

**Electronic Supplementary Information. Appendix 1. Preparation and characterization of self-supported films of BaTiO<sub>3</sub>.**

Amorphous layers of BaTiO<sub>3</sub> were deposited at room temperature by RF oxygen/argon (80/20 v/v,  $4 \times 10^{-3}$  mBar) plasma sputtering from a stoichiometric target on (100)-oriented n-type Si substrates ( $280 \pm 20$   $\mu\text{m}$  thick,  $1\text{-}10 \text{ } \Omega \cdot \text{cm}$ ), which had been previously covered with a 20 nm thick MgO layer<sup>11</sup>. The MgO layer was deposited by RF oxygen plasma ( $5 \times 10^{-4}$  mBar) sputtering from a pure Mg target (Semiconductor Materials, 99.99%) followed by annealing in air for 3 hrs at 700 °C. According to SEM (Leo Supra 55VP) and XRD (Rigaku D-max/B goniometer equipped with a thin film attachment) measurements performed in  $\theta$ - $2\theta$  and  $2\theta$  (incidence angle  $3^\circ$ ) modes, the MgO layer was completely crystalline and consisted of platelet-shaped grains 20-50 nm in diameter that had no preferred crystallographic orientation. The surface roughness of the MgO layer was below 5 nm.

The chemical composition of the amorphous BaTiO<sub>3</sub> was verified by energy dispersive X-ray fluorescence spectroscopy (EDS, Oxford, approximate measurements) and X-ray photoelectron spectroscopy (XPS, Kratos, precise measurements). Calibration for both techniques was performed with respect to stoichiometric BaTiO<sub>3</sub> (Semiconductor Materials, 99.95%). Only the films for which the deviation from stoichiometry was smaller than 0.2% were used for the experiments. Anisotropic local etching of Si substrates with an aqueous solution containing 50% (NH<sub>2</sub>)<sub>2</sub> and 2% KOH (w/w) at 90 °C for 5 hrs<sup>28</sup> produced 150-250  $\mu\text{m}$  square windows with self-supported films (films **B**) tethered at their edges (Fig. 1a). The silicon etching solution does not attack the MgO layer. The MgO layer from films **B** can be removed with an aqueous solution containing 3% acetic acid (w/w) (20 min at room temperature) forming films A. This solution does not attack either amorphous BaTiO<sub>3</sub> or Si. According to XPS, the etching processes do not contaminate either the front or back surfaces of the film and complete removal of both Si and MgO, whenever required, was achieved.

Heating of the self-supported films was performed in air in a horizontal oven under isothermal conditions maintained with a spatial uniformity better than 0.01 °C/mm. Following each stage of the heating treatment, the preservation of the chemical composition of the films was monitored by XPS. No deviation from stoichiometry as a result of heat treatment was found.

The surface morphology of the films was analyzed with atomic force microscopy (AFM, Topometrics). The crystallinity of the self-supported films was characterized by transmission wide angle X-ray diffraction (WAXD,  $90^\circ$  incidence angle,  $2\theta$  -detection limits =  $20\text{-}50^\circ$ ), by electron diffraction (ED in TEM) and by high resolution transmission electron microscopy (HRTEM, Phillips CM-120).

The spectral dependence of the optical absorption of each film was measured with a Varian Cary 50 Probe UV-Vis spectrophotometer before and after each step of the heating process. The optical band gaps were estimated by linear fitting of  $\ln(\mathbf{I})^2 - E$  for a direct band gap and of  $\ln(\mathbf{I})^{1/2} - E$  for an indirect band gap<sup>29</sup>, where  $\mathbf{I}$  is the optical absorption of a film and  $E$  is the photon energy. Since,  $\mathbf{I}$  is a product of the film thickness and the optical absorption coefficient this procedure is adequate.

The method of deducing the film thickness from the internal interference maxima observed in the optical absorption spectra is described in Electronic Supplementary Information Appendix 2.

### Electronic Supplementary Information. Appendix 2. Measurements of film density by the internal interference technique.

A typical optical absorption spectrum of a thin self-supported BaTiO<sub>3</sub> film is shown in Fig. 1. A2. The spectrum contains minima and maxima corresponding to the internal interference effect. The wavelengths corresponding to the minima and the maxima are given by:

$$\lambda_{\min} = \frac{4d \cdot n}{2k+1} \quad \text{and} \quad \lambda_{\max} = \frac{2d \cdot n}{k} \quad (\text{B1})$$

where  $d$  is the film thickness,  $n$  is the refractive index,  $k$  is the integer order of the minima or maxima. The wavelengths corresponding to  $k=1$  are not accessible; therefore the orders of the minima and the maxima were determined by the following procedure. The shifts of the positions of the minima and maxima due to heating are small with respect to the distance between them. Therefore the assigned values of  $k$  should remain unchanged. Prior to substrate removal the refractive index of the as-deposited films can be measured exactly ( $\pm 0.2\%$ ) by ellipsometry (Rudolph,  $\lambda=634.2$  nm) performed at multiple angles ( $60^\circ$ ,  $65^\circ$ ,  $70^\circ$ ). Within an accuracy of  $\approx 10\%$  the thickness of the films prior to substrate removal can be determined with a surface profiler. Using these two measurements, the order  $k$  of the minimum or maximum closest to 634.2 nm can be determined for the self-supported films. This also provides the exact thickness ( $\pm 0.5\%$ ) of the films before heating and permits assignment of  $k$  for all observable minima and

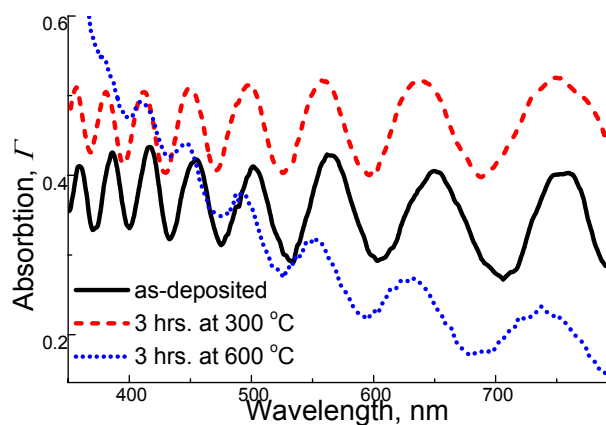


Fig. 1.A2. Example of a transmission optical spectrum of a self-supported film.

maxima. From the shift of the positions of the minima and maxima after heating, one can find the product  $d \cdot n$  for each observable minimum or maximum.

According to the Clausius-Mossotti equation the ratio of densities  $\frac{\rho_1}{\rho_2}$  of two films having similar chemical composition (i.e. polarizability) with refractive indices  $n_1$  and  $n_2$  should follow the relation:

$$\frac{\rho_1}{\rho_2} = \left( \frac{n_1^2 - 1}{n_1^2 + 2} \right) \left( \frac{n_2^2 + 2}{n_2^2 - 1} \right) \quad (\text{B2})$$

Assuming that the expansion is isotropic, one obtains  $\frac{\rho_1}{\rho_2} = \left( \frac{d_2}{d_1} \right)^3$  and  $\left( \frac{d_2}{d_1} \right)^3 = \left( \frac{n_1^2 - 1}{n_1^2 + 2} \right) \left( \frac{n_2^2 + 2}{n_2^2 - 1} \right)$ .

The thickness,  $d_1$ , and the refractive index,  $n_1$ , are known for each amorphous film at room temperature,

and the optical path  $l_2=(d_2 \cdot n_2)$  is known for the same films after annealing. Then the refractive index  $n_2$  must satisfy:

$$\left(\frac{l_2}{n_2 d_1}\right)^3 = \left(\frac{n_1^2 - 1}{n_1^2 + 2}\right) \left(\frac{n_2^2 + 2}{n_2^2 - 1}\right) \quad (\text{B3}),$$

and the relative density of the films can be calculated. The refractive index of the films depends on the wavelength; therefore, the minima and the maxima are not equally spaced and the procedure was performed for three minima and maxima at the longest wavelengths possible. Then a statistical average was calculated with 95% confidence level.