

Ferroelectric Domain Architecture for Novel Devices

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We investigated the sub-microscale to nanoscale engineering of the ferroelectric domain structure and surface morphology of LiNbO_3 and LiTaO_3 single crystals with scanning force microscope. Domain structures with tailored patterns were fabricated by controlling the magnitude of the bias voltage, polarity, and treatment time applied to these samples while scanning them with the conductive cantilever. The fabricated structures and surface potential of tailored domains were revealed by piezoresponse force microscopy mode and Kelvin probe force microscopy mode, respectively. The $-Z$ -faces of tailored domain structures were subjected to selective chemical etching under appropriate conditions to construct surface structures with shape originating in these patterns. The surface-structure architectures of the ferroelectric crystals can be ranged from the sub-micro scale to nanometer scale and could be used in the future to create additional unique templates and devices.

Key words: LiNbO_3 , LiTaO_3 , Domain engineering, Scanning force microscopy, KFM

1. INTRODUCTION

Lithium niobate (LiNbO_3 : LN) and lithium tantalate (LiTaO_3 : LT) are ferroelectric materials that possess excellent electro-optical, nonlinear-optical, piezoelectric and pyroelectric properties. Therefore, they are an attractive functional material for potential use in light-wavelength-conversion, light-modulation, hologram-memory and micro electromechanica system (MEMS) devices. In some of devices, domain structures of the ferroelectric crystals are artificially fabricated, leading to induce functions. For example, second harmonic generation (SHG) [1] and optical parametric oscillation (OPO) devices have been fabricated by utilizing quasi phase matching (QPM) [2], which is induced by the formation of periodically poled domain structures at the microscale level. Thus, the availability of technology to arbitrarily fabricate domain structures in ferroelectric crystals is one of important factors affecting the development of these optical devices. In addition, the availability of technology that allows us to arbitrarily fabricate surface morphology is also important in helping us develop these functional devices. In fact, lithographic techniques have already been used to artificially construct periodically polarization-reversed structures on a micro-scale in LN crystal. Recently, scanning force microscopy (SFM) has made it possible to perform domain engineering on a submicro-scale and even nano-scale [3-12], which is difficult by conventional lithographic techniques. The capability of engineering domain structures and surface structures into arbitrary shapes on a nano-scale should make it possible to improve not only conventional function devices but also to create devices that operate under new concepts

using nano-scale advantage.

We have investigated the sub-microscale to nanoscale domain engineering of ferroelectric crystals through SFM [10-12], which enables the polarization of ferroelectric domains to be locally inverted. In this paper, we describe pattern processing of domain in LN and LT crystals by SFM and the pattern processing of surface structures by the chemical etching of those patterned domain structures. We also describe the surface potential distribution of tailored domain structures by SFM.

2. EXPERIMENT [10, 12]

A single crystal of stoichiometric LN and LT was grown with a double-crucible Czochralski method with an automatic powder supply system [13]. The LN and LT single crystals, which have single 180° -domain structures (polarization is parallel to Z-axis), were cut perpendicular to the Z-axis. Gold films were deposited on one side (+Z-face) of the cut plate-crystals and the covered faces were attached onto metal substrates using conductive paste. The crystals on the metal substrates were polished to approximately $3 \mu\text{m}$. The domain inversion of these samples was achieved by applying an appropriate dc bias voltage between the conductive cantilever and metal substrates, where the cantilever was grounded. The patterns of the inverted domain structures were fabricated by scanning the $-Z$ -faces of samples with the cantilevers while applying appropriate voltages. We imaged the fabricated patterns of the inverted structures in piezoresponse force microscopy (PFM) mode. The surface potential of engineered domain structures were also imaged by Kelvin probe

force microscopy (KFM) mode. The influenced of piezoelectric effect on the surface potential was examined by changing temperature of samples in vacuum.

We also examined the etching properties of the LN and LT crystals on nano-scale levels with SFM in order to know an appropriate etching condition for fabricating surface structure architectures. First, the Z-cut LN and LT crystals, which have anti-parallel polarization of domains, were etched in various mixtures of hydrofluoric acid (HF) aqueous solution (46% in water) and nitric acid (HNO₃) aqueous solution (60% in water) for different periods at 20 °C. Because -Z-face of the domain was preferentially etched, the etching rate can be determined by measuring the etch depth of the -Z-face. Then, the LN and LT samples subjected to domain patterning with SFM were etched using the mixture of HF and HNO₃ acids solution, and the tailored surface structures after etching were observed in the SFM topographic mode.

3. RESULTS AND DISCUSSION

3.1 Domain engineering

We examined the shapes of inverted domains in LN and LT samples under different bias voltages and over different periods of time [10,12]. When the treatment time was fixed, the inverted domains grew lineally as the voltage increased. On the other hand, when the bias voltage was fixed, the domains grew as the treatment times increased. Thus, inverted domains of arbitrary size can be fabricated with SFM by controlling the bias voltage and treatment time. As treatment time or bias voltage was decreased, a domain size can be decreased; however, the inverted domain at a certain size become unstable and disappeared with time. This may be because the domain could not grow penetrating through from the bottom to the surface. This critical size depended on the thickness of the samples. In this study, the

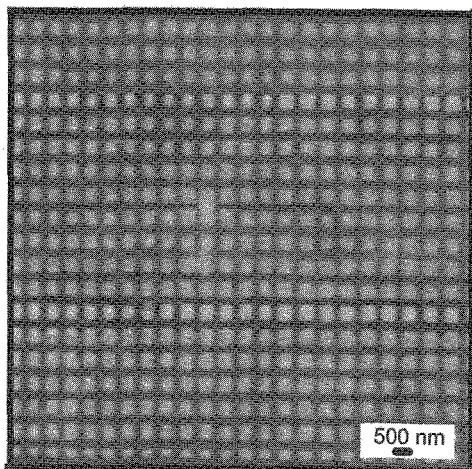


Fig.1 PFM images of domain structure fabricated by SFM. The dark and light sections correspond to +Z- and -Z-faces, respectively.

samples polished to a thickness of approximately 3 μm were used, the critical size was approximately 400 nm.

We fabricated inverted domain structures with tailored patterns by scanning with a conductive cantilever on the LN and LT samples while applying the appropriate voltage. Figure 1 has an example of fabricated domain structures with a lattice pattern. The lattice pattern of the inverted domain (represented by black area) was fabricated by scanning the sample with the cantilever at the rate of 500 nm/s, while applying a voltage of $V = -60$ V. The line width of the inverted domain in the pattern was approximately 500 nm.

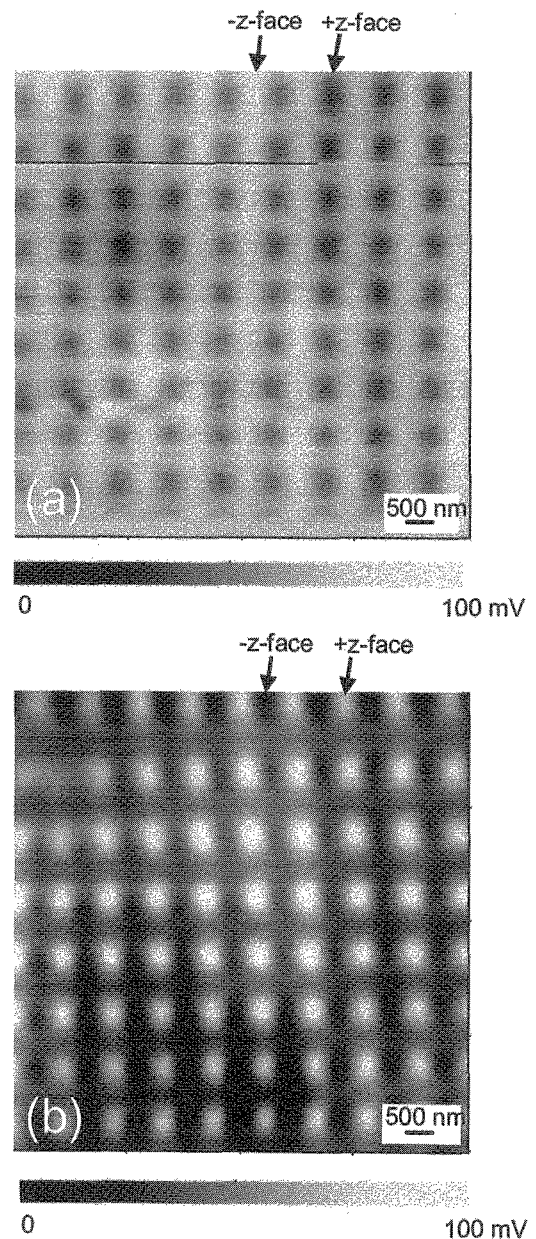


Fig. 2: Surface-potential-distribution images of the tailored domain with lattice pattern observed by KFM in a vacuum after heating to 60°C: (a), and after heating to 120°C and cooling to 60°C: (b)

3.2 Surface potential of tailored domains

Using SFM in KFM mode, we examined the surface charge distribution of the fabricated domain structure with tailored pattern. First, a surface-charge-distribution of the domain structure with a lattice pattern consisting of the -Z face line with the 500 nm width was measured at room temperature in room air, but the surface -charge image corresponding to the domain structure could not be obtained. In a vacuum, we were likewise unable to obtain a clear image at room temperature, but when making measurements while heating the sample to 60°C, we obtained a surface-charge image of lattice pattern (Fig. 2 (a)). The surface potential of lattice-shaped domain is higher than surrounding surface potential even though the domain is fabricated with the -Z-face. The reason for this is as follows. At room temperature, the negative potential of the -Z-face becomes neutralized by a covering of positively charged material. But at 60°C, a pyroelectric effect decreases the spontaneous polarization (negative potential) of the -Z-face with the result that the positive potential of the material covering the surface comes to dominate. In addition, the sample was heated to 120°C and cooled to 60°C, the surface potential of lattice-shaped domain is lower than surrounding surface potential, as shown in Fig. 2 (b). This is because the covering of positively charged material was removed at high temperature (120°C), and the spontaneous polarization (negative potential) of the -Z-face comes to dominate after cooling to 60°C. These KFM results demonstrate that surface potential of tailored domain structure can be controlled by changing the temperature in vacuum.

3.3 Chemical etching

We have examined the etching properties of the LN and LT crystal on nano-scale level. LN and LT samples that had anti-parallel domain polarization were etched by mixtures of HF and HNO₃ aqueous solutions. The -Z surface experienced different etch rates corresponding to different HF concentrations and temperatures, whereas the +Z surface remained almost unetched in all the experiments. The steps formed by preferential etching [12, 14, 15] at the boundary of the +Z and -Z surfaces were very sharp. For each sample, the etch depths were measured. Figure 3 (a) and (b) show the relationship between the etch depth and the treatment time of LN and LT crystals etched in different ratios of HF and HNO₃ aqueous solution at 20°C. The etch depth of both crystals for all ratios of HF and HNO₃ aqueous solution increased linearly as the treatment time increased. Both LN and LT crystals had different etch depths corresponding to different ratios of HF and HNO₃ aqueous solution for same treatment time. These results indicate that the etch depth can be controlled in the nanoscale by changing of treatment time and HF concentration.

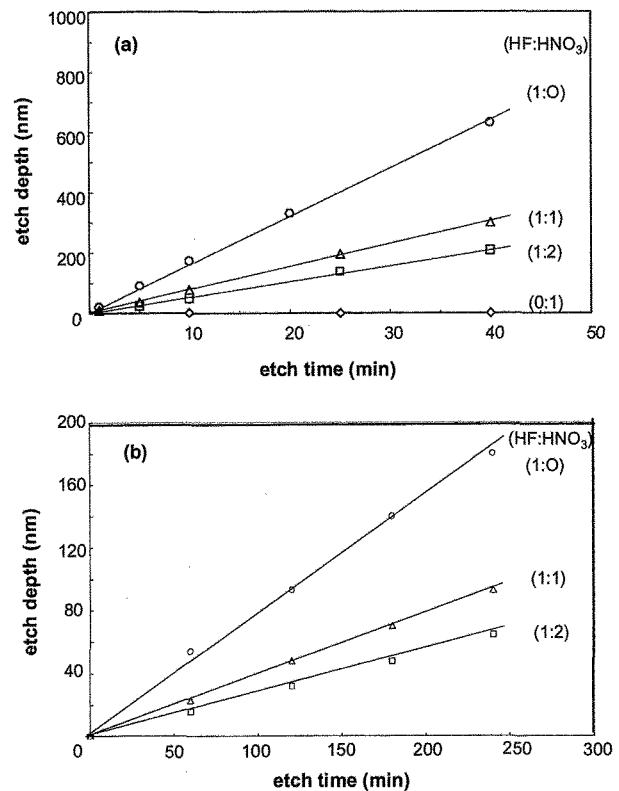


Fig. 3: Etch depth of -Z-face versus etch time when etching LN: (a) and LT: (b) samples in mixed aqueous solutions (HF:HNO₃ = 1:0, 1:1, 1:2, 0:1) at 20°C.

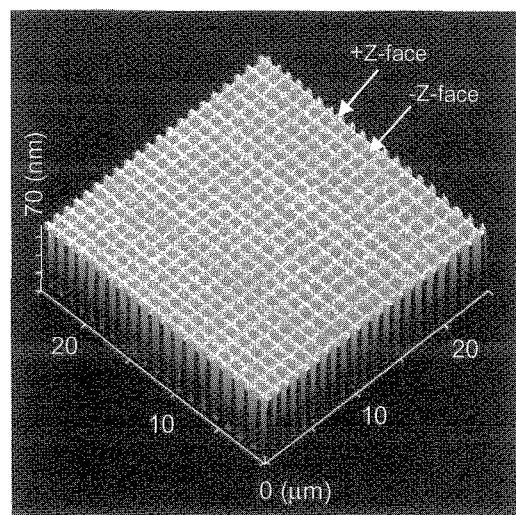


Fig. 4: 3D topographic image of an LN sample with a domain structure patterned into a lattice structure (Fig. 1) after etching for 12 minutes at 20°C in a mixed aqueous solution (HF:HNO₃ = 1:2).

3.4 Surface structuring

We examined the possibility of the surface structural fabrication on LN and LT by making use of its chemical etching properties [10, 12, 16]. Figure 4 (a) shows an example of spatial topographic micrographs of the surface structures after etching of the LN sample with tailored domain structure (Fig. 1 (a)) for 12 minutes at 20°C in a mixed aqueous solution (HF:HNO₃ = 1:2). The -Z-face within the pattern was selectively etched resulting in the fabrication of a surface structure with a lattice shape consisting of line with a width and height of about 500 nm and 80 nm, respectively.

4. CONCLUSION

We demonstrated the sub-microscale to nanoscale engineering of the ferroelectric domain structure and surface morphology of LN and LT single crystals with SFM. The engineered domain structures and surface structures should open up the development of new devices that capitalize on the superior features of this material. This study has shown that domain-structure tailoring of LN and LT using SFM can be followed by selective chemical etching under appropriate conditions to fabricate surface structures on a nano-scale level that reflect that pattern. Such surface architectures exhibit periodic changes in the index of refraction suggesting application as a photonic crystal. Because of electro-optical effect and piezoelectrical effect, a photonic crystal using ferroelectric material can be used to vary optical characteristics and even move a surface by application of an external electric field. In addition, because of pyroelectric effect, the surface potential of a tailored domain holds the potential of being used as a nanoscale template.

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