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Observation of ferroelectric microdomains in $LiNbO_3$ crystals by electrostatic force microscopy

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Abstract

Mechanochemically Polished surface of d.c. poled $LiNbO_3$ crystals are observed by electrostatics force microscopy (EFM) which is performed by applying a d.c. voltage to the tip. EFM is confirmed to be suitable for a non-destructive inspection of submicron size 180º domains (+ domains) in –z plane. It is revealed by EFM that the –z plane has a positive charge and the + domains are charged negative in the air. A possibility is proposed that the Li_2 deficiency is an origin of the + domains. © 1999 Elsevier Science B.V. All right reserved.

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1. Introduction

Characterization of 180º microdomains, remaining at poled ferroelectric materials, is required for integrated optical and microelectronic devices in which nonlinear effects of a single domain crystal are applied. It is, however, impossible to detect submicron size 180º domains less than 0.2 μm in diameter, in chemically etched ferroelectric crystals even under differential interference optical microscope (DIOM). On the other hand, it is easy to observe uneven submicron size objects on mechanochemically polished surfaces by atomic force microscopy (AFM) . $LiNbO_3$ crystals are one of the most important ferroelectric oxides for the use in numerous opto-electronic devices, like surface acoustic wave (SAW) filters [1], SAW deflectors [2] and optical waveguide modulators [3]. Usually, domains in $LiNbO_3$ can be eliminated by electrical poling. However, it is not yet clarified completely whether 180º microdomains could remain and of which influence is the deviation of composition from non-stoichimetry in $LiNbO_3$ [4]. Moreover, Until now, there exist no technical reports on observation of submicron size domains in spite of extensive and sophisticated investigations for ferroelectric materials by multi-mode AFM [5-14]

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In this paper, for the first time we report on submicron size 180° domain found in mechanochemically polished surfaces of d.c. poled $LiNbO_3$ cyrstals by electrostatic force microscopy (EFM), which is performed by applying a low d.c. voltage to the tip under an interleave scan.

2. Experimental

AFM and EFM observations were carried out on 0.5 mm thick –Z plates of SAW grade $LiNbO_3$ crystals (Nippon Mektron) [15] and on those of optical grade ones (Crystal Technology) ,where –Z plate or plane means that the positive electrode was set on the surface normal to the c-axis in poling the sample. The180° domains with diameters > 0.2 μm were observed in both –Z and +Z plates of the SAW grade samples under DIOM (Optiphot, Nikon). However, in the optical grade samples, such domains were not observed, obviously, due to the decreased diameter below the resolution limit of 0.2 μm.

In advance of the observations, Mechanochemically polished surfaces of the sample were washed in pure water with a surfactant by cotton swab, rinsed with an alcohol-rich aqueous solution and dried up instantly by spraying an inert gas Then the samples were put on a conducting tape adhered to the metal table in order to attain a rapid removal of surface charges induced by a d.c. voltage and to make them applicable to the tip for the EFM observation. The use of a static eliminator (Model-PB160M, Fisa) was also required to neutralize the Charge originated by a small change of room temperature during the analysis. At first, a topographic study was performed using images of the tapping mode AFM (TMAFM: NanoScope 」 a, Digital Instruments) in the height- and AFM-amplitude-modes with a standard tip for EFM having a resonance frequency F_0 in the range of 66-90 kHz (Nanoprobe-MESP, 225 μm long). The drive frequency applied to the tip was always tuned in a frequency lower than F_0. Whereas the TMAFM image in the height-mode taken under condition of a constant force, that in the AFM-amplitude-mode was obtained under non-interleave scan at a tip voltage of 0 V and it is near the differential variation of that in the height-mode. Secondly, TMAFM scope traces in the height-and EFM-amplitude-modes were observed. For that we changed the lift scan height, d.c. voltage and its polarity of the tip, under an interleave scan fixed on a certain domain obtained by the TMAFM image in the height-mode. Finally, TMAFM images in the height- and EFM-amplitude-modes were observed under an interleave scan in unfixed mode. All images were taken at a scan rate of 1 or 2 Hz.

3. Results and discussion

The 180° domains in –z plane of the SAW grade Samples, obtained by DIOM, shows frequently round and sometimes triangular shape which is convex and charged positive. We call them + domains because of the positive charged surface which is rather diffisult to be chemically etched in $LiNbO_3$ crystals. DIOM images in + z plane were obtained except for Domains being concave and charged negative. For those the AFM images was used which clearly analyzed the –z plane. The present EFM probe could not always works well for concave structures.

Fig.1 shows TMAFM images in the height-and AFM-amplitude-modes near the area observed by DIOM. The density of the + domain which are more than 0.2 μm in diameter is estimated to be roughly 6×10^4 /mm^2. Fig. 2a shows a TMAFM image in the height-mode for the area indicated by a square in Fig. 1 and a scope trace in the height-mode under the interleave scan fixed at y-distance of 1.5 μm in the upper image, where the strong contrast around one domain is due to the overdump of a cantilever. Fig. 2b-d shows scope traces in the EFM-amplitude-mode at tip voltages of 0 V, + 4 V, and -4 V, respectively, under the same scan as that in Fig. 2a. These traces are obtained for a lift scan height of 30 nm against the domain height of about 10 nm. The electric field between the sample and the tip is estimated to be about 0.2 MV / mm for 4 V. A base line of the trace in EFM-amplitude-mode at the tip voltage of + 4 V is elevated up to about one division and only a trace curve of the + domain falls down in comparison with that at 0 V. That is the reverse at the tip voltage of - 4 V. Because the drive frequency is tuned in a lower side of the tip resonance frequency, an elevation of the trace line

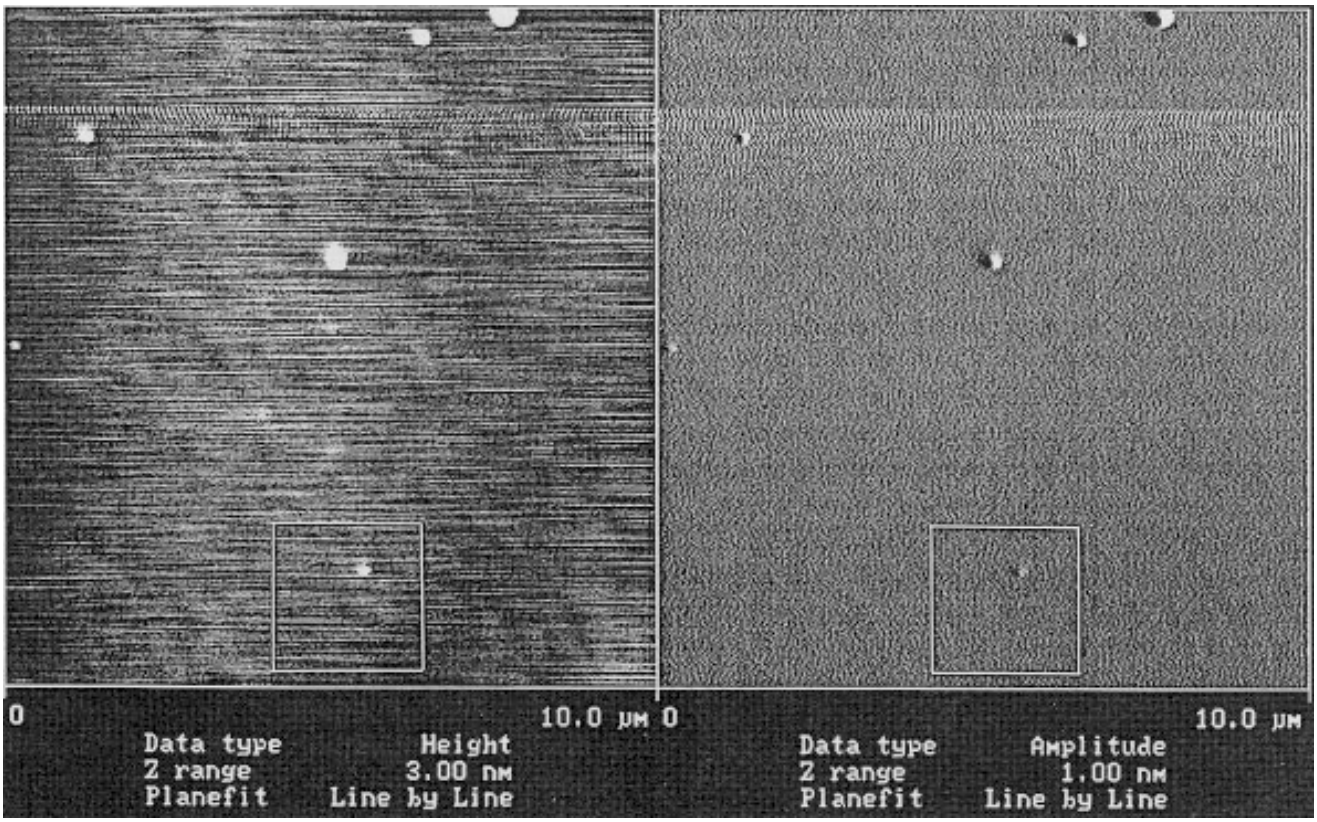


Fig. 1. TMAFM images in the height- and AFM-amplitude-modes at a scan rate of 1 Hz

means a repulsive force. These results indicate that the surface is charged positive and the domains negative. In other words the -z plane of SAW grade $LiNbO_3$ has a positive charge and the + domains in it are charges negative in the air contrary to the original charge. A physical adsorption may cause such a reverse charge, e.g., physisorptions of H^+ ions on the surface and OH^- ions on the + domain. Besides, Fig. 2a indicates in height-mode scope trace that the roughness of the Mechanochemically polished surface is within 1 nm.

Fig. 3 shows TMAFM images in the height- and AFM-amplitude-modes-in -z plane of the optical grade sample which displays no domains under DIOM. Several convex and domain-like objects are found in the images. It has to be noted that the objects in this area are frequently two- and occasionally three-fold paired. It may be due to the formation mechanism of the object. The dentistry of the objects, which are less than 0.2 µm in diameter, is estimated to be roughly $2 \times 10^6/mm^2$. In EFM observation of the samples a remarkable relaxation phenomenon was exhibited in the image obtained by the d.c. voltage tip, which did not appear in that of the SAW grade samples. This phenomenon may be due to the high receptivity caused by a high quality of the optical grade sample, e.g., impurity concentration of Fe and transition metals less than 1 ppm and well-Controlled heat treatment in poling and annealing Therefore, the interleave scan at 0 V was taken at Least for 20 min as a relegation time in changing the d.c. voltage, especially its polarity.

Fig. 4a shows a TMAFM image in the height-Mode for the area indicated by a square in Fig. 3 and a scope trace in the height-mode under the interleave scan fixed at y-distance of 0.96 µm in the upper image. The strong contrast around four domains is due to the overdump of a cantilever. Fig. 4b-d show scope traces in the EFM-amplitude-mode at tip voltages of 0 V, + 3 V, and - 3 V, respectively, under the same scan as that in Fig. 4a. These traces are obtained for a lift scan height of 50 nm against a height of the domain-like object of about 30 nm. The electric field between the sample and the tip is

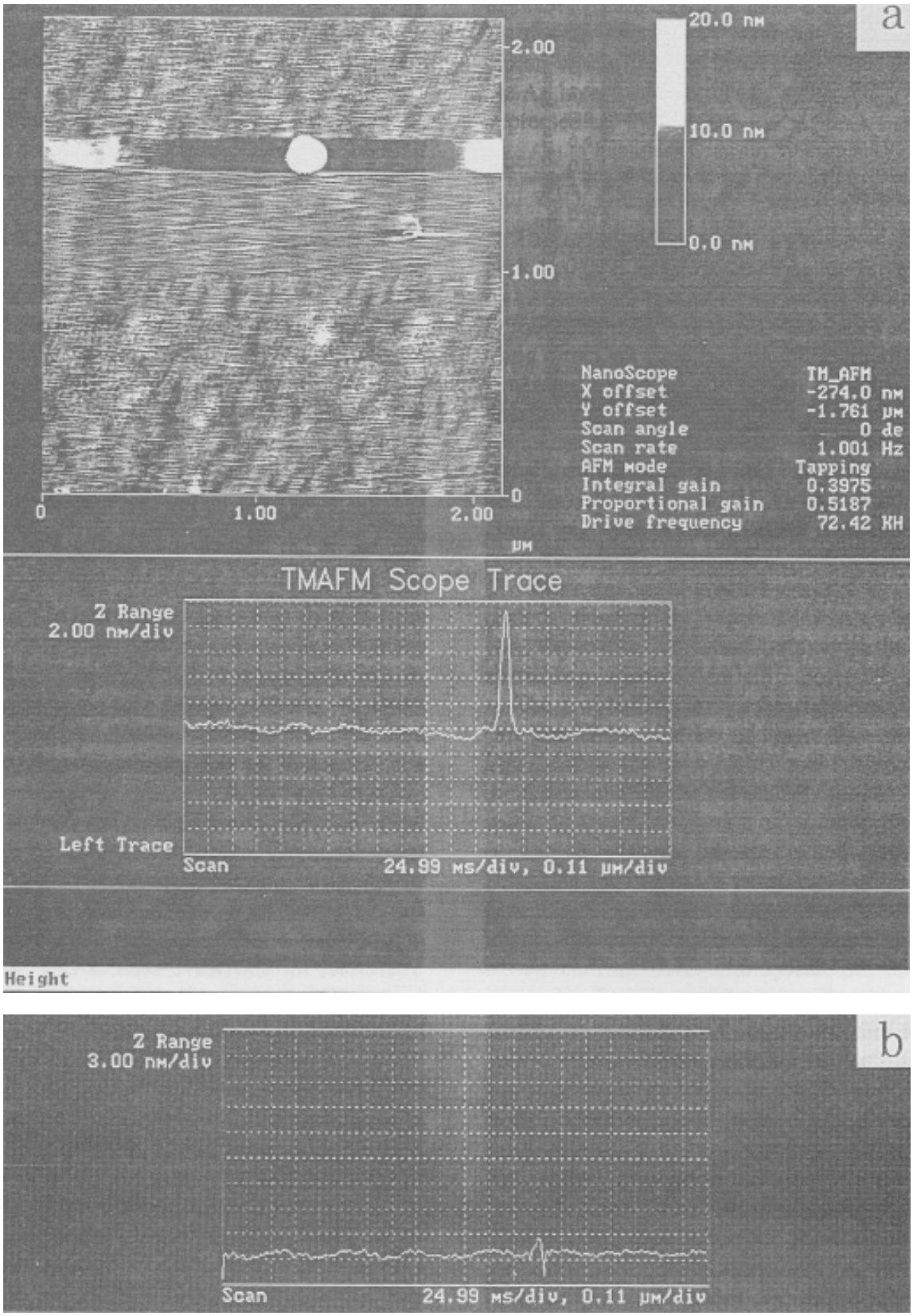
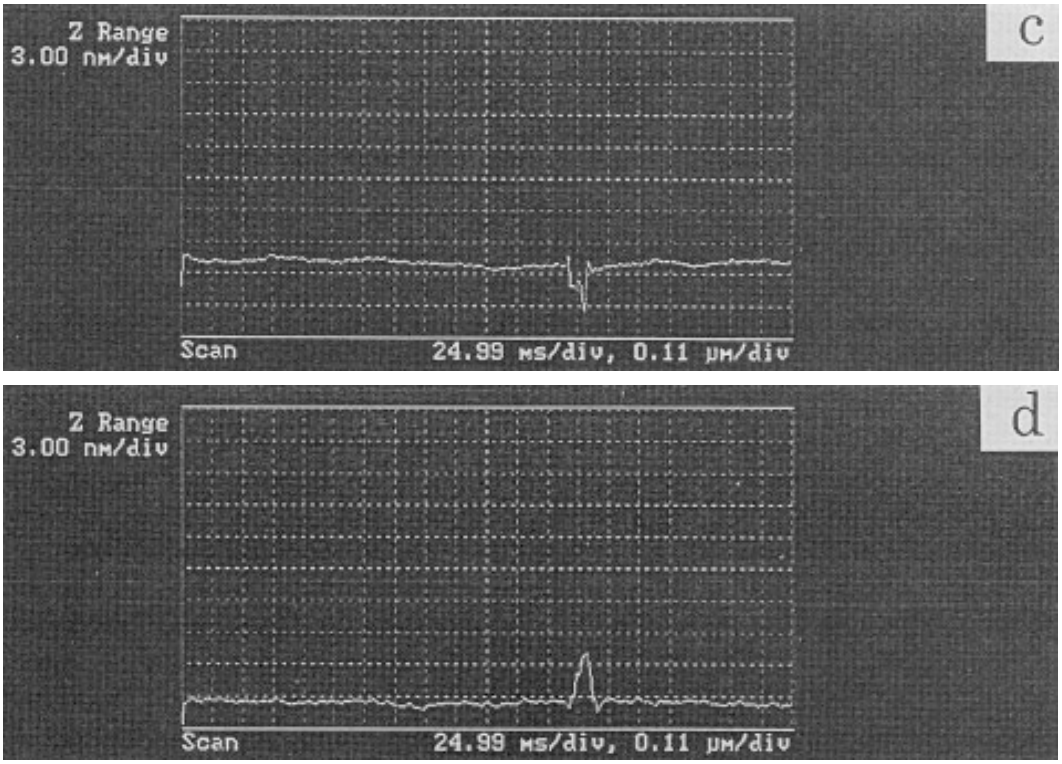


Fig. 2. TMAFM image and scope trace in the height-mode (a), and scope traces in the EFM-amplitude-mode at tip voltages of 0 V (b), + 4 V (c) and -4 V (d) under the interleave scan at a rate of 1 Hz, where the scope traces are taken under the scan fixed at the ordinate of 1.5 μm in the TMAFM image which is observed under unfixed scan.



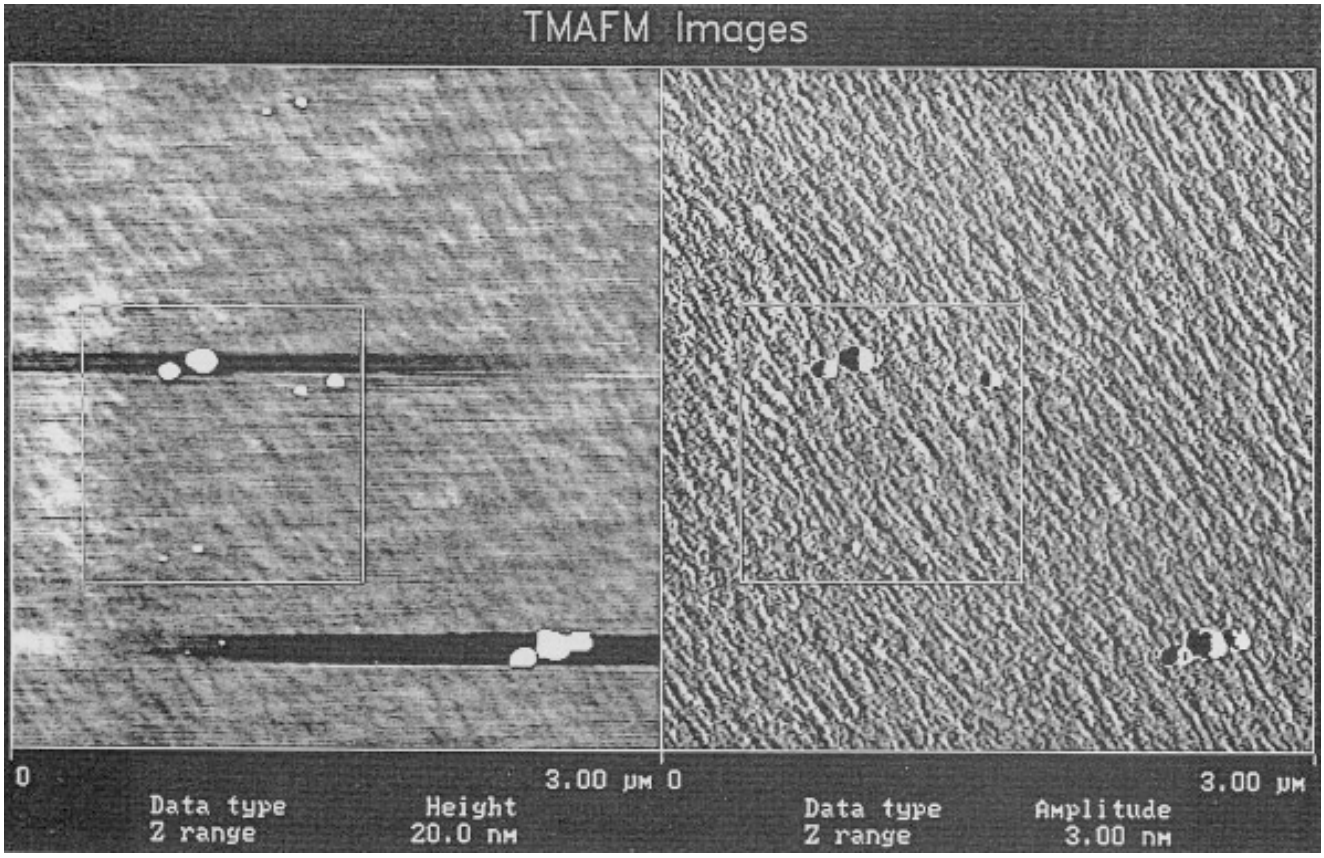


Fig. 3. TMAFM images in the height- and AFM- amplitude-modes in -z plane of an optical grade sample at a rate of 1 Hz

estimated to be about 0.15 MV / mm for 3 V. The results indicate that the -z plane is charged positive and the object negative as well as the SAW grade sample reveals, though they are vague in the level change of the + domain in comparison with those in Fig. 2. It is found in Fig. 5, however, that the TMAFM images in the EFM-amplitude-mode under the interleave scan in unfixed mode display drastic change at a tip voltage lower than 3 V, even if the level variation in the scope traces is very small.Two domains at the right hand are hardly detected due to their small height in the EFM\amplitude-mode image. The lightness of two domains at the left hand is high at the tip voltage of - 2 V, middle at 0 V, and low at + 2 V, which seems, fortunately, to correspond to the relative difference of the levels between the surface and the + domain in each scope trace in the EFM-amplitude-mode. The TMAFM image in

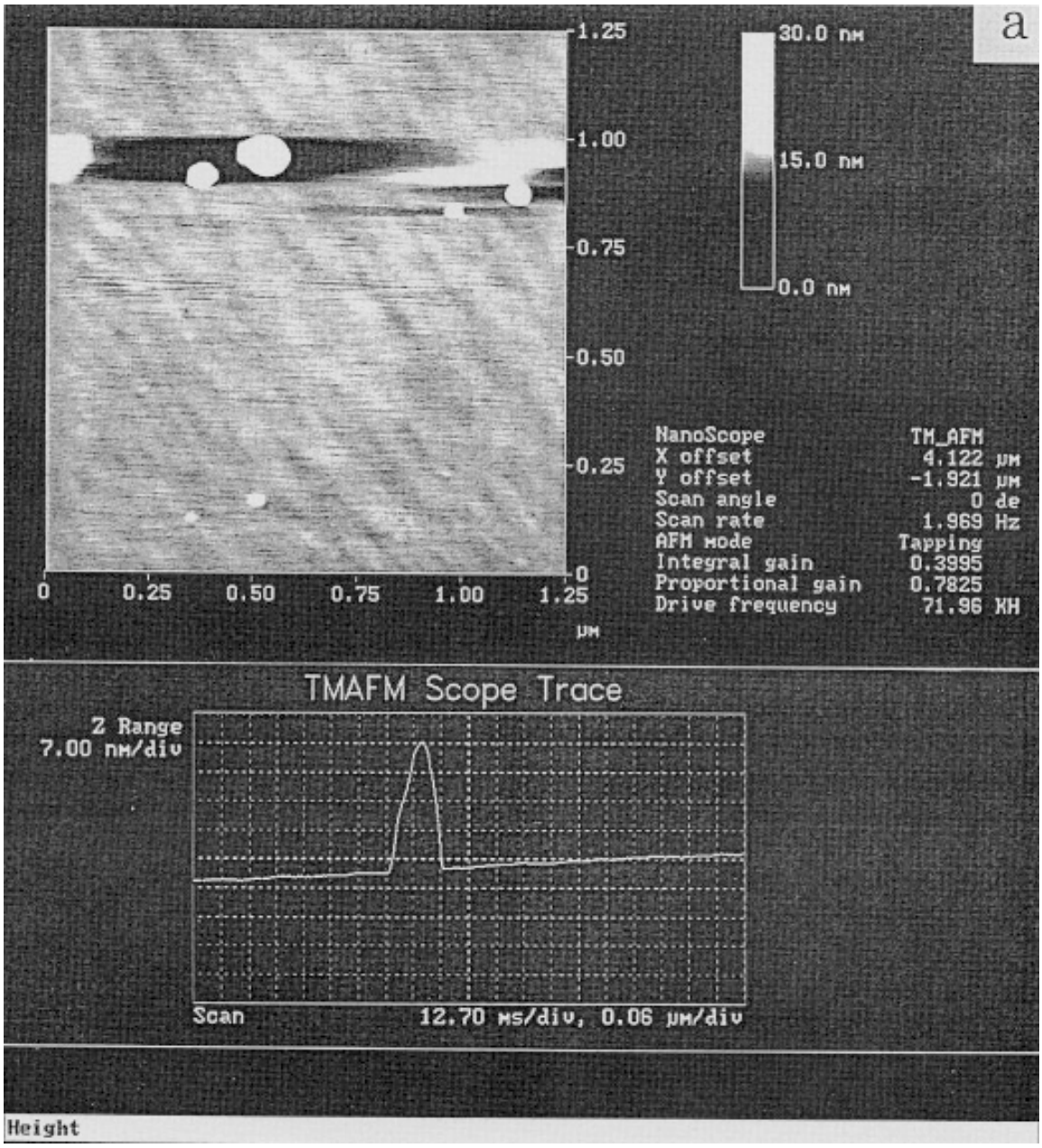


Fig. 4. TMAFM image and scope trace in the height-mode (a), and scope traces in the EFM-amplitude-mode at tip voltages of 0 V (b), + 3 V (c) and -3 V (d) under the interleave scan at a rate of 2 Hz, where the scope traces are taken under the scan fixed at the ordinate of 0.96 µm in the TMAFM image which is observed under unfixed scan.

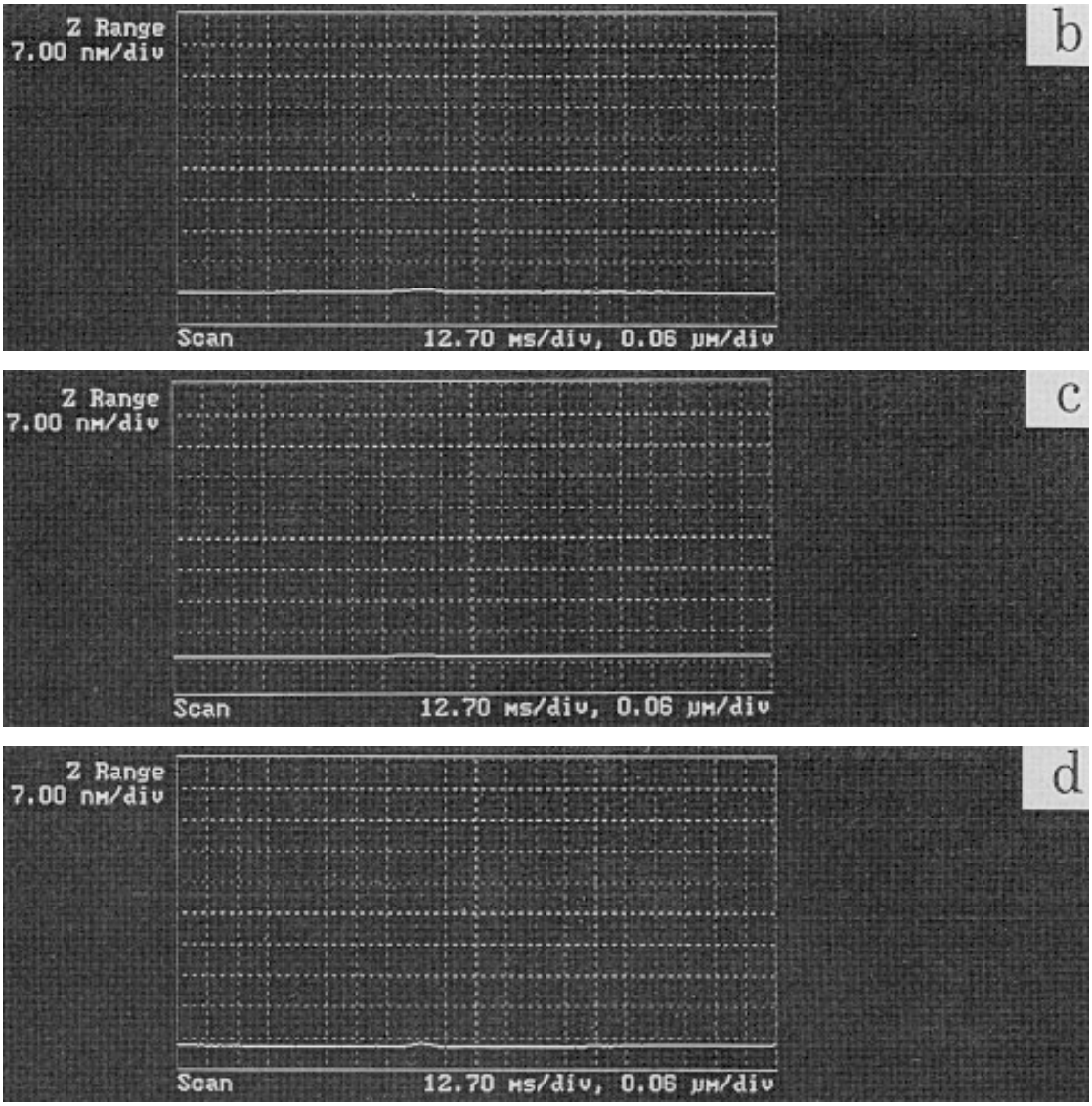


Fig. 4 (continued)

the EFM-amplitude-mode shows a very sensitive variation in color or lightness which is, generally, not relative but on the whole, while the level change in the scope trace in that mode is significant but its sensitivity is reduced down to one hundredth in order to catch the signals in the scope measurement range. However, the lightness of the objects corresponds to the relative level in the scope trace and is much more enhanced, if lightness of the surface is almost constant independently of the tip voltage. Fig. 5 is one of the case.

The object of less than 0.2 μm in diameter in the Optical grade sample are suggested to be + do - Mains, because the TMAFM image is very similar to that in the SAW grade sample. Although EFM observation has been performed on trial for BaTiO3 films, which have many submicron size 180° domains [5] and the roughness of the surface within 0.5 nm [16], clear images have not yet been detected for the domains in the (001) plane regardless of the domain size. The image is especially unstable by applying the voltage to the tip. $BaTiO_3$ surfaces are active, because both barium and titanium oxides have catalyses, and a chemisorption may occur in the surface, while $LiNbO_3$ surfaces are inert and may have only a physisorption.

A trail estimation is made for 180° domains remaining in d.c. poled $LiNbO_3$ crystals grown with

the congruent composition Li_2O / (Li_2O + Nb_2O_5) =48.5 ± 0.1% [17]. A surface density of the Li_2O deficiency δ is roughly calculated by the following equation:

$$\delta = \{ (N_A/V_M) \cdot t \} \times 1.5 \times 10^{-2}$$
$$= 2.8 \times 10^{11} /mm^2$$

where N_A = Avogadro number = 6.0×10^{23}, V_M= molar volume of $LiNbO_3$ = 32×10^3 mm^3 [18], and t = roughness of the sample surface = 1×10^{-6} mm (see Fig. 2a). Therefore, the value in the braces is a surface density of the $LiNbO_3$ molecules. The size of a Li_2O molecule is estimated to be roughly 0.4 nm in diameter from the Li^+ and O^{2-} ionic radii, which are about 0.06 and 0.14 nm, respectively. Consequently, the area is about $4\pi \times 10^{-2}$ nm^2. The area may be a center of the nucleation of microdomains, having a coercive field higher than the other area in poling under 30-50 μA / mm^2 at 1433-1483 K, and grow in the heating and annealing responsible to the sample receptivity. Mean diameters of the 180° domains in the SAW and optical grade sample are about 0.4 and 0.08 μm in our analysis, so the averaged area of them are $4\pi \times 10^4$ nm^2 and $16\pi \times 10^2$ nm^2, respectively. Surface densities of the domains realized in the SAW and optical grade samples δ_1 and δ_2 are estimated to be

$$\delta_1 = \delta / 4\pi \times 10^4 / 4\pi \times 10^{-2} = 3 \times 10^5 / mm^2$$

and

$$\delta_2 = \delta / 16\pi \times 10^2 / 4\pi \times 10^{-2} = 7 \times 10^6 / mm^2 .$$

These values are in good agreement with the values obtained by the EFM observation, 6×10^4 /mm^2 and 2×10^6 / mm^2, respectively. In other words this suggests a possibility that the prigin of the mi-

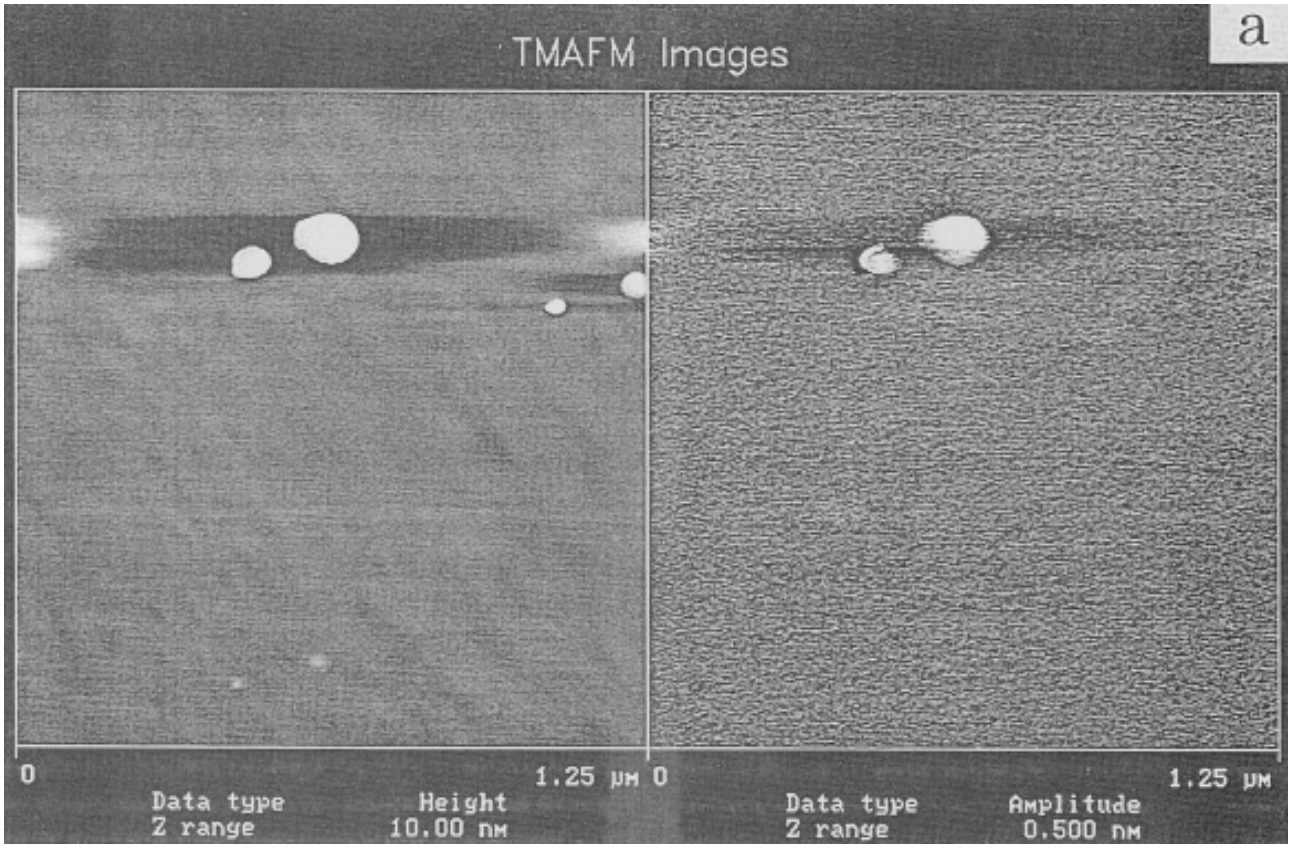


Fig. 5. TMAFM images in the height-and EFM-amplitude-modes under the interleave scan in unfixed mode at tip voltages of 0 V (a), +2 V (b), and -2 V (c) at a scan rate of 2 Hz in the same area as that of the TMAFM image in Fig. 4: The reason why a left a smaller domain of the two at the left hand is brightest and shows no change regardless of the tip voltage is due to the overlap effect of the adjacent domain.

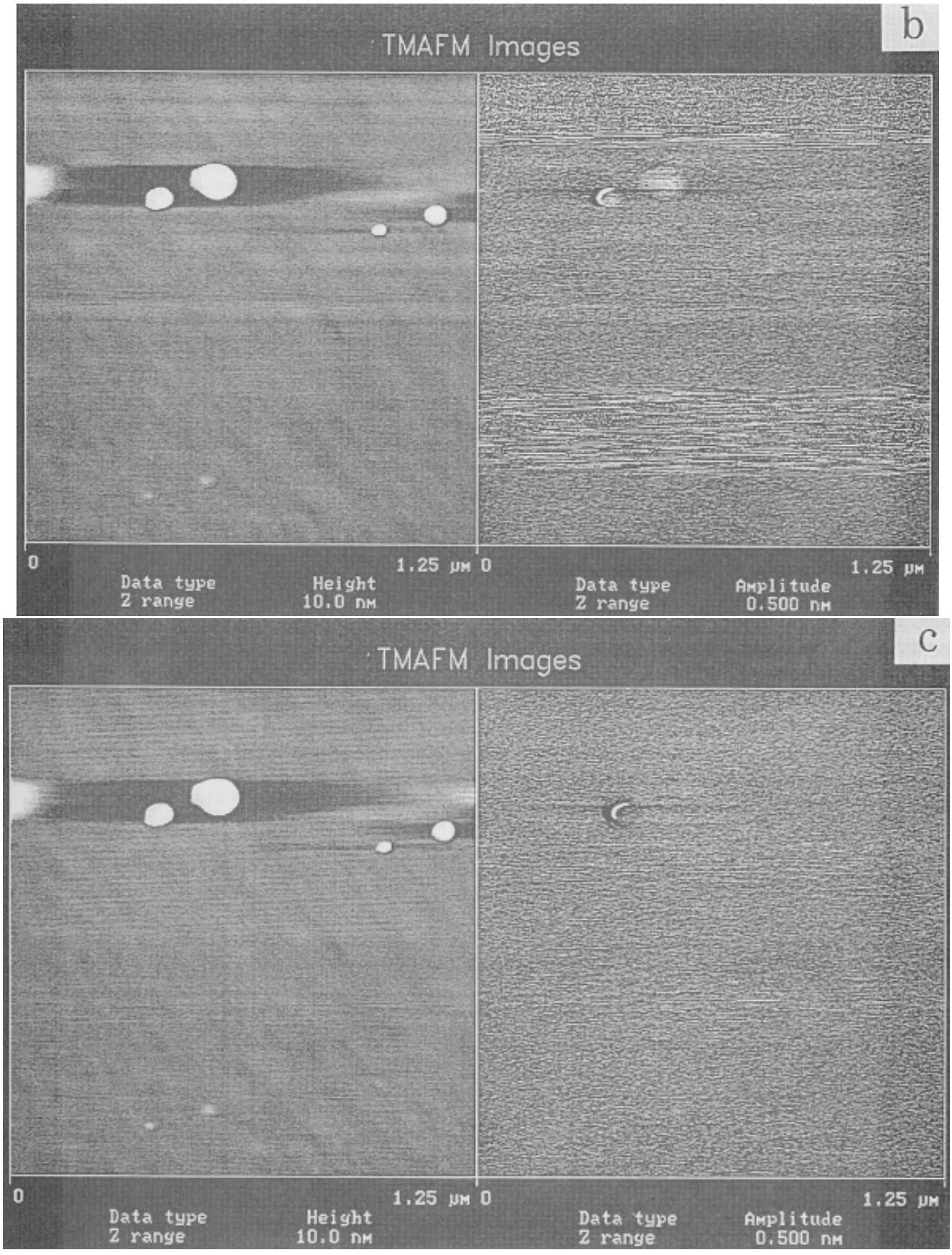


Fig. 5. (continued)

crodomains in $LiNbO_3$ could be due to the Li_2O deficiency. For the exact clarification of such mechanism, however, future aimed studies on samples poled under different electric fields (or currents) and with different deviations from stoichiometry should be required

4. Conclusions

SAW grade $LiNbO_3$ samples show many 180º Domains (+ domains) of more than 0.2 μm in diameter in -z plane under DIOM. The + domains in the EFM-amplitude-mode. Objects of less than 0.2 μm in diameter in -z plane of the optical grade sample show very similar images to the + domains in the SAW grade sample. At present, the EFM observation is thought to be useful for a non-destructive inspection of submicron size 180º domains, though this method requires that sample surface in inert. In future, surface potential probe method under well-controlled temperature and atmosphere conditions, being more intelligent than the EFM,is expected as a hopeful technique in many multi-mode AFM methods for a direct observation of the static Charge of the submicron size objects in ferroelectrics materials.

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