Supporting Information

Self-Limiting Atomic Layer Deposition of Barium Oxide and Barium Titanate Thin Films Using a Novel Pyrrole Based Precursor

Shinjita Acharya,[1,] ǂ Jan Torgersen,[1,*] ǂ Yongmin Kim,[1] Joonsuk Park,[5] Peter Schindler,[1] Anup L. Dadlani,[2] Martin Winterkorn,[1] Shicheng Xu,[1] Stephen Walch,[1] Takane Usui,[3] Christian Schildknecht[4] and Fritz B. Prinz[1,5]*

1. Department of Mechanical Engineering, Stanford University, CA, 94305, USA
2. Department of Chemistry, Stanford University, CA, 94305, USA
3. BASF Corporation, Union, NJ 07083, USA
4. California Research Alliance (CARA), BASF Corporation, Berkeley, CA 94720, USA
5. Department of Material Science and Engineering, Stanford University, CA, 94305, USA

ǂ These authors contributed equally to the work.

Supporting Figures:

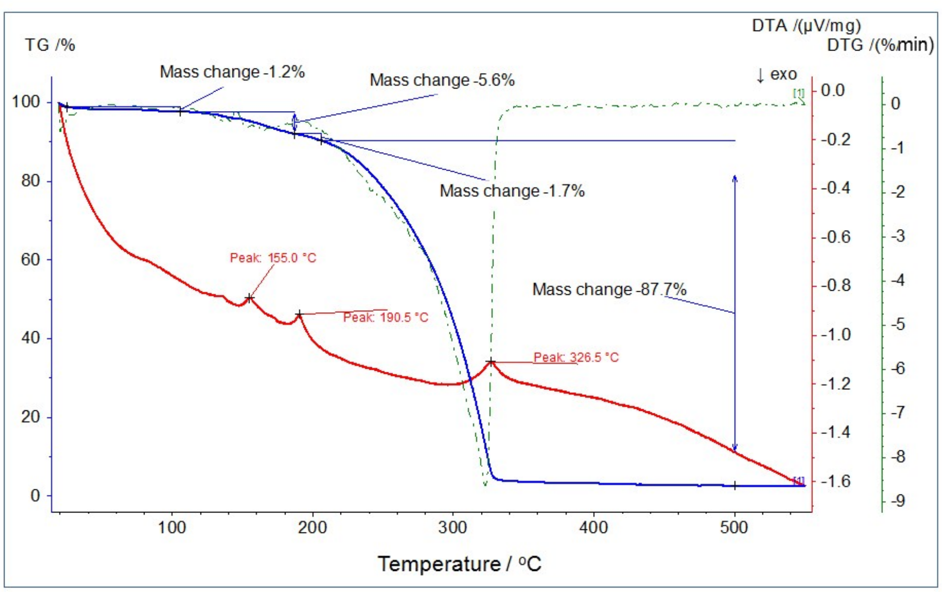

Fig. S1. Thermogravimetric (TG) plot of the py-Ba precursor.

Calculation of pressure differential:

The quantity of a gas can be indicated by way of its mass or its weight in the units of measure normally used for mass or weight. In practice, however, the product of p and V is often more interesting in vacuum technology than the mass or weight of a quantity of gas. The pV flow through any desired piping element, i.e. pipe or hose, valves, nozzles, openings in a wall between two vessels, etc., is indicated by the equation $Q = \Delta P * C = (P_1 - P_2)\ C$ [1] where Q is the total throughput by convection. P_1 and P_2 are the upstream and downstream pressures. Here in our case, the pressure of the precursor cylinder and the chamber. ΔP is the difference of P_1 and P_2. C is the conductance (volume/time). For example, the conductance of a simple orifice is $C = 15d^2$ (where d is the diameter of the orifice). The pressure P_1, 10^{-4} bar (75mTorr), is the precursor vapor pressure at 180 ^{o}C, P_2, the base pressure (before injecting precursor) is 0.1 Torr. Considering C to be constant, the amount of precursor dose delivered has been calculated accordingly.

Ellipsometry mapping:

The growth-per-cycle (GPC) and thickness standard deviation plotted in Fig. 2 and 3 of the manuscript are measured on 7 different spots on the wafer as depicted in Fig. S3.

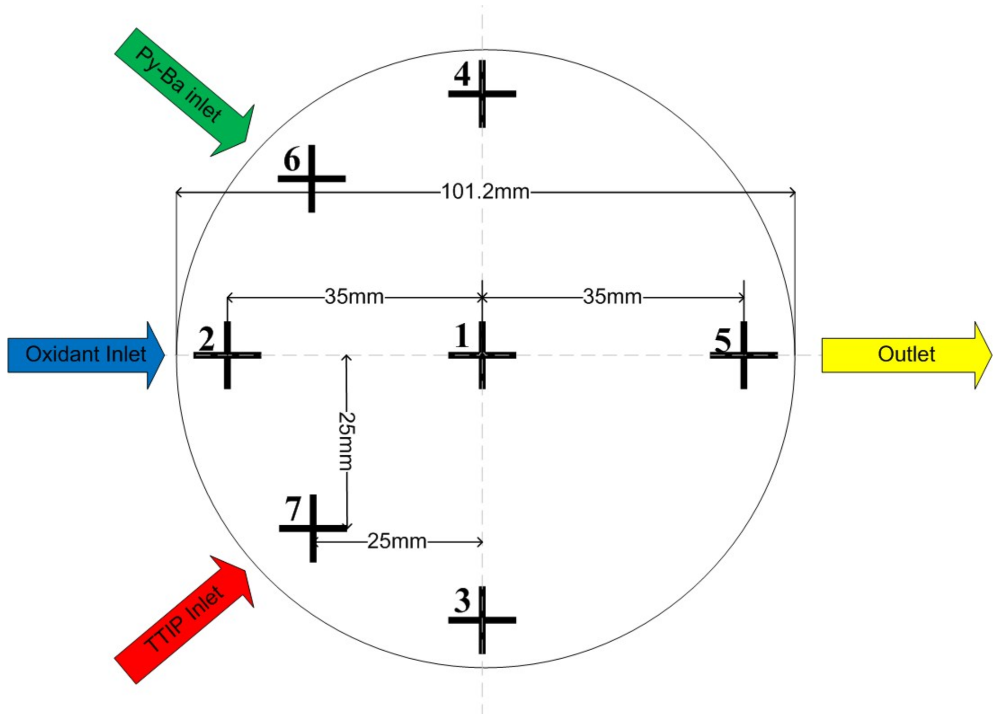

Fig. S2. Spectroscopic ellipsometry measurement procedure for obtaining the thickness and GPC standard deviation on 4-inch Si <100> wafers.

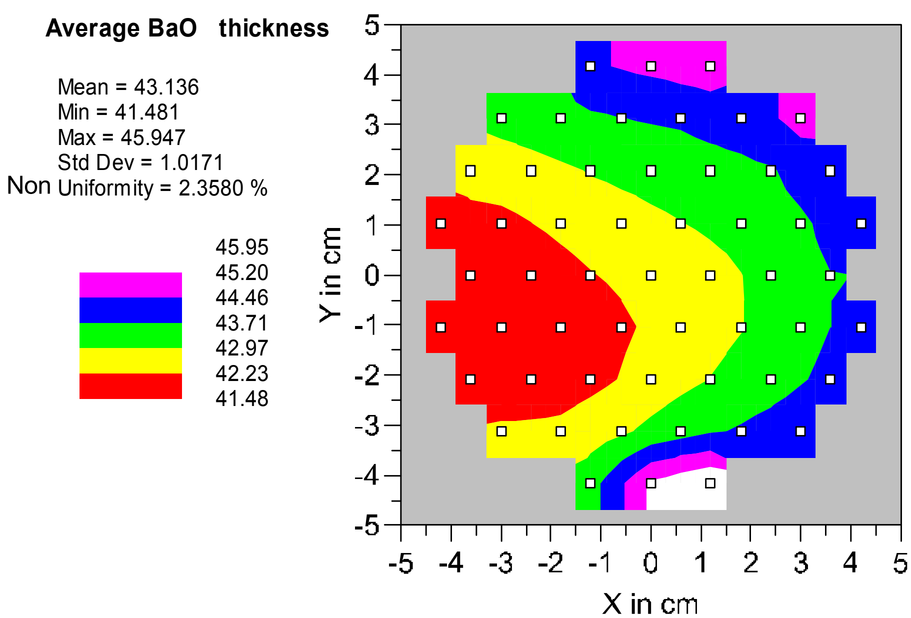

Fig. S3. Color mapping for thickness distribution of BaO on a 4inch wafer as obtained from a 55 point spectroscopic ellipsometry measurement.

For comparison, 20 cycles of Al_2O_3 deposition using trimethylaluminium (TMA) and H_2O according to a well-known recipe was performed on a four inch wafer in our reactor. The thickness was 19 Å and the standard deviation was 0.6 Å as shown below. Considering that the radii of Ba atoms and Ba-O bond distances are much larger than Al atoms and Al-O bond distances, we can claim that the BaO uniform thickness distribution (deposited using py-Ba and H_2O) strongly supports the self-limiting growth mode.

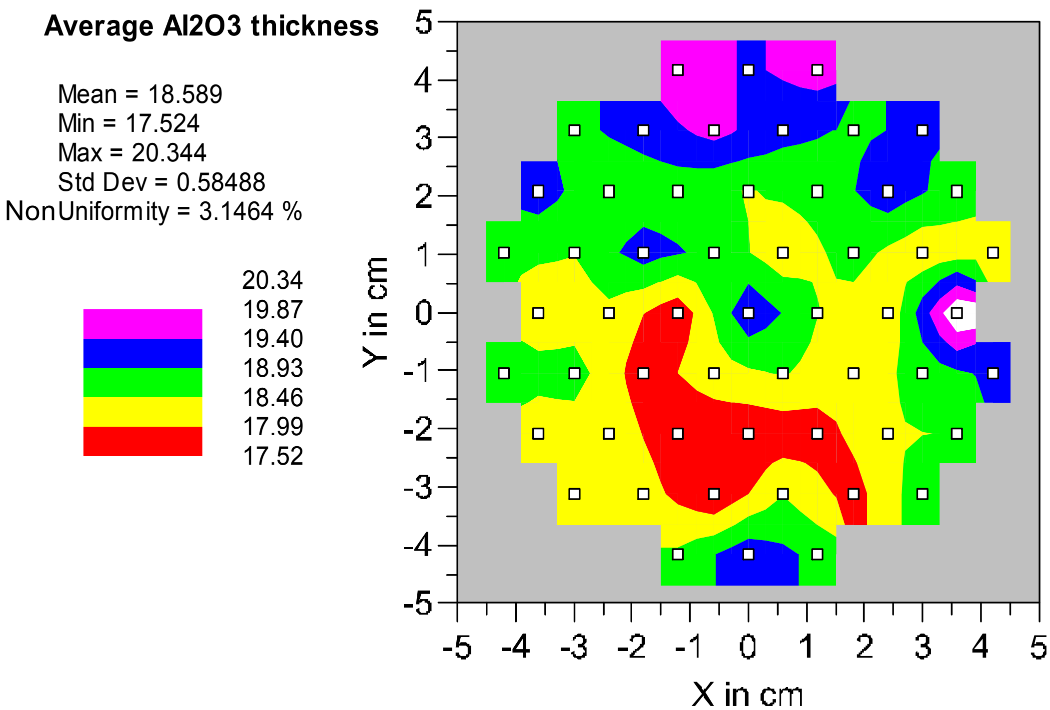

Fig. S4. Color mapping for thickness distribution of Al_2O_3 film (20 cycles of TMA and H_2O) on a 4-inch wafer as obtained from a 55 point spectroscopic ellipsometry measurement.

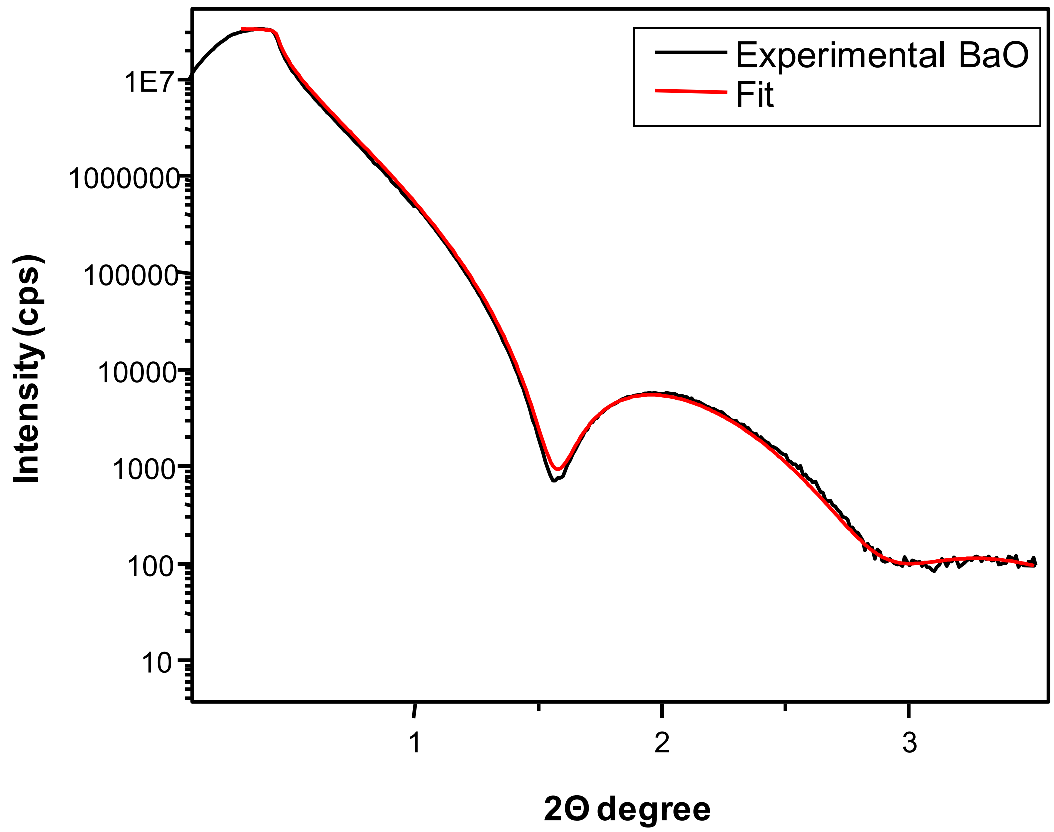

Fig. S5. X-Ray reflectivity (XRR) spectra of BaO and the corresponding fit (100 cycles of py-Ba and H_2O).

Thickness	Roughness	Density
4.8 nm	1.06 nm	4.76 g/cm^3

Table S1. Thickness, roughness and density measured from XRR.

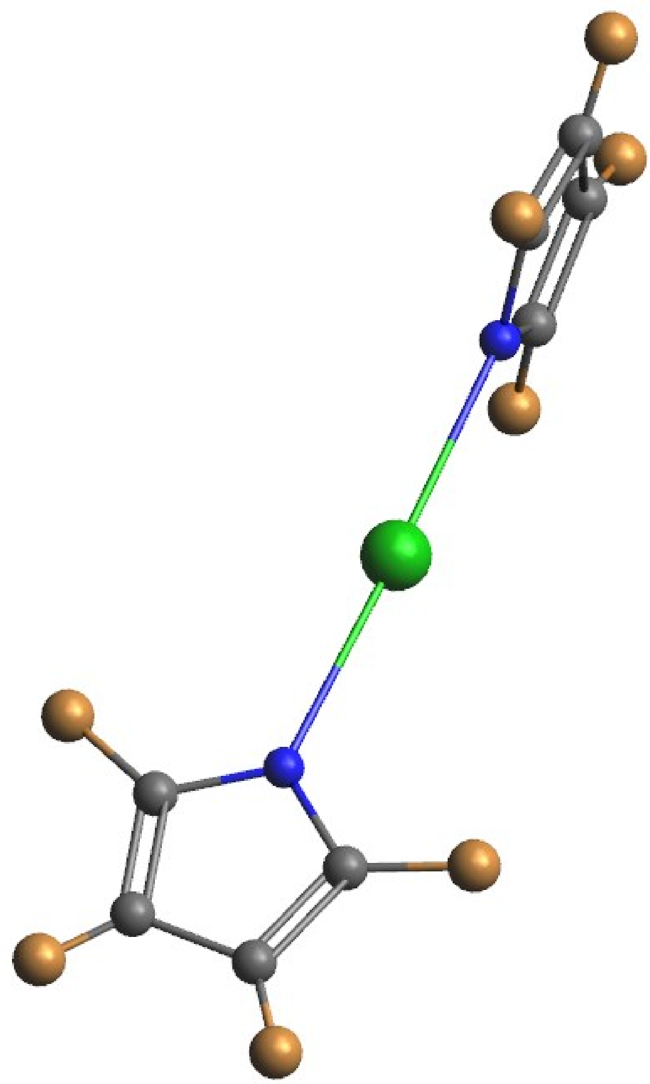

Fig. S6. Optimized py-Ba precursor with DFT, Gaussian 09 package. The Ba-N bond distances are 2.709 Å, the N-Ba-N angle is 177.9°; Ba atom is represented as green, N as blue, C as gray and proprietary substituents on the pyrrole ring as brown.

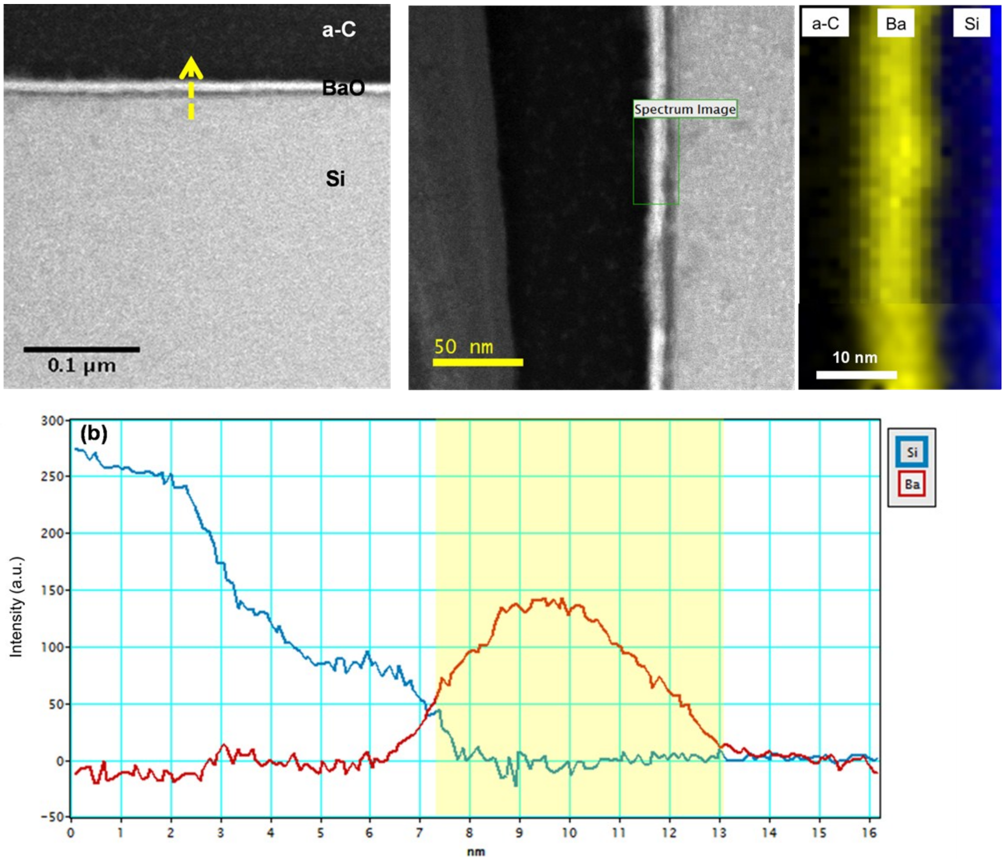

Fig. S7. (a) Representative STEM-EELS image for the interface region showing that STEM-EELS line scan along yellow arrow mark has been done. The dark region is amorphous C, and lighter one is BaO film. (b) STEM-EELS line scan profile from Si-L edge and Ba-M edge signals. The yellow shaded region is chosen to calculate the thickness of the BaO film at the interface. Note that a small Si bump between Si substrate and BaO comes from SiO2 layer. (c) STEM-EELS mapping (right) showing the elemental distribution at the interface and STEM-ADF ((Annular Dark Field) image (left) showing the area that the STEM-EELS mapping was performed.

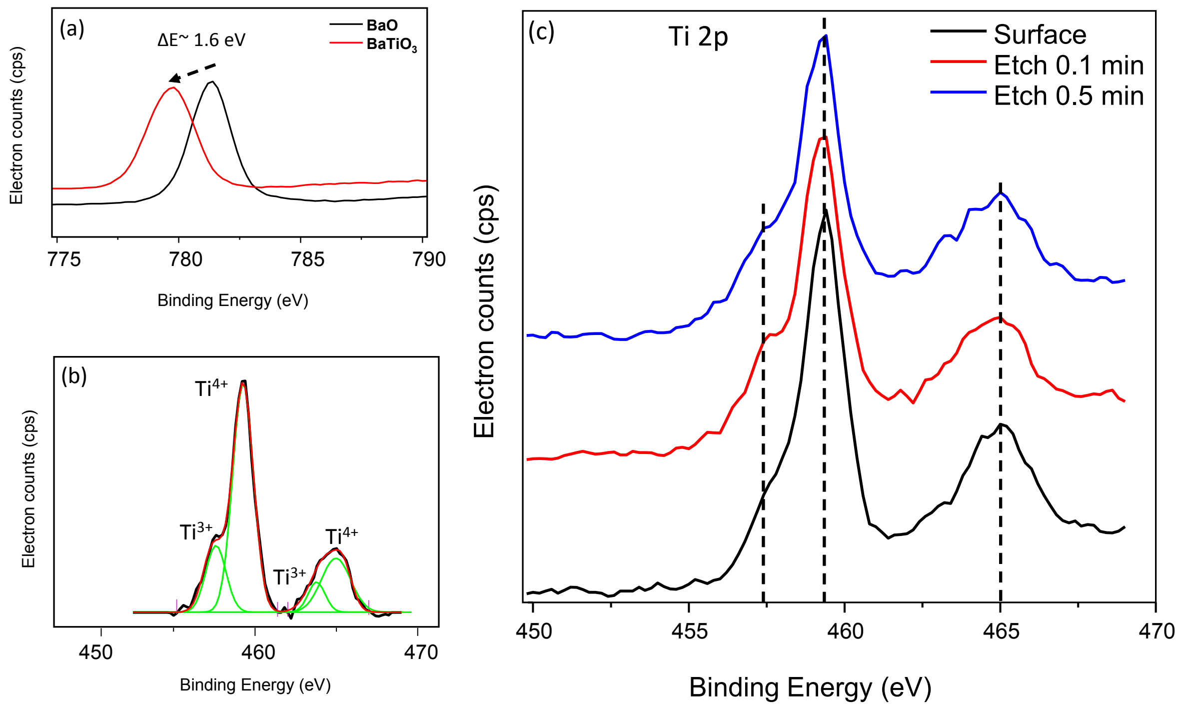

Fig. S8. High resolution XPS of (a) Ba 3d peak in pure ALD BaO and ALD BTO and the B.E shift to a lower value by ~ 1.6 eV shows a lower oxidation state consistent with BTO. (b) Deconvolution of Ti 2p peak in BTO shows different oxidation states of Ti like Ti^{3+} apart from predominant Ti^{4+} state. (c) The Ti-2p peaks at the surface, after 0.1 min and 0.5 min of sputtering respectively showing a uniform composition in the bulk of the film.

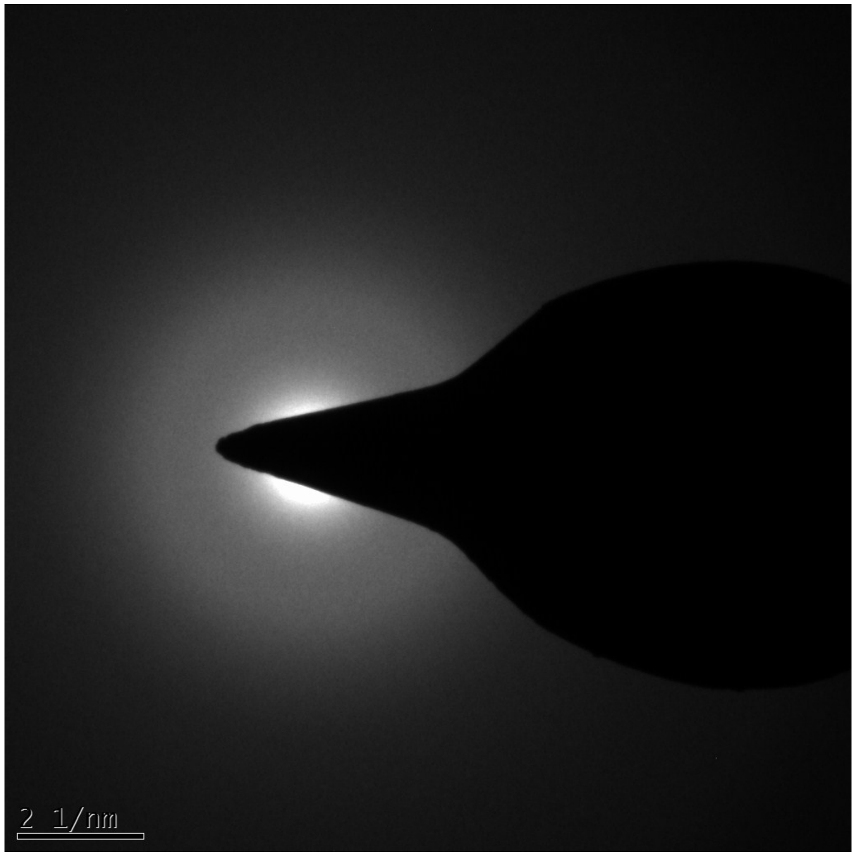

Fig S9. Selected area TEM diffraction (SAD) pattern of ~7 nm thick BTO film.

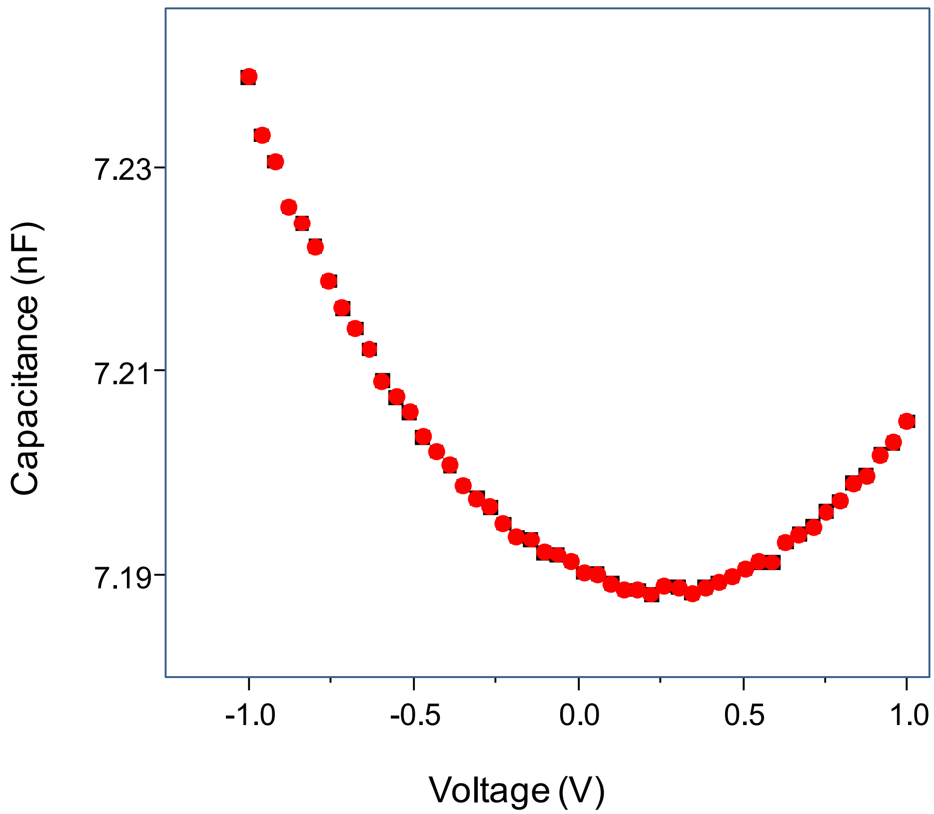

Fig. S10. Representative capacitance-voltage (C-V) characteristics of BTO thin film (20 nm) at 1 kHz frequency. The capacitor area defined by the top electrode was $(0.68*10^{-3})^2$ m^2.

Supporting Reference:

(1). Fundamentals of Vacuum Technology. Book chapter. 00.200.02 Kat.-Nr. 199 90