that between one pad electrode and one tip electrode as in the SPM experiments. The different distributions of the electrical field between electrodes can be seen from the top view showing in the above figure, even though, it is reasonable to claim that the strength of the electrical field, as well as the potential drop at the electrode/insulating film interface, would vary with the change of the distance between two electrodes. Resistive switching at the nanoscale is essential for miniaturizing the memory devices, and C-AFM technique is an ideal tool for studies in this field. In this work, the experimental geometry with a C-AFM tip is supposed to (and also evidenced to) make the tip/sample junction and the interfacial effects become vital for the resistive switching performance, which to some extent resembles the resistive switching cell with the electrode area of hundreds of nanometers.

[1] Waser R, Aono M. Nanoionics-based resistive switching memories[J]. Nature materials, 2007, 6(11): 833-840.
[2] Strukov D B, Snider G S, Stewart D R, et al. The missing memristor found[J]. nature, 2008, 453(7191): 80-83.
[3] Kwon D H, Kim K M, Jang J H, et al. Atomic structure of conducting nanofilaments in TiO2 resistive switching memory[J]. Nature nanotechnology, 2010, 5(2): 148-153.
[4] Yang J J, Pickett M D, Li X, et al. Memristive switching mechanism for metal/oxide/metal nanodevices[J]. Nature nanotechnology, 2008, 3(7): 429-433.
[5] Hsiung C P, Liao H W, Gan J Y, et al. Formation and instability of silver nanofilament in Ag-based programmable metallization cells[J]. ACS nano, 2010, 4(9): 5414-5420.
[6] Sawa A. Resistive switching in transition metal oxides[J]. Materials today, 2008, 11(6): 28-36.

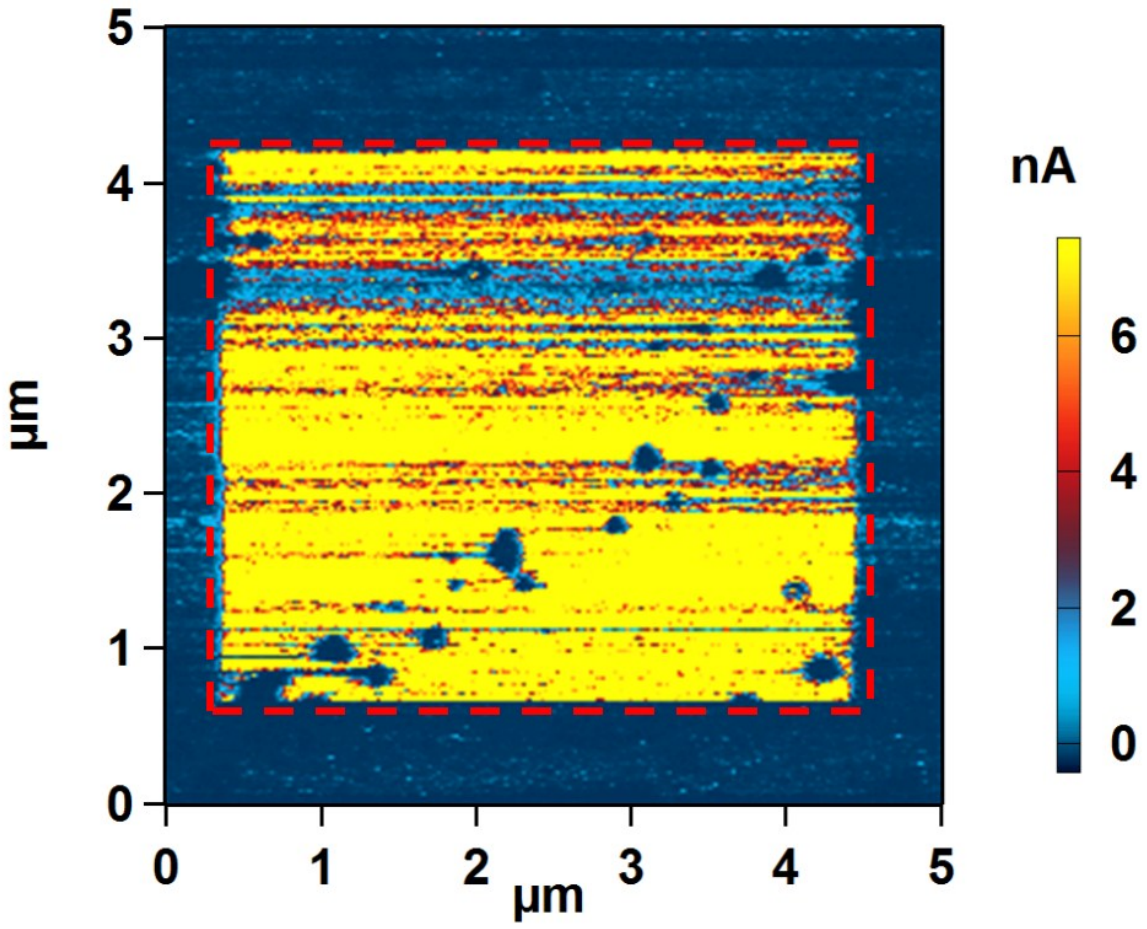



Figure S1. Current image obtained by C-AFM with a scanning voltage of 2 V. Before this scanning, area within the dashed box is pre-written by -6 V to switch the sample stack into LRS. The higher current within the box suggests that LRS can be maintained when switch off the voltage, which means the sample stack in our study is non-volatile.

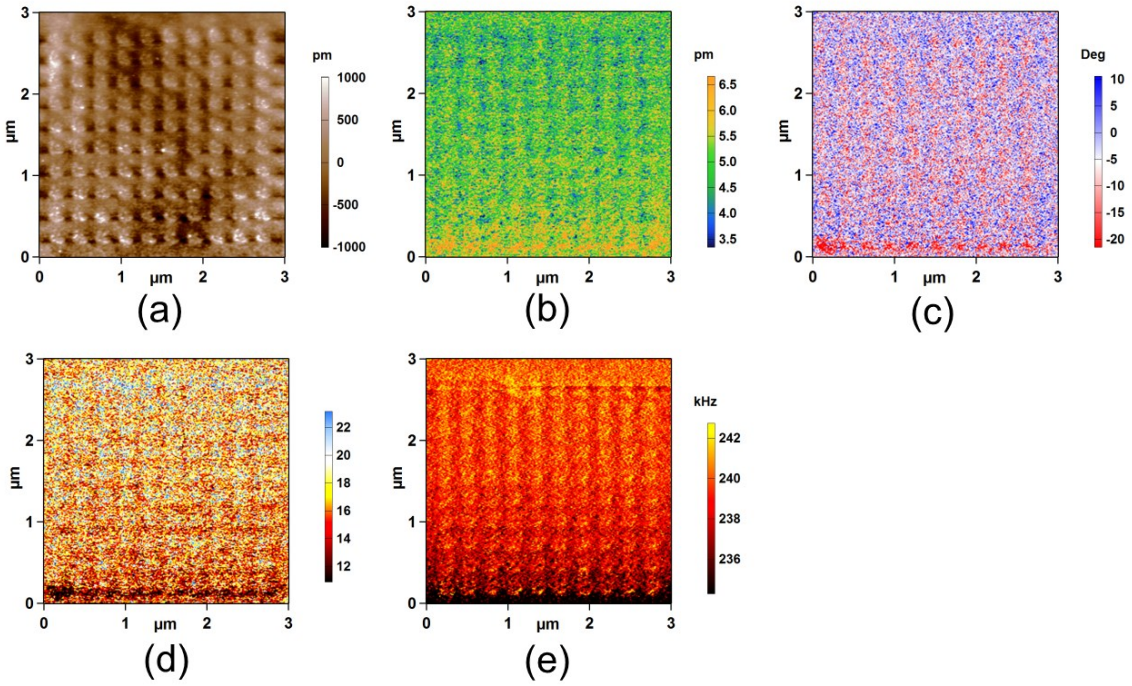



Figure S2: ESM images after applying voltages with an amplitude of 6 V: (a) topography, (b) amplitude, (c) phase, (d) Q-factor, and (e) resonance frequency.

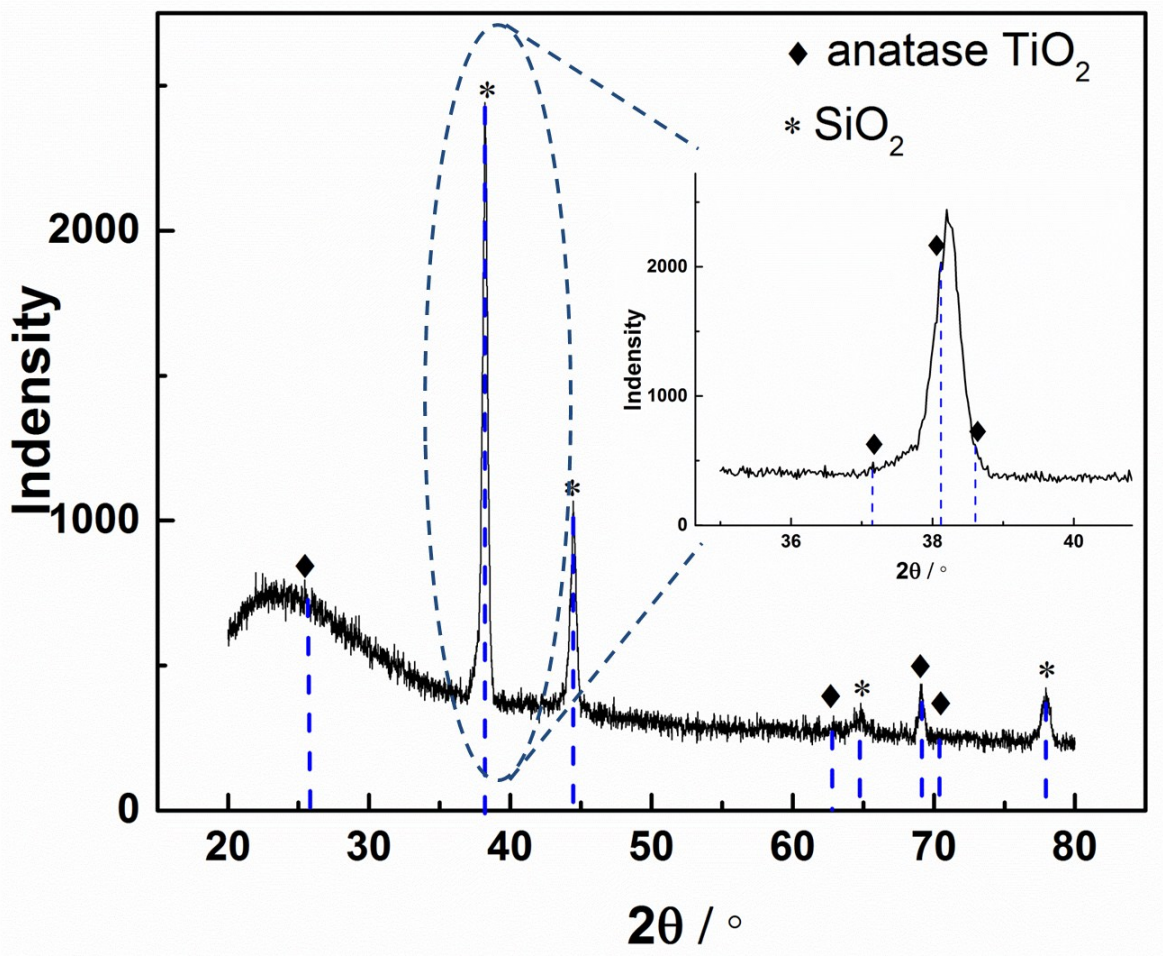



Figure S3: XRD pattern of $TiO_2$, showing a centrosymmetric anatase structure.

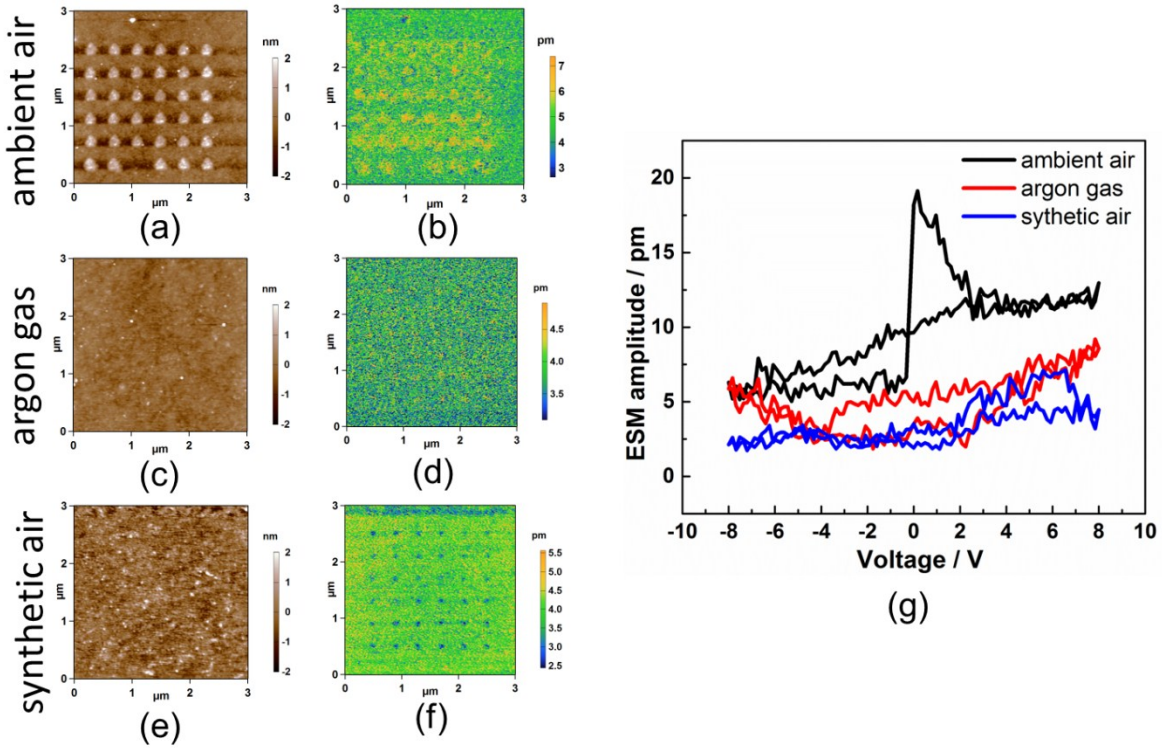



Figure S4: (a)-(f) Topographic images and ESM amplitude images after applying a 6 V dc voltage on a 6 × 6 grid in different environments. This dc voltage was deliberately extended for a long duration of 10 s to facilitate electrochemical processes underneath the SPM tip. (g) ESM amplitude loops as a function of environments.