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Imaging and engineering the nanoscale-domain structure of a $Sr_{0.61}Ba_{0.39}Nb_2O_6$ crystal using a scanning force microscope

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We have investigated the ferroelectric domain structure formed in a $Sr_{0.61}Ba_{0.39}Nb_2O_6$ single crystal by cooling the crystal through the Curie point. Imaging the etched surface structure using a scanning force microscope (SFM) in both the topographic mode and the piezoresponse mode revealed that a multidomain structure of nanoscale islandlike domains was formed. The islandlike domains could be inverted by applying an appropriate voltage using a conductive SFM tip. Furthermore, a nanoscale periodically inverted-domain structure was artificially fabricated using the crystal which underwent poling treatment. © *2002 American Institute of Physics.* [DOI: 10.1063/1.1506945]

Strontium barium niobate (SBN) is a promising ferroelectric material that exhibits large piezoelectric, electrooptic, nonlinear optic and pyroelectric coefficients, and is being considered for applications such as second-harmonic generation (SHG),[1,2] optical parametric oscillation (OPO), and microelectromechanical system (MEMS)[3] devices. Microscale and even nanoscale-domain engineering of a ferroelectric single crystal has recently attracted great interest,[4,5] because the fabrication of such OPO, SHG, and MEMS devices relies on the engineering technique. The emission of the quasi-phase-matching (QPM)-SHG has been demonstrated by forming a periodically inverted-domain microstructure in the SBN crystal.[1,2]

Recently, it has also been found that SHG emission was generated from an as-grown SBN crystal, in which the periodically inverted-domain structure was not formed artificially.[6] This is possible because a multidomain structure is naturally formed in the SBN crystal upon cooling through the Curie point (T_c), and these domains partially satisfy the QPM condition. On the basis of observations made using a transmission electron microscope, the formation of nanoscale 180° domains with the polarization that is parallel to the *c* axis of the SBN crystal has been revealed.[7] However, the domain structure formed in the SBN crystal has not been investigated due to the difficulty in domain visualization using conventional optical microscopy.

We have investigated the imaging and engineering of the domain structure in the SBN crystal using a scanning force microscope (SFM). Imaging the etched SBN surface in both the topographic and piezoresponse[8–10] modes of the SFM revealed the nanoscale multidomain structure. Inversion of the nanoscale domains was achieved by applying an appropriate dc bias voltage using the conductive SFM tip.[8,9,11] Furthermore, we have artificially formed the nanoscale periodically inverted-domain structure in the SBN crystal using the SFM. It was difficult to fabricate the nanoscale domain patterns by conventional electric-field poling using lithographically defined electrodes.[4,12]

A high-quality single crystal of $Sr_{0.61}Ba_{0.39}Nb_2O_6$ (SBN:61) was grown by a newly developed double-crucible Stepanov method.[13] The composition corresponds to that of the congruent melt in the $SrNb_2O_6-BaNb_2O_6$ system, thus, the SBN:61 crystal is much easier to grow than SBN crystals with other compositions ($Sr_xBa_{1-x}Nb_2O_6$:$0.25 \leqslant x \leqslant 0.75$). The as-grown SBN:61 crystal was annealed at 1350 °C for 24 h and was then cooled to room temperature in the furnace. The crystal was cut perpendicular to the *c* axis and was polished using alumina-particle and colloidal-silica aqueous solutions. Then, the polished crystal was etched in an HF aqueous solution at room temperature for 15 min. Imaging of the domain structure on the etched SBN surface was achieved using the SFM in two different modes. First, the etched surface was scanned in the topographic mode. The domain structure could be revealed in the topographic mode because of the different etching behaviors of the positive and negative polarized faces of domains. Second, the conductive SFM tip was scanned to perform domain-structure imaging in the piezoresponse mode with an applied ac bias voltage of 10–14 V (peak to peak) at a frequency of 10 kHz. If the bias voltage decreased less than 10 V, it was impossible to perform the domain imaging in the mode. The conductive SFM cantilever made of a tetrahedral silicon tip with a radius of less than 25 nm, which was coated with platinum/titanium metals, was used. The resonance frequency and spring constant were 70 kHz and 2 N/m, respectively. The piezoresponse mode was expected to be able to directly image the domain structures with nanoscale resolution. The piezoresponse and topographic SFM modes were used as complementary methods to confirm nanoscale domain structure in the SBN crystal.

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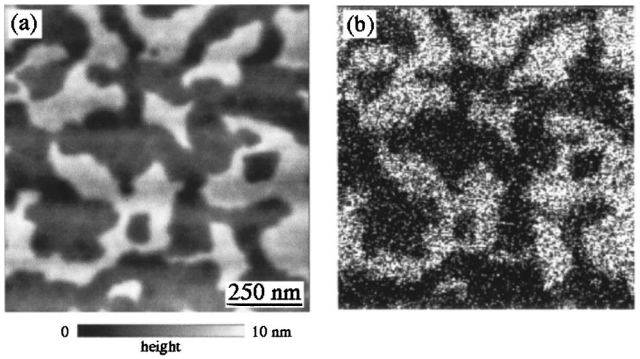

FIG. 1. SFM images of the HF-etched SBN crystal (a) in the topographic mode and (b) in the piezoresponse mode. White and black areas in (a) and (b) represent the negatively and positively polarized faces of the domains, respectively.

The domain inversion of the SBN crystal was achieved by applying an appropriate dc bias voltage using the conductive SFM tip. The SBN sample was prepared by the following procedure. A gold film was deposited on one side of the *c*-cut SBN crystal. The gold-coated surface was fixed on a metal substrate using conductive paste, and the SBN crystal on the metal substrate was polished using the alumina-particle and colloidal-silica aqueous solutions. The dc bias voltage (V_s) was applied between the conductive SFM tip and the metal substrate, where the tip was grounded. When the tip was scanned on the SBN sample of less than 50 μm the thickness in the piezoresponse mode with an applied ac bias voltage of 10 V, the domains in the scanned area were partially inverted without applying V_s. Thus, the SBN sample of an approximately 70 μm thickness was used for examining the domain inversion. A nanoscale periodically inverted-domain structure was also fabricated by scanning the conductive tip with application of V_s on the SBN sample. Before the patterning, the crystal underwent poling treatment under the electric field of 400 V/mm, which is larger than the coercive field ($E_c \cong 250$ V/mm), using the liquid electrodes at room temperature.

Figure 1(a) shows a topographic SFM image of the etched SBN crystal. The unetched area, white in Fig. 1(a), resembled an island structure with the feature size of several hundred nanometers. Cross-sectional analysis of the image revealed surface profile variations of approximately 10 nm. The preferential etching of the SBN crystal was caused by the etching rate anisotropy of 180° domains parallel to the *c* axis, which was previously observed in $LiNbO_3$,[14] $LiTaO_3$,[15] and $Pb_{1-x}Ba_xNb_2O_6$[16] crystals. In order to determine the polarity of the etched regions, the SBN crystal which underwent the conventional poling treatment,[17] in which negatively and positively polarized faces were formed artificially, was etched in the HF solution. The positively polarized face was determined to be preferentially etched. Thus, the white areas in Fig. 1(a) represent the negatively polarized faces of the domains, that is, they correspond to polarization pointing down into the figure plane.

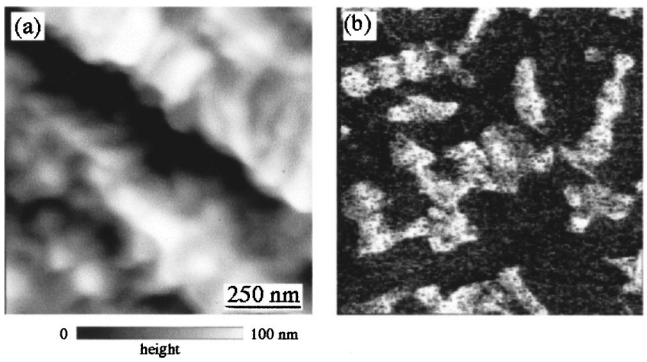

FIG. 2. SFM images of the alumina-polished SBN crystal (a) in the topographic mode and (b) in the piezoresponse mode.

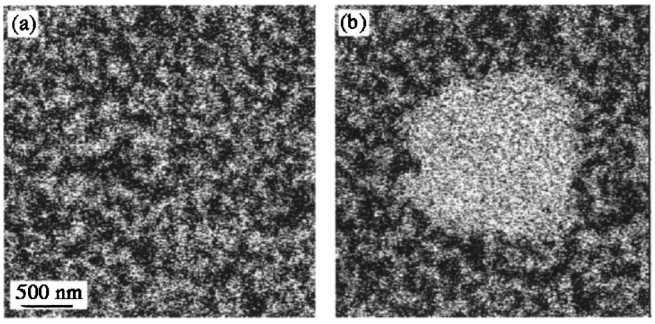

FIG. 3. Piezoresponse images showing the inversion of domains in the thin SBN crystal (a) before and (b) after application of the bias voltage of −30 V.

The same region was imaged in the piezoresponse mode. As shown in Fig. 1(b), the piezoresponse image agrees well with the structure revealed in the topographic image. By monitoring the phase shift between the piezoresponse signal and the modulating voltage, it was determined that the bright regions in Fig. 1(b) corresponded to the negatively polarized faces of the domains, which is consistent with the results of etched topography. The piezoresponse mode was also used to image the islandlike structure in the unetched SBN sample. Figure 2(a) shows a topographic image of the sample with a high surface roughness of approximately 100 nm; the surface structure was prepared by applying only the polishing treatment using the alumina particle solution. No domain structure could be seen in the topographic mode. In spite of the high surface roughness, the piezoresponse imaging revealed the nanoscale islandlike domain structure [Fig. 2(b)]. This suggests that the piezoresponse signal seen in Fig. 1(b) is not an artifact due to the topography. Namely, these SFM observations demonstrate that the nanoscale multidomain structure does exist in the SBN crystal.

The E_c value of the SBN crystal as obtained by a conventional hysteresis measurement using liquid electrodes of diameter 4 mm (saturated LiCl solution in water) was determined to be approximately 250 V/mm at room temperature. A required voltage for inverting the domain was calculated to be more than ± 17.5 V for the sample with a thickness of 70 μm when the liquid electrodes are used. However, it is difficult to estimate the required voltage for inverting the domain when the conductive SFM tip is used as the electrode due to the complex field distribution. In our study, the bias voltage of $V_s = -30$ V, which is much larger than the value of −17.5 V, was applied to the SBN sample by scanning the tip at a rate of 1000 nm/s over a small area of 1000×1000 nm^2. Subsequently, the domain inversion was visualized in the piezoresponse mode. Figures 3(a) and 3(b) show the multidomain structure of the SBN crystal before

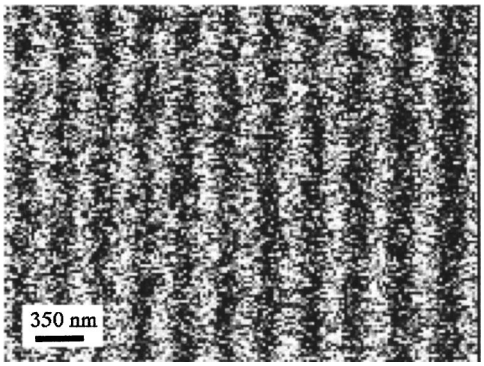

FIG. 4. Piezoresponse images showing the periodically inverted-domain structure with approximately 350 nm period width.

and after application of the bias voltage, respectively. The treated domains in a small area (a square of about $1000 \times 1000\,\mathrm{nm}^2$) in Fig. 3(b) in a scanning area of $3000 \times 3000\,\mathrm{nm}^2$ were fully inverted, as shown by the change in contrast from black to white. The surface polarity of the inverted domain should be negative, and its contrast is again consistent with the results of the preferential etching shown in Fig. 1. Furthermore, the nanoscale periodically inverted-domain structure could be artificially fabricated in the SBN crystal. Before the patterning, the crystal underwent poling treatment under the electric field of 400 V/mm using liquid electrodes at room temperature. The bias voltage of $V_s = -30$ V was repeatedly applied to the sample as the conductive tip was scanned with equal interval of 350 nm at a rate of 1000 nm/s. Subsequently, the periodically inverted-domain structure with approximately a 350 nm period width was formed, as shown in Fig. 4.

In conclusion, we have investigated the domain structure of the SBN crystal using the topographic and piezoresponse modes of the SFM. It was found that the 180° nanoscale islandlike domains were naturally formed upon cooling through the Curie point to room temperature. The domains could be inverted by applying an appropriate voltage using a conductive SFM tip. Furthermore, the nanoscale pattern of the periodically inverted-domain structure could be fabricated by controlling the tip scanning. We believe that the nanoscale domain patterning of ferroelectric single crystals, such as the SBN crystal, using the SFM has great potential for creating functional devices.

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