**Supplementary Information**

**Resistive Switching Properties of Epitaxial $BaTiO_{3-\delta}$ Thin Films Tuned by After-Growth Oxygen Cooling Pressure**

*Yooun Heo[1], Daisuke Kan[2], Yuichi Shimakaw[2, 3], and Jan Seidel*[1]*

Yooun Heo, Jan Seidel
School of Materials Science and Engineering
University of New South Wales, Sydney, NSW 2052, Australia

Daisuke Kan, Yuichi Shimakawa
Institute for Chemical Research, Kyoto University, Gokasho, Uji, Kyoto, 611-0011, Japan

Yuichi Shimakawa
Japan Science and Technology Agency, CREST, Uji, Kyoto 611-0011, Japan

* Corresponding author e-mail: jan.seidel@unsw.edu.au

### AFM topography scans

Our $BaTiO_{3-\delta}$(BTO) thin films exhibit smooth surface topologies as shown in the following AFM topography scan image of a sample cooled at 50μTorr (Figure S1). This image is representative of all our oxygen deficient BTO samples in our studies.

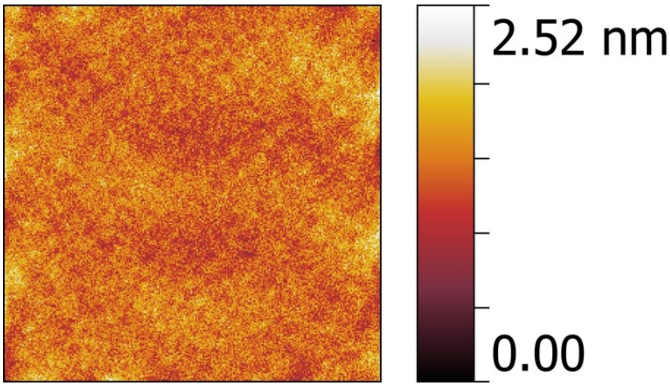


**Figure S1.** Topography image of BTO film cooled at 50μTorr with a root-mean-square surface roughness of 0.25nm

### Resistive switching characteristics of $BaTiO_{3-\delta}$ cooled at large oxygen pressure

In fact, the BTO thin film cooled at the largest oxygen cooling pressure (100Torr) also exhibits clear rectifying characteristics and hysteretic behaviour with two resistance states at the same voltage for up and down bias sweep. However, current levels are extremely low compared to other samples cooled at low oxygen pressure. We show a representative set of local I-V curve curves of 100Torr sample on a semi-log scale in Fig. S2. In the box of the figure, the sweep voltage ranges are shown for the I-V curves.

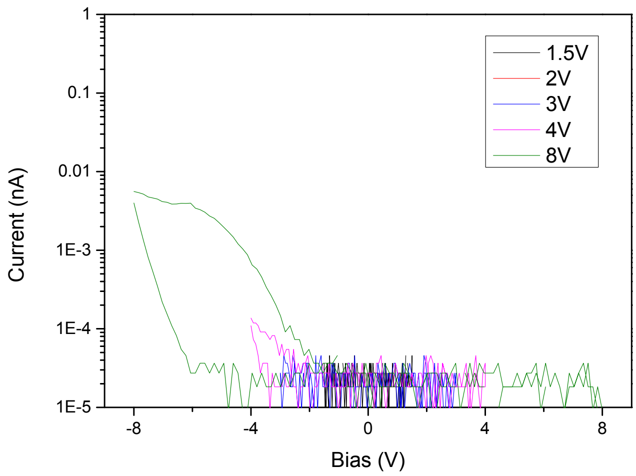


**Figure S2.** Locally acquired *I-V* curves of resistive switching behavior for the as-grown BTO film cooled at 100Torr oxygen pressure.

## Fitting of I-V curve to Schottky model

In a standard semiconductor Schottky barrier model, e.g. thermionic emission model, the current I under forward bias is expressed as a function of the bias voltage V as the following:

$$I = I_o exp\left(\frac{eV}{nk_BT}\right), \tag{S1}$$

$$I_o = A^* ST^2 exp\left(-\frac{e\varphi_B}{nk_BT}\right) \tag{S2}$$

$$A^* = \frac{4\pi em^* {k_B}^2}{h^3} \tag{S3}$$

where e is the electron charge, n an ideality factor, S the diode area, $k_B$ Boltzmann's constant, T the temperature, A* Richardson's constant, $\phi_B$ the Schottky barrier heights, m* the effective mass, and h Planck constant. Therefore, if the thermionic emission process is predominant in the conduction process, I is expected to increase exponentially with V, meaning the log I-V curves should be a straight line. For the reverse bias (negative bias), the log I-V curves in the LRS (HRS) during up (down) sweep can be well-fitted to a straight line in the lower voltage region as shown in Figure S2. Therefore, thermionic emission process can be considered predominant in the conduction mechanism. Moreover, the ideality factors can be calculated based on the I-V curves by rearranging the equations and these results are discussed in the manuscript. From the intersection of I at V=0 in log I-V characteristics, the effective Schottky barrier heights $\phi_B$ can also be estimated by approximations by using equations S2 and S3. However, since the series resistance of the interfacial layer gives rise to the large ideality factor, the standard equations S4 and S5 of a Schottky barrier model cannot provide reliable $\phi_B$ values.

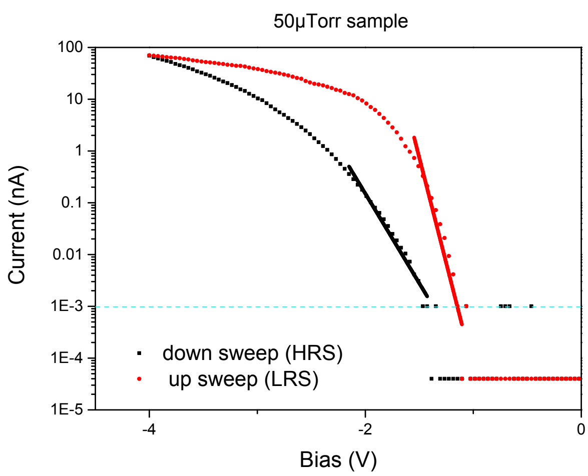


**Figure S3.** Linear fitting of the log I-V curve in the low voltage region for 50μTorr sample

**I-V curve measurements over a period of time**

We measured I-V curves of our oxygen deficient BTO samples at different times to see the impact of oxygen vacancies on the conductivity and the observed resistive switching properties. At early stage from the fabrication, we observed clear rectifying and hysteretic characteristics of I-V curves. On the other hand, after an 8 month period of time, no measurable current was observed due to the dispreading or removal of oxygen vacancies. A representative result is shown below in Figure S3 for as-grown state of BTO thin film cooled at 50μTorr

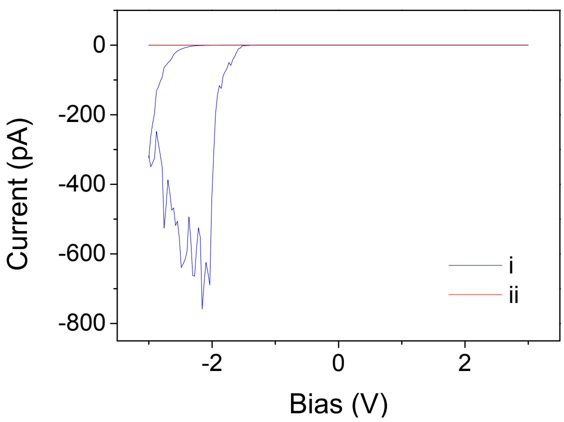


**Figure S4.** Comparison of I-V characteristics over a period of time:

(i) at early stage, (ii) after roughly 8 months' time since fabrication