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FERROELECTRICS

Evidence of 90° polarization switching in polycrystalline macro-domains of self-supported $BaTiO_3$ films

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Abstract It was shown previously that the self-supported films of nanocrystalline (30–80 nm) $BaTiO_3$ spontaneously split into regions, within which the direction of spontaneous polarization of each grain is aligned as closely as possible to some average direction. These regions, called polycrystalline macro-domains, may be of two types: (1) those with out-of-plane polarization and (2) those with in-plane polarization. In-plane macro-domains exhibit in-plane optical anisotropy which can be monitored using cross-polarized transmitted light. This property was utilized in the current work to study the influence of temperature variation on macro-domains. According to the temperature dependence of the intensity of cross-polarized transmitted light, the films could be divided into three groups: (group 1) those films that did not exhibit strong changes in intensity; (group 2) those that exhibited a strong and abrupt change at a temperature between 20 and 120 °C; and (group 3) those that upon heating exhibited a gradual increase in the intensity of the cross-polarized transmitted light. The observed changes were reversible and consistent with a 90° rotation of the *c*-axis of some grains, which caused reversible changes in the macro-domain structure.

Introduction

The formation of polydomain structures in ferroelectrics has been the subject of numerous studies which concentrated primarily on epitaxial thin films due to their scientific and practical importance. In such films, the force leading to the formation of the elastic domains is the mechanical stress induced by the interaction of the film with the substrate (clamping) [1–10]. The equilibrium polydomain structure is such that the film experiences the least strain and, thereby, the minimum elastic energy. The fraction of each type of domain in a polydomain structure is defined by the type of mechanical constraints and by the number of possible crystallographic variants (e.g., three for the cubic–tetragonal phase transition or four for the cubic–rhombohedral phase transition). Epitaxial films are usually grown at temperatures above the paraelectric–ferroelectric transition. Therefore, a polydomain structure appears upon cooling through the transition to the ferroelectric phase. Once formed, the polydomain structure may then change in response to change in temperature due to the changes in spontaneous strain.

In polycrystals, the situation is significantly more complex. If each grain were to form a single domain independent of the neighboring grains, the grains would become geometrically incompatible with each other. In order to minimize the internal stress resulting from this incompatibility, each grain splits into domains so that following formation of the intragrain polydomain structure, geometrical incompatibility is minimized. If the grains are too small to contain more than a single domain, the transformation into the ferroelectric phase will either produce a polycrystal with high intergrain stress [11] or the intergrain stress may suppress the phase transition completely [11, 12].

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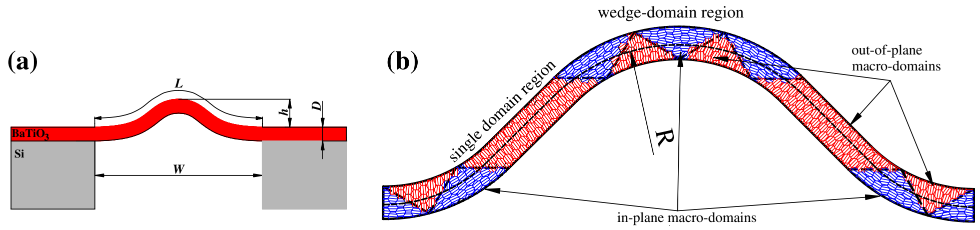

Fig. 1 **a** Scheme of a self-supported tethered film; **b** Polycrystalline macro-domains forming linear and wedge-ordered regions in a uniaxially buckled film of nanocrystalline ferroelectric BaTiO$_3$. The direction of the stripes in each grain denotes the direction of the *c*-axis: in-plane (*blue regions*) or out-of-plane (*red regions*). The film shape is determined by a combination of arcs (*wedge-ordered regions*) and planes (*linear regions*) [13]. The *dashed lines* denote the boundaries between the macro-domains

However, a different type of behavior was recently demonstrated in thin films of BaTiO$_3$ (Fig. 1a) that are self-supported, i.e., substrate-free, but tethered at the edges to a window etched in a Si substrate. Though tethered, such films are not clamped and are free to buckle. It was shown that single-domain nm-sized ferroelectric grains in a buckled, polycrystalline, self-supported film of BaTiO$_3$ (Fig. 1a) can minimize intergrain stress by forming regions within which the crystallographic axes of the neighboring grains are similarly aligned [13, 14] (Fig. 1b). These spontaneously formed regions of hundreds to thousands of grains, called polycrystalline macro-domains, are elastic in nature and mimic elastic domains in crystals [7]. The direction along which the grains align during formation of a macro-domain depends only on the external mechanical constraints. Therefore, the number of possible variants for polycrystalline macro-domains is unlimited. This property constitutes the most important difference between polycrystalline macro-domains and elastic domains in single crystals. The latter are limited to a small number of variants. Subsequent investigation revealed that within the temperature range of 20–100 °C, self-supported BaTiO$_3$ films with macro-domains exhibit a pyroelectric effect, which is enhanced 10–50 times with respect to that of bulk BaTiO$_3$ under similar conditions [14, 15]. Enhancement of the pyroelectric effect cannot be attributed to the transition from the tetragonal (ferroelectric) to the cubic (paraelectric) phase at $T = 124$ °C. Therefore, we hypothesized that an increase in temperature caused a 90° rotation (switching) of the polar axis in some of the grains and that this polarization switching contributed to the pyroelectric current. This is analogous to the polarization rotation responsible for the "giant" piezoelectric effect observed in some lead zirconium titanate compounds [16–18]. The goal of the study presented below is to provide experimental evidence that 90° polarization switching indeed takes place in self-supported BaTiO$_3$ films.

Polycrystalline macro-domains in a uniaxially buckled self-supported film of BaTiO$_3$

Although formation of macro-domains was first observed in square-shaped self-supported films of BaTiO$_3$, we used a uniaxially bent film as a useful qualitative model [13, 14]. In a uniaxially buckled, self-supported film of BaTiO$_3$, two types of macro-domains are formed [13]: (1) those with the *c*-axes of the grains aligned as closely as possible with the perpendicular to the film ("out-of-plane" macro-domains) and (2) those with the *c*-axes of the grains aligned as closely as possible with the film plane ("in-plane" macro-domains). To minimize the elastic energy, these two types of macro-domains self-organize into alternating triangular (wedge-shaped) regions, in-plane and out-of-plane macro-domains, similar to the wedge-shaped domains observed in bent single crystal plates (Fig. 1b) [19, 20]. These wedge-domain regions have the contour of a circular arc. The curvature radius, *R*, of the arc is fixed by the crystallographic parameters of the tetragonal lattice, *a* and *c*, and the film thickness, *D*, as $R_{\mathrm{eq}} = D/((c/a) \cdot g - 1)$, where $g < 1$ is a constant that takes into account the fact that the film is polycrystalline and that the *c*-axes of the grains cannot be aligned perfectly in one direction. For a film with randomly oriented grains, this constant is $g = 0.86$ [14]. Those parts of the film that do not contain wedge-domain regions tend to have minimal curvature, i.e., remain flat. These flat regions contain a single out-of-plane macro-domain. Thus, the overall shape of a uniaxially buckled film with macro-domains is determined by a combination of arcs (wedge-domain (WD) regions) and flat sections (single out-of-plane macro-domain (SD) regions). When the film is heated, the *c*/*a* ratio decreases [21]. As a result, the equilibrium radius of the WD regions increases. Since the edges of the film are tethered; increase in the equilibrium radius of the WD-regions should result in the expansion of the WD-regions at the expense of the SD regions.

Detection of the rearrangement of the polycrystalline macro-domains

It was shown earlier that in-plane macro-domains can be visualized [13, 14]. Tetragonal (ferroelectric) $BaTiO_3$ displays a large difference in refractive index in the directions perpendicular and parallel to the crystallographic *c*-axis [22]. Therefore, in-plane macro-domains possess in-plane optical anisotropy and linearly polarized light passing through in-plane macro-domains becomes elliptically polarized. Consequently, if viewed in cross-polarized transmitted light, in-plane macro-domains appear as bright areas [13]. Out-of-plane macro-domains do not display optical anisotropy in cross-polarized transmitted light. Since only WD-regions contain in-plane macro-domains, only they contribute to the intensity of the transmitted cross-polarized light. Therefore, the average intensity of the transmitted cross-polarized light over the whole film is proportional to the area occupied by WD-regions and to the degree of in-plane optical anisotropy.

Experimental

Self-supported nano-crystalline films of $BaTiO_3$ tethered to a window in a Si substrate were prepared as described in references [13, 14]. The film thickness $d = 500 \pm 50$ nm and the film had a square shape with side 200 ± 50 μm. The film–window misfit strain, $u_{mf} = (L - W)/W$ (Fig. 1a), determined from the buckling height [23] was found to be within the range of $u_{mf} = 0.1–3\%$ (Fig. 1a). The thickness of the self-supported films was inferred from optical transmission spectra [24]. An X-ray diffraction pattern acquired in transmission mode (0.625°/h) indicated that, on average, the films contained randomly oriented crystallites of a perovskite phase (Fig. 2). Due to the small amount of material in a self-supported film (200 × 200 × 0.5 μm), the intensity of the XRD peaks was too low to distinguish between the cubic and tetragonal phases. However, the pyroelectric effect observed in such films [13, 15] required that the films be in the tetragonal phase. The grain size deduced from the width of the (111) diffraction peak was ≈30 ± 10 nm, which was close to the value deduced from the scanning electron microscopy images, 40 ± 10 nm (Fig. 3). At the beginning of each measurement, the films were first rotated to find the position of minimum transmitted cross-polarized light I_{ct} averaged over the whole film. The films were then subjected to heating or cooling (0.1 °C/min, −20 °C +150 °C) with a custom-made micro-heater mounted in an optical microscope, and the average intensity (I_{ct}) was recorded as a function of temperature using a photodiode detector (Fig. 4). In addition, the phase difference ($\Delta\phi$) of the light passing through a single WD region was determined by collecting the light only from this region and rotating the sample while measuring the maximum and the minimum values of transmitted light intensity. The square root of the ratio of these values gives tan $\Delta\phi$.

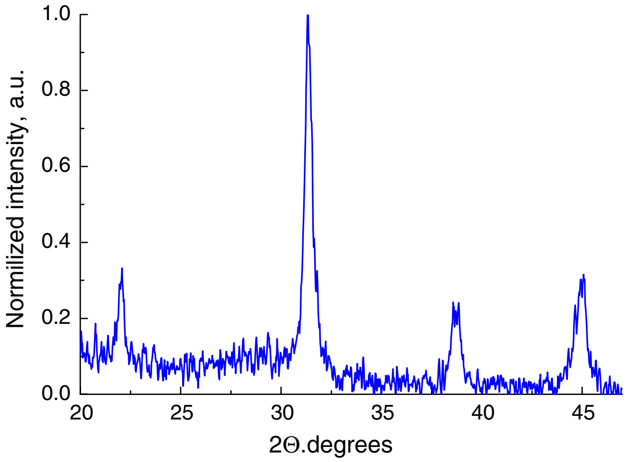

Fig. 2 Transmission XRD pattern of a self-supported $BaTiO_3$ film

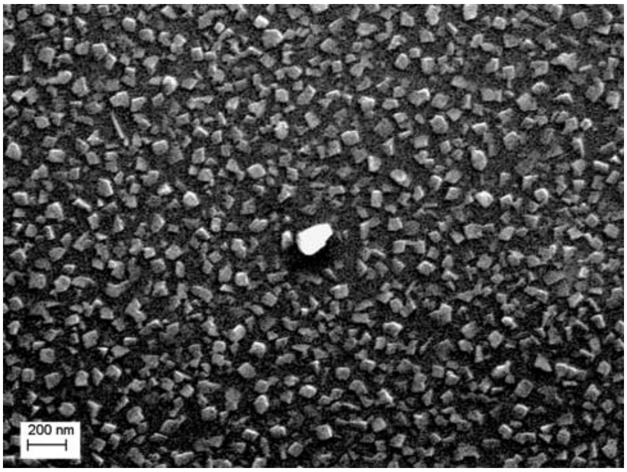

Fig. 3 SEM micrograph of a self-supported $BaTiO_3$ film

Results

According to the temperature dependence of I_{ct}, the films could be divided into three groups: (group 1) those films that did not exhibit significant changes in I_{ct} (Figs. 4, 5a–c; Fig. 4a–c in Ref. [13]); (group 2) those that exhibited a strong and abrupt change in I_{ct} at some temperature, T_b, between 20 and 120 °C (Figs. 4, 5d–f; Fig. 8 in Ref. [14]), and (group 3) those films that upon heating exhibited a gradual increase in I_{ct} (Figs. 4, 5g–i). Above ∼150 °C, none of the films exhibited detectable optical anisotropy and all films of group 1 and some of group 2 exhibited a

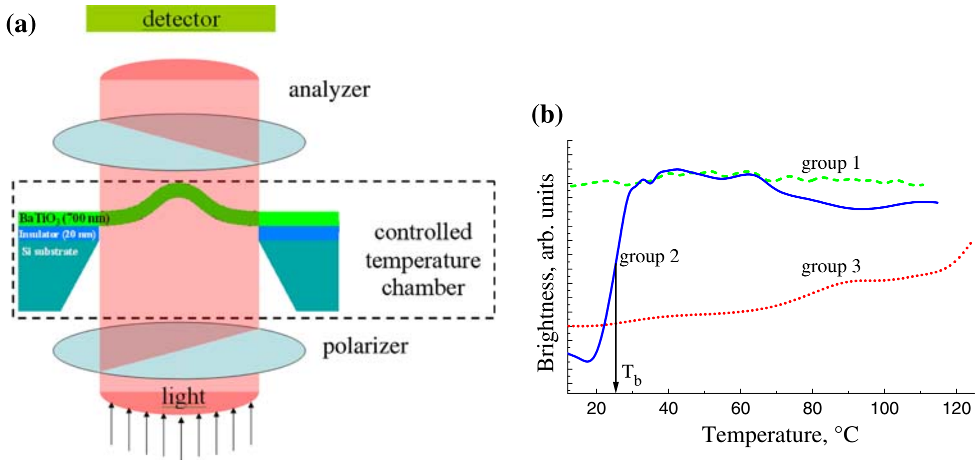

Fig. 4 **a** Scheme of the observation of the self-supported films with cross-polarized light; **b** Examples of the temperature dependence of the average intensity of the cross-polarized light passing through the self-supported films of $BaTiO_3$. The changes are fully reversible

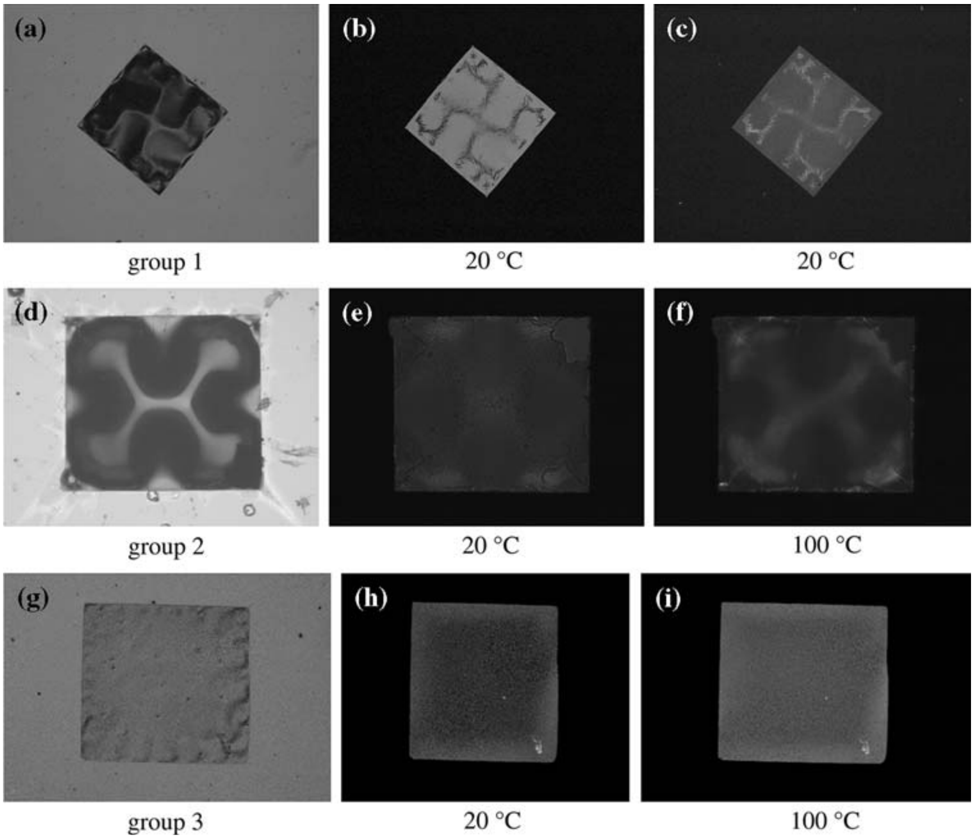

Fig. 5 Optical microscopy images of 500 ± 50 nm thick $BaTiO_3$ films. **a**–**c** A film of group 1 (width 200 µm). **a** Top view in reflected light; **b** and **c** the same film viewed in transmitted cross-polarized light at 20 °C. In (**b**) the polarizer is oriented vertically (diagonally with respect to the film). In (**c**) the polarizer and analyzer are rotated by 45°. One can see that all parts of the films are birefringent but with different directions of the optical axes. Neither the image nor the intensity of the transmitted light change upon heating. The film changed shape and disintegrated at ≈150 °C. **d**–**f** A film of group 2 (width 200 µm). **d** Top view in reflected light. **e** and **f** the same film viewed in transmitted cross-polarized light at 20 °C and at 100 °C, respectively. The polarizer is oriented parallel to the film side. **g**–**i** A film of group 3 (width 180 µm). **g** Top view in reflected light. **h** and **i** the same film viewed in transmitted cross-polarized light at 20 °C and at 100 °C, respectively. The polarizer is oriented parallel to the film side

noticeable change in shape, presumably caused by the transition from the tetragonal to the cubic phase (Fig. 4 in Ref. [13]). All changes in I_{ct} were reversible. The films with misfit strain of $u_{mf} > 0.4\%$ contained optically anisotropic regions which caused the linearly polarized transmitted light to acquire a phase difference $\Delta\phi \sim 10$–20° (Fig. 5a–c and f; Fig. 4 in Ref. [13]). It was also found that all films with $u_{mf} > 2\%$ belonged to group 1 and all parts of these films exhibited strong in-plane optical anisotropy (Fig. 5a–c). The films of group 2 and 3 contained areas with and without optical anisotropy (Fig. 5).

Discussion

The phase difference ($\Delta\phi = 10–20°$) of the transmitted light is significantly larger than what can be explained on the basis of the bending strain caused by film buckling. The radius of curvature of the films is $R_b > 100\ \mu\text{m}$ [13]; therefore, the bending strain is limited to:

$$u_b = D/(2R_b) \approx 0.25\%. \quad (1)$$

Applying the Clausius–Mosotti equation to a refractive index of $n \approx 2.4$ ($\lambda = 500$ nm) and a bending strain of 0.25%, one finds that the maximum change in the refractive index induced by the bending strain is [24]:

$$\Delta n < \left(\frac{2B+2}{1-B}\right)^{1/2} - n = 0.007, \quad \text{where } B = \left(\frac{n^2-1}{n^2+2}\right)(1-u) \quad (2)$$

The phase shift of the transmitted light that can be induced by the in-plane anisotropy of the refractive index, Δn, is given by:

$$\Delta\phi < 360° \cdot D \cdot \Delta n/\lambda \quad (3)$$

For the case of bending stain, Eq. 3 yields a phase shift of 2.6°, which is far smaller than the observed value of 10–20°. In the visible region, the difference in refractive index parallel to the *c* and *a* crystallographic axes is 2–2.5% [22]. According to Eq. 3, this difference in refractive index may produce a phase difference of 13–28° if the linearly polarized light propagates perpendicular to the *c*-axis. Since this estimate closely matches the experimentally observed value of 10–20°; one may conclude that the regions of the films exhibiting strong optical anisotropy are indeed the WD-regions because only they contain in-plane macro-domains [13, 14]. Since all parts of the group 1 films exhibited optical anisotropy, the films of this group contain only WD-regions, whereas the films of group 2 and 3 contain both WD- and SD-regions.

For a single crystal of $BaTiO_3$, the difference in refractive index parallel to the *c*- and *a*-axes *decreases* upon heating [25]. Therefore, the *increase* of I_{ct} observed upon heating the films of group 2 and 3 is an indication that the *c*-axes of some grains switch from the out-of-plane to the in-plane direction. This leads to the conclusion that upon heating, the out-of-plane macro-domains are transformed into in-plane macro-domains and upon cooling the process is reversed, i.e., WD-regions can convert into SD and vice versa. Furthermore, the abrupt change in I_{ct} observed in the films of group 2 implies that there are conditions under which small changes in temperature can cause large changes in macro-domains. We attribute the differences in the behavior of the three groups of films to the fraction of WD- and SD-regions. From the above analysis, it follows that the films of group 1 contain only WD-regions at all temperatures. Since upon heating, the SD-regions convert into the WD-regions, one can conclude that the abrupt change in the birefringence observed in the films of group 2 marks the temperature T_b (Fig. 4b) at which SD-regions disappear completely. This hypothesis is supported by the fact that above T_b the birefringence is constant. Since the birefringence of the films of group 3 increases continuously upon heating until the phase transition is reached, one can assume that in these films, some SD-regions persist at all temperatures at which the tetragonal phase is stable.

In summary, our data provide strong evidence that temperature variation can cause rapid changes in the structure of polycrystalline macro-domains. These changes occur via 90° polarization switching in some grains and it is this polarization switching that is responsible for the enhancement of the pyroelectric coefficient in self-supported films of $BaTiO_3$ [15].

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