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Domain patterns on ferroelectric Rh:$BaTiO_3$ single crystals

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Abstract

Single crystal growth and domain structure of Rh:Barium titanate ($BaTiO_3$) have been investigated. Rh doping in $BaTiO_3$ is effective for the growth of bulk crystals without twin formation. Atomic force microscope (AFM) and optical microscope studies reveal the formation 180° and 90° domains on the grown crystals. It has been observed that the complex 180° domain structure with typical size of around 20 μm exists in the c-domain of {0 0 1} face of Rh doped $BaTiO_3$ crystals.

Keywords: $BaTiO_3$ single crystals; Ferroelectric domains; AFM

1. Introduction

Ferroelectric materials possess broad range of unique properties, such as high dielectric permittivity, high piezoelectric constant and electromechanical coupling, and high pyroelectric coefficient, etc. and are widely used in industrial, military, health care and domestic applications including piezoelectric ignition devices, ultrasonic transducers, micropositioning devices, high-dielectric-constant capacitors, explosive-to-electrical transducers, wide-aperture electro-optic shutters, colour filters, and ferroelectric RAM [1–4]. Recently, these materials have been intensively studied due to their promising applications in microelectronic devices as well as in smart-sensing and self-actuating micro-systems [5,6]. If one can design, fabricate, and/or control the domain structures and polarization switching, it is possible to have full advantage of ferroelectric materials in manufacturing modern electronic and mechatronic devices. Hence, it is of great importance to understand and predict the ferroelectric domain structures and polarization switching when such materials are subjected to external electrical and/or mechanical loading. Scanning force microscopy (SFM) offers the possibility to detect and even manipulate polarization domains on ferroelectric surfaces down to the nanoscale range, useful for both practical applications and the study of ferroelectric and related structural phenomena at the submicroscopic scale [7].

Domain structure of ferroelectrics consists of domains with different orientations and boundaries between the domains, which are called domain walls. Sufficiently high electrical and/or mechanical fields can switch polarizations by 180° or about 90° from one polar axis to another and thus result in domain nucleation, domain wall motion, domain switching and/or a complete change in the domain structure. Barium titanate ($BaTiO_3$) is a well-known (for many years) crystal and has been widely applied in the field of optical waveguide and holographic storage due to its good electro-optic, acousto-optic properties. However, growth of bulk crystals by flux technique is limited by the butterfly twin formation. Several dopants have been attempted and twin-free crystals have been grown [8,9]. The present investigation reports the domain structure studies of Rh doped $BaTiO_3$ single crystal, which gives fast response time and more active in near infrared region [5,6] compared with pure $BaTiO_3$, one of the most extensively studied ferroelectric materials up to now.

2. Experiment

The Rh doped $BaTiO_3$ single crystals were grown by high temperature solution growth technique with KF flux. The

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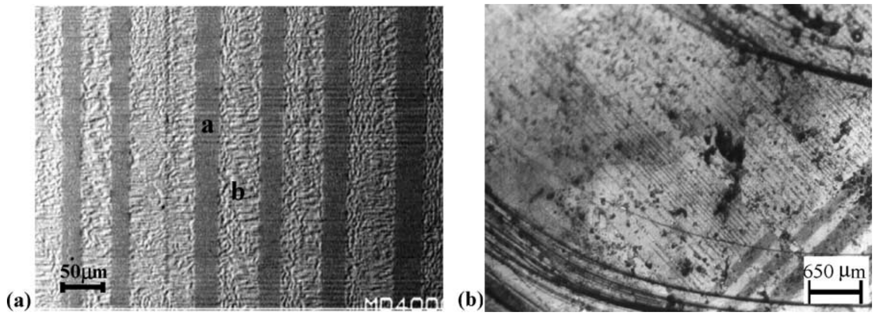

Fig. 1. Domain structure observed in Rh:$BaTiO_3$ (a) 180° domains (b) 90° laminar wedges.

growth aspects have already been reported [8]. The grown crystals were oriented by X-ray Laue pattern and (0 0 1) slices were cut and polished for domain observation. Domain patterns were observed using optical polarized microscope and atomic force microscope (AFM). A commercial AFM (Seiko Instruments SPA 300, Japan) was used for the measurements. The scanned head allowed a maximum scan area of 150 μm. The samples were scanned by contact topography and piezo-response mode with an applied ac bias voltage of 18 V. Compared with the conventional techniques for domain structure observation, atomic force microscopy has several advantages with wide range in *X*–*Y*-direction and high resolution in *Z*-direction. This technique is a promising tool for studying the morphology of the sample without any surface treatment with high spatial resolution. In particular, the development of piezoelectric scanner enables observation of surface over a wide range. The observation of nanometer to micrometer ferroelectric domains with required resolution in the *Z*-direction is possible.

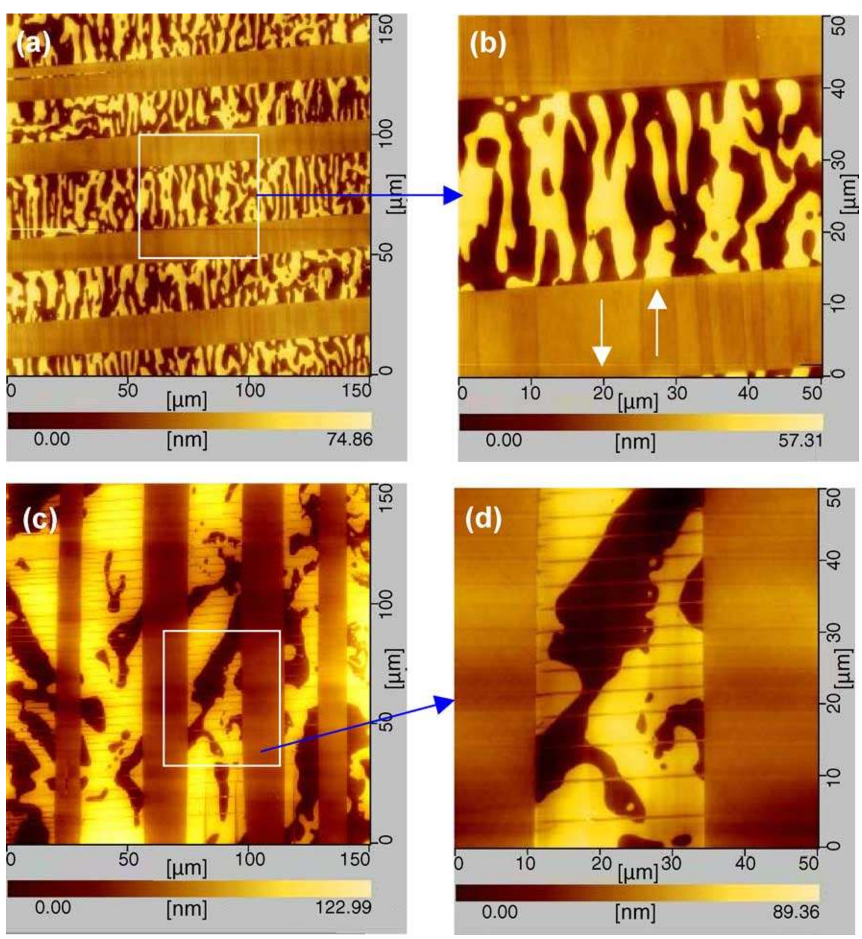

Fig. 2. Topographic AFM images on polished samples of Rh:$BaTiO_3$: (a and b) 1.0 mol.% of Rh and (c and d) 5.0 mol.% of Rh. The homogeneous patterns and the complex island like patterns are 90° parallel a–c domains. The complex islands like patterns are 180° c–c domains.

3. Results and discussion

In $BaTiO_3$ the c-domains are seen to be dark between crossed polarizers while the a-domains polarized in other directions are birefringent and appear to be bright provided polar axis of the crystal and polarizer axes are not coplanar. The contrast observed between a- and c-domain is the result of difference in charge density (ρ) and dielectric constant (ε). The contrast might also be produced by the difference in $\varepsilon_{\perp}$ and $\varepsilon_{||}$. Fig. 1a shows typical ferroelectric a- and c-domains observed through optical microscope on the crystals grown from different Rh concentrations after chemical etching using concentrated HCl [10]. The regions "a" and "b" represent the contrast between domains: a-domains look "bright" and the c-domains are "dark" [11]. The 'a' region consists of small anti-parallel domains, but the 'b' region has large anti-parallel domains. Domain boundaries may be distinctly recognized at the images. The definite order of the boundaries depends on the sample orientation. The 'a' and 'b' regions are divided by the $\langle 1\,0\,0 \rangle$ straight line. In the tetragonal phase, a–c domain walls are observed as straight lines along $\langle 1\,0\,0 \rangle$ in $\{0\,0\,1\}$ face. The morphology of the domains depends primarily on the cooling rate around ferroelectric phase transition region ($T_c = 130\,^{\circ}C$). The c-axis is the optic axis of the tetragonal phase and platelet was viewed normal to this face. Fig. 1b shows the 90° wedges, which are generally formed during the cubic to tetragonal phase transition and are aligned along the [1 0 1] direction. As the 90° twinning is incompatible with the tetragonal symmetry of the crystal, appearance of 90° twins should be a consequence of inhomogeneous mechanical stresses and their redistribution in the crystal.

At room temperature Rh doped $BaTiO_3$ crystals have symmetry with P_s oriented along the c-axis, however the P_s can lie along a number of axes, which are equivalent in the high temperature cubic phase. Thus it is possible for adjacent domains to be polarized at 90° to each other in the tetragonal phase at room temperature as depicted in the strain free model [12]. The condition for stable formation of such domains is the continuity and matching of the lattice at the boundary.

Fig. 2 shows the domain patterns of (0 0 1) plane of the unpoled tetragonal Rh doped $BaTiO_3$ crystal. The irregular fingerprint domain patterns were observed by atomic force microscope in the piezoresponse mode. These fingerprint patterns have previously been observed using scanning force microscope SFM [11]. Two kinds of domain patterns are found in Fig. 2a–d. Fig. 2a shows a homogeneous pattern and the other shows the complex island like pattern. Iwata et al. [13] observed similar patterns on PZN–20%PT crystals.

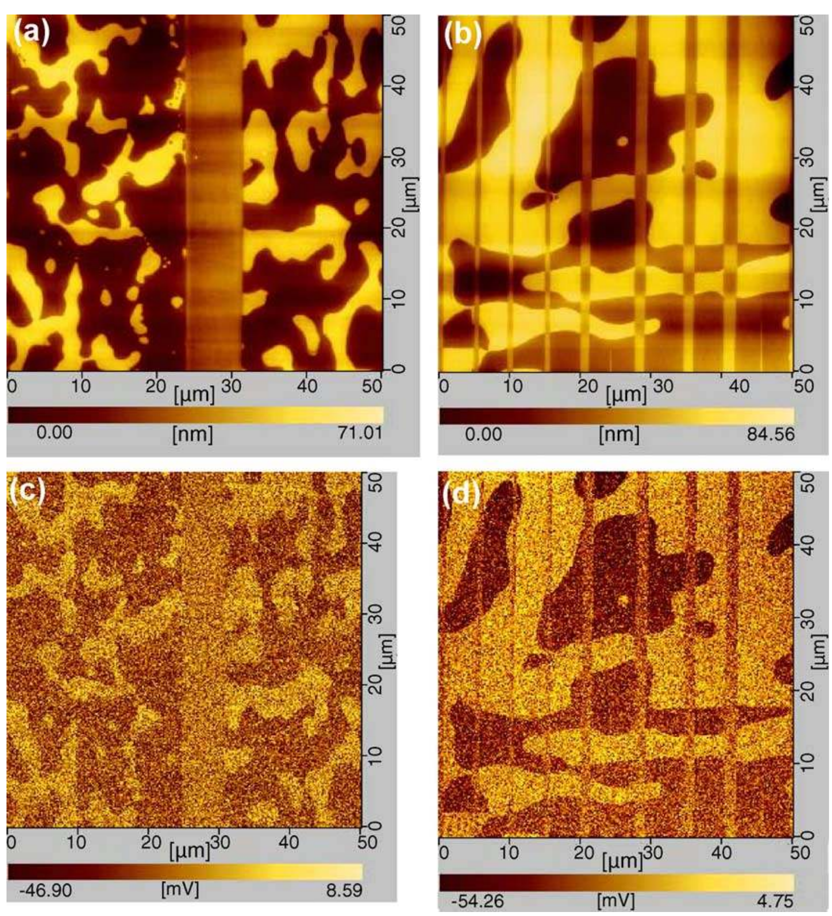

Fig. 3. Topographic AFM images on polished samples of Rh:$BaTiO_3$ with (a) 1.0 mol.% and (b) 5.0 mol.% of Rh, which show the difference in domain size. (c and d) Domain patterns taken by piezoresponse mode for the same area of topographic image (a and b).

The sample was polished to a thickness of 50 μm in order to distinguish a- and c-domains. It is inferred that the homogeneous patterns and the island-like patterns correspond to a- and c-domains, respectively. In the island like pattern the ferroelectric 180° domain walls have an arbitrary orientation. It is seen in the c-domain of Fig. 2a that there are two regions with bright and dark contrast corresponds to upper and lower height level, respectively. It is possible to identify the direction of spontaneous polarisation in the c-domain using electrostatic force microscope by measuring the surface potential due to the charge of the pyroelectric polarisation on the (0 0 1) plane. It is observed that the bright region corresponds to the tail of the polarisation and the dark region corresponds to the head of the polarisation. On the other hand the positive end (head) of the polarisation is etched rapidly in $BaTiO_3$ with the mixture of HCl and HF while the negative (tail) end of the polarization is etched very slowly [10].

Both the 90° and 180° domain structures have been observed on Rh doped $BaTiO_3$ single crystals. Fig. 2b and d show the enlarged portion of Fig. 2a and c respectively. It is found that complex 180° domain structure with a typical size of the ∼10–20 μm exists in the c-domain on the (0 0 1) plane of 1.0 mol.% of Rh in $BaTiO_3$. It seems that the domain size is slightly larger for higher concentration of Rh (Fig. 3a and b). Moreover, thin (size ∼1 μm) straight homogeneous a-domains embedded in the complex c-domains have been observed for low concentration of Rh (Fig. 3b). Fig. 3c and d show the domain patterns observed by piezo-response mode on the same area of topographic images (Fig. 3a and b). The reciprocal 90° domains are embedded in a- and c-domains (Fig. 2d). In the tetragonal lattice, the 90° domain walls coincide with tetragonal (1 0 1) plane, and the angle between a- and c-domain is ∼94°. Eng et al. [14] have reported that the brightness variation is due to the inclination of a-domain into the c-domain in the tetragonal $BaTiO_3$.

4. Conclusions

Ferroelectric domain patterns of Rh doped $BaTiO_3$ single crystals have been investigated. Both 90° and 180° domain structures have been observed by optical microscope and AFM after etching the sample using HCl. 90° laminar wedge domain patterns have also been observed. Complex island-like patterns correspond to positive and negative c-domains and homogeneous patterns correspond to a-domain have clearly been observed by AFM in both contact topography and piezo-response mode. It is observed that the complex 180° domain structure with a typical size of the ∼10–20 μm exists in the c-domain on the (0 0 1) plane of Rh doped $BaTiO_3$ crystals.

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