Electronic Supplementary Material (ESI) for Nanoscale.
This journal is © The Royal Society of Chemistry 2018

Supporting Information for:

Extended cation solubility in atomic layer deposited nanocrystalline $BaTiO_3$ thin films and its strong impact on the electrical properties

Matthias Falmbigl[1], Igor A. Karateev[2], Iryna S. Golovina[1], Aleksandr V. Plokhikh[1], Thomas C. Parker[3], Alexandre L. Vasiliev[2], and Jonathan E. Spanier[1,4,5]

[1]Department of Materials Science & Engineering, Drexel University, Philadelphia, Pennsylvania 19104, USA

[2]National Research Center "Kurchatov Institute", Kurchatov Square 1, Moscow 123182, Russia

[3]US Army Research Laboratory, Aberdeen Proving Ground, Maryland 21005, USA

[4]Department of Electrical & Computer Engineering, Drexel University, Philadelphia, Pennsylvania 19104, USA

[5]Department of Physics, Drexel University, Philadelphia, Pennsylvania 19104, USA

X-ray reflectivity fitting results

Table S1. Fitting results for the XRR-data on Si-substrates after deposition for all four samples using a superlattice model and the Motofit program.[1] The deposition sequence was: $(Ti(iOPr)_4$-$H_2O)$ x 40 + [(4 x $(Ba(iPr_3Cp)_2)$-H_2O) x y + $(Ti(iOPr)_4$-$H_2O)$ x z] x 10.

Ba/Ti-ratio	**0.8**	**0.92**	**1.01**	**1.06**
y, z	25, 55	25, 50	25, 46	25, 42
SiO_2-layer, Å	15.3	20.3	14.5	10.1
TiO_2-layer (1) , Å	13.5	13.0	12.0	12.0
$Ba(OH)_2$-layer, Å	34.6	36.5	37.9	37.8
TiO_2-layer (2) , Å	18.2	17.2	15.2	13.7
GPC ($(Ti(iOPr)_4)$, Å	0.3	0.3	0.3	0.3
GPC $(Ba(iPr_3Cp)_2)$, Å	0.3	0.4	0.4	0.4

Atomic force and scanning electron microscopy

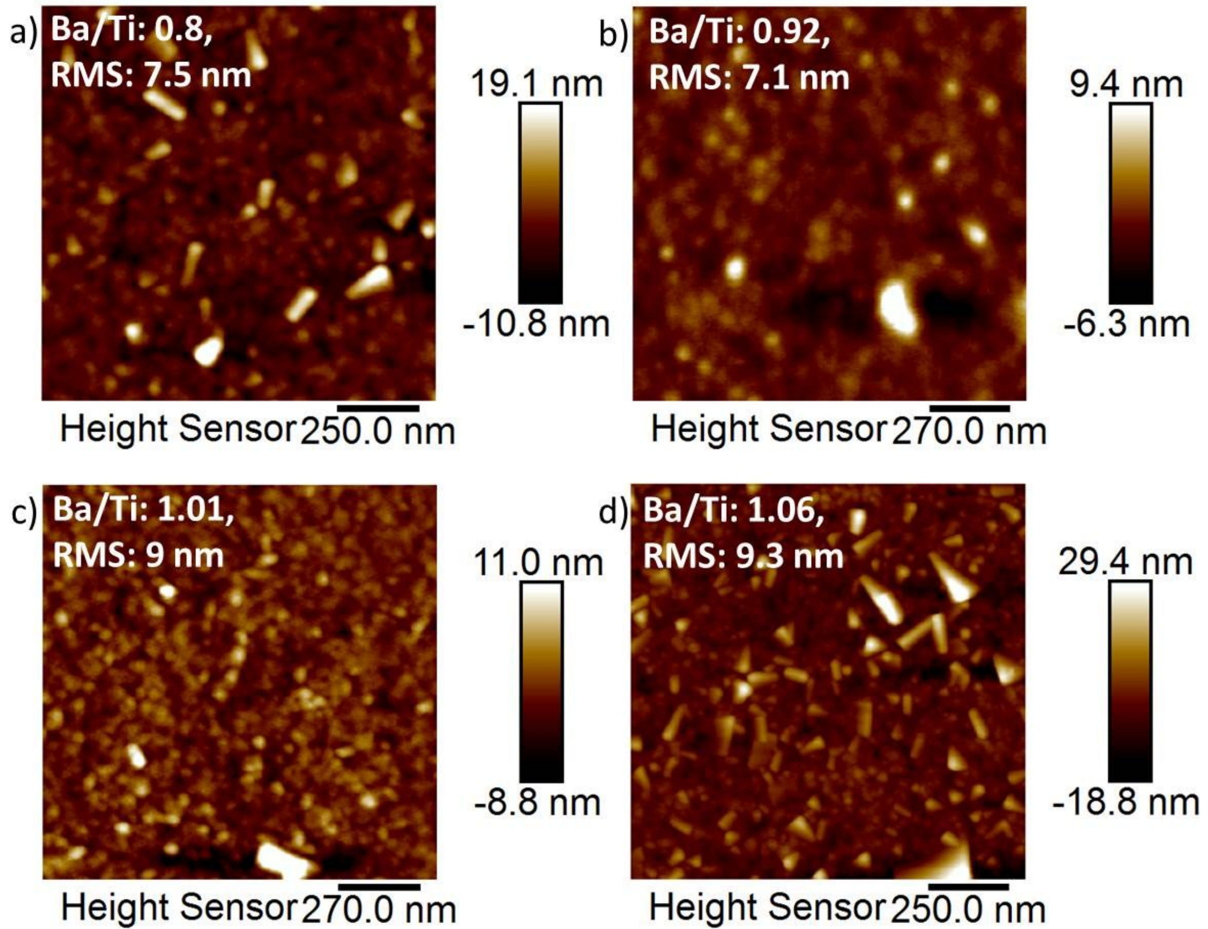

Fig. S1. AFM images of the film surface of films with varying Ba/Ti-ratio: a) 0.80, b) 0.92, c) 1.01, and d) 1.06. The areas were selected avoiding the abnormally large grains. The root mean square roughness is provided for each image.

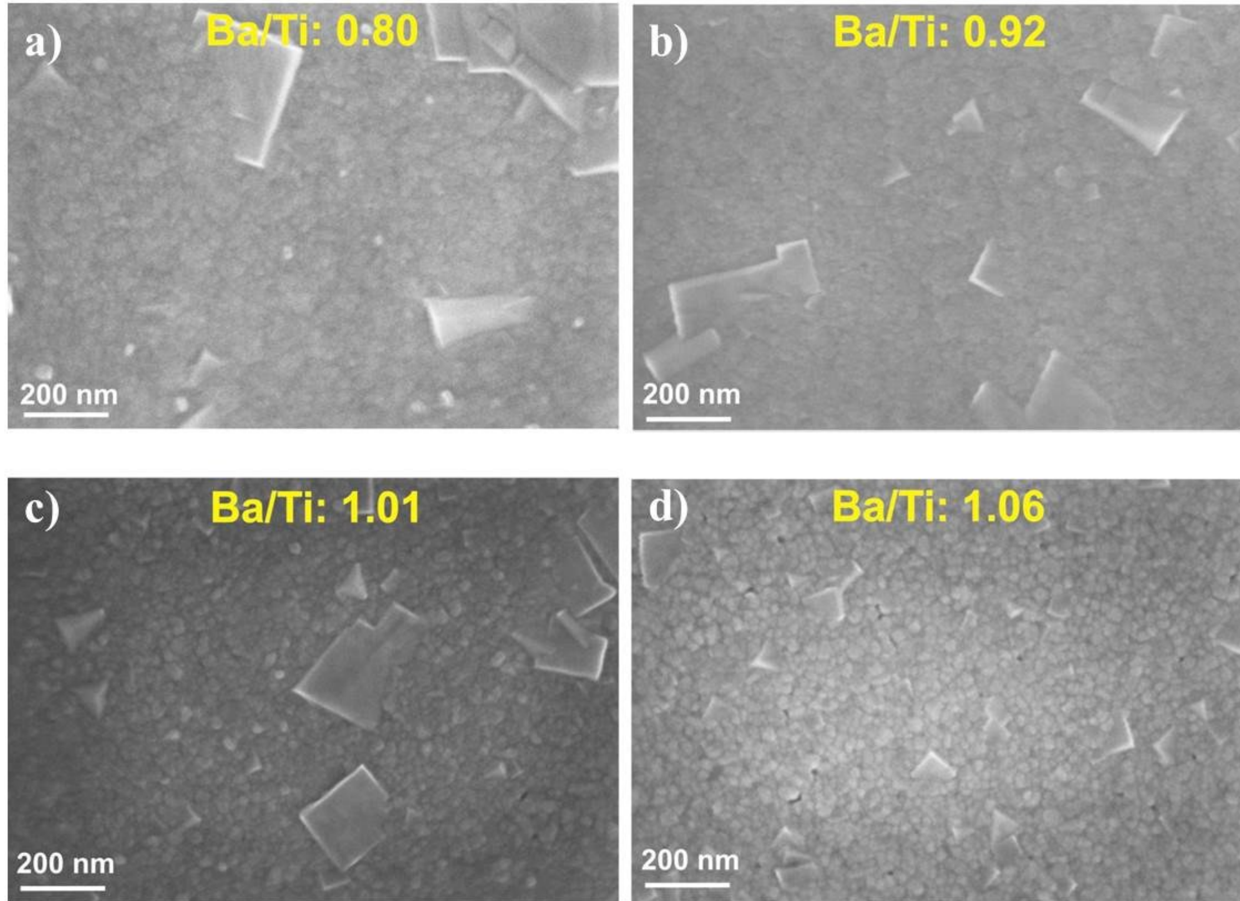

Fig. S2. SEM images collected at 10 kV on Pt(111)/Ti/SiO_2/Si(100) substrates for the films with Ba/Ti-ratios of a) 0.80, b) 0.92, c) 1.01, and d) 1.06 after annealing at 750°C.

The grain sizes were evaluated from the smaller matrix grains and the large facetted grains of an unknown phase were not included. These large grains are not observed under the Pt-electrodes, which were sputtered onto the film surface before the annealing step. First results for these large grains indicate a Ba-rich phase, most likely α-$Ba(OH)_2$, which forms during the crystallization of $BaTiO_3$ at the surface. Further investigations to identify these large grains are ongoing.

Table S2. Average grain sizes evaluated from the AFM and SEM images displayed in Figs. S1 and S2.

Ba/Ti-ratio	**Average grain size from AFM,** ***nm***	**Average grain size from SEM,** ***nm***
0.80	40(10)	40(10)
0.92	44(10)	45(10)
1.01	41(10)	49(10)
1.06	38(10)	42(10)

EF-TEM results

In order to evaluate the non-uniformity of the Ba/Ti-ratio for each sample the distribution of the cation ratio at each spot measured by EF-TEM was fitted using a Gaussian function. In all cases 4 areas similar to ones used in Fig. 6 were evaluated. Only for the sample with a Ba/Ti-ratio of 0.8 2 areas were used. The full width at half maximum (FWHM) for each composition, which directly reflects the non-uniformity, is displayed in Fig. S3.

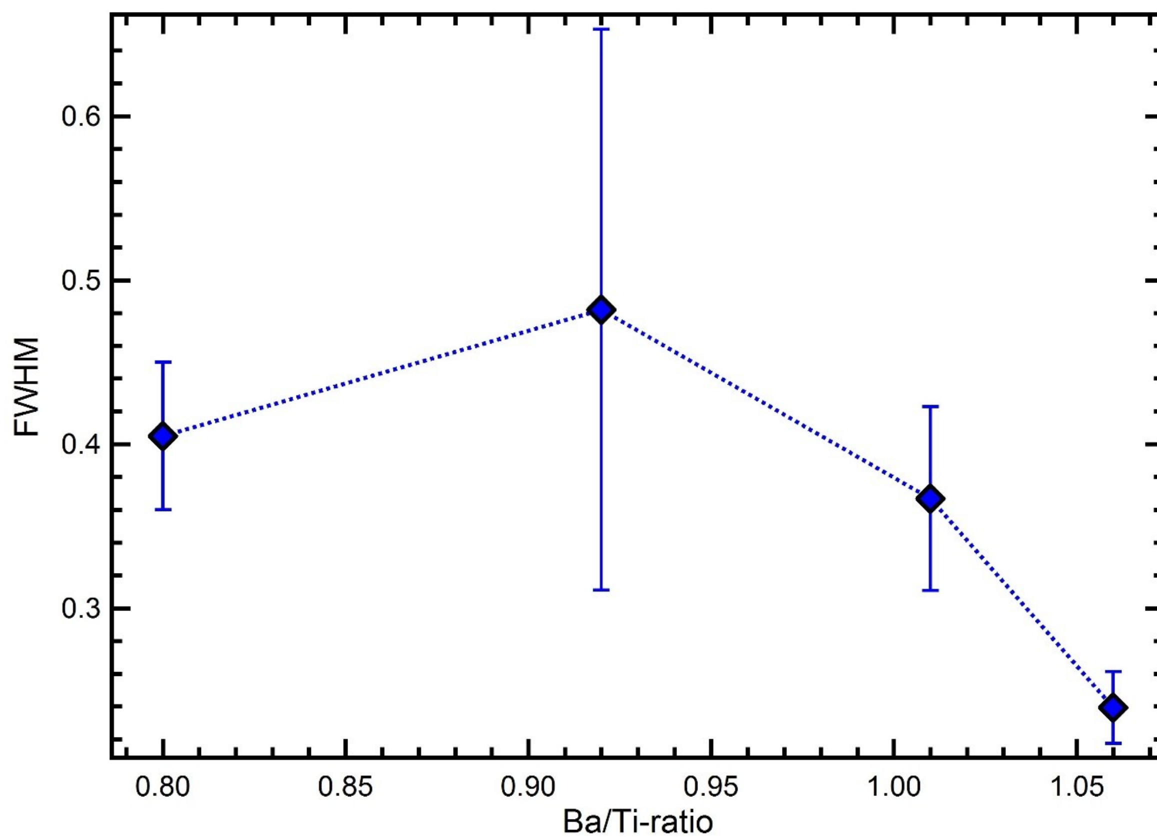

Fig. S3. FWHM of a Gaussian function fitted to the Ba/Ti-ratio distribution from EF-TEM for each sample.

Physical Properties

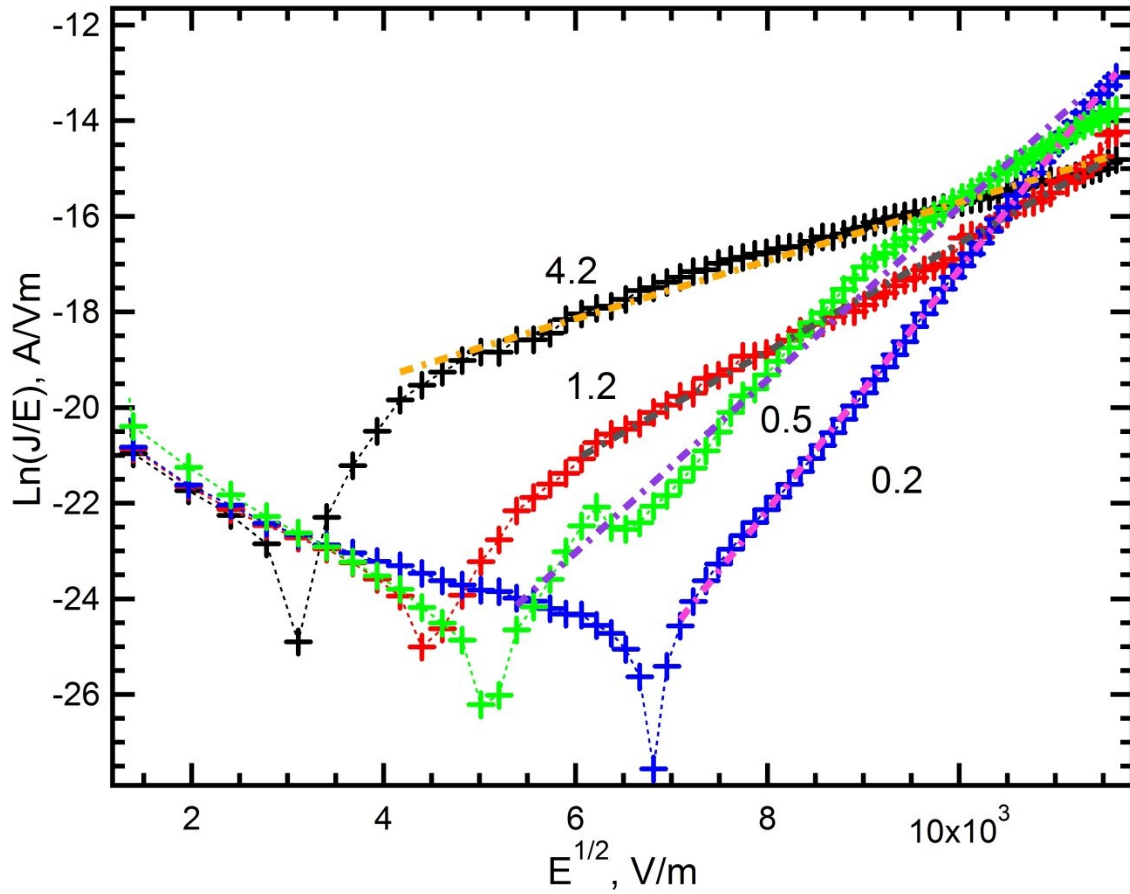

Fig. S4. Dependence of Ln(J/E) vs. $E^{1/2}$ for all four samples applying a positive bias. The dashed lines correspond to fits to the modified Schottky equation by Simmons,[2] and the values are the resulting value for the optical dielectric constant.

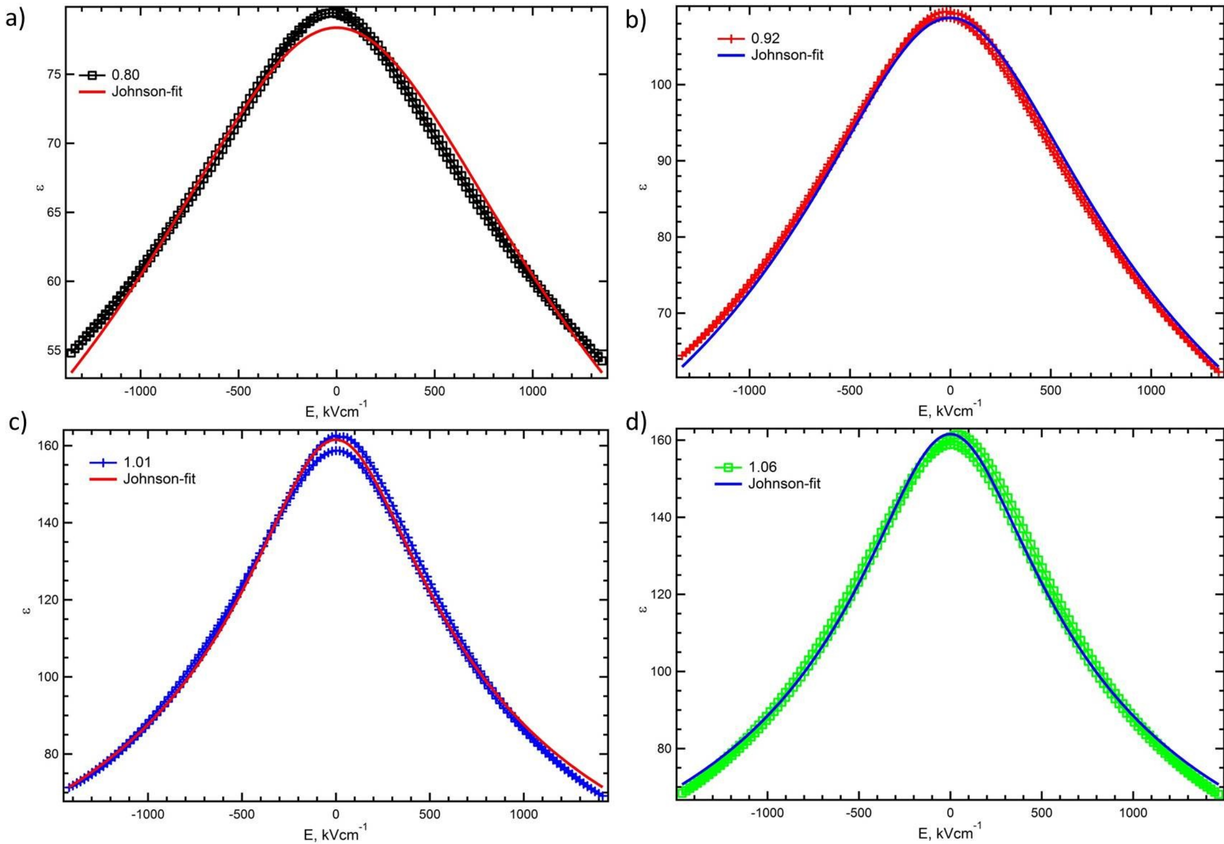

Fig. S4. Dependence of the dielectric constant on the applied electric field for Ba/Ti-ratios of a) 0.8, b) 0.92, c) 1.01, and d) 1.06. The lines represent least-squares fits to the Johnson model.[3]

References:

1. Nelson, A. Co-refinement of multiple-contrast neutron/X-ray reflectivity data using MOTOFIT. *J. Appl. Crystallogr.* **39,** 273–276 (2006).

2. Simmons, J. G. Richardson-Schottky effect in solids. *Phys. Rev. Lett.* **15,** 967–968 (1965).

3. Johnson, K. M. Variation of Dielectric Constant with Voltage in Ferroelectrics and Its Application to Parametric Devices. *J. Appl. Phys.* **33,** 2826–2831 (1962).