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SCANNING ELECTRON MICROSCOPY OBSERVATION OF THE VOLTAGE CONTRAST IMAGE OF THE FERROELECTRIC DOMAIN STRUCTURE IN THE $LiNbO_3$ CRYSTAL

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Abstract

This paper reports a scanning electron microscopy study of the formation of the voltage contrast image of the ferroelectric domain structure in the $LiNbO_3$ crystal. We investigated the formation of the pyroelectric voltage contrast image of the regular domain structure. For our experiment, we used ZY cut of a $LiNbO_3$ crystal which had a regular domain structure with a domain width of ~ 55 μm. The regular domain structure in the $LiNbO_3$ crystal was formed by the method of thermo-electrical treatment after growth. The pyroelectric voltage contrast image of the regular domain structure in the scanning electron microscope was formed by applying the pyroelectric effect along polar axis Z. The difference in the voltage contrast in the neighboring domains connect with opposite directions of polar axis Z in the neighboring domains. It is shown that the voltage contrast of the ferroelectric domain structures is defined by the physical properties and orientation of the ferroelectric crystals.

Key Words: Voltage contrast, ferroelectric domain structure, pyroelectric effect.

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Introduction

Ferroelectric lithium niobate ($LiNbO_3$) is widely used in opto- and acousto-electronics because of its optical, piezoelectric, electro-optic, elastic, photoelastic, and photorefractive properties. Recently, the ferroelectric domain structures, which usually are formed spontaneously during the process of the ferroelectric crystal growth, were the defects in the crystals for opto- and acousto-electronic applications. Today, the regular domain structures in the ferroelectric crystals are widely used for excitation and reception of high-frequency surface acoustic waves, processing of radio signals [9], and generation of harmonics of laser radiation [5, 6]. Three methods are used to form the regular domain structures in the ferroelectric crystals with domain widths ~ 1-100 μm: (**1**) fabricating of the regular domain structures by the method of crystal growth with doped melts [7]; (**2**) formation of the regular domain structures by the method of thermoelectrical treatment after growth near Curie temperature at the conditions of the temperature gradient and electric field [1]; and (**3**) formation of the regular domain structures by using direct electron-beam writing [8]. For observation of the ferroelectric domain structures in an optical microscope, it is necessary to etch the ferroelectric crystals in acids and to form the topographical relief since the neighboring domains have different etching velocities along the polar axis in the crystals [2, 4]; this is a destructive method. On the other hand, scanning electron microscopy (SEM) can be used as a method of the non-destructive control, because the interaction of the electron beam with the ferroelectric crystal surface is defined by the physical (electrical, thermal) properties of the crystals. The ferroelectric crystals are very interesting for investigations in the SEM as they have the extremely large dielectric, pyroelectric and piezoelectric properties [10]. Using well known electrophysical properties of the ferroelectric materials, it is possible to control the values and signs of the electrical charges on the ferroelectric crystal surface, and by doing this, it is possible to control the secondary electron emission from the crystal surface. We have investigated the secondary electron emission from the surface of the ferroelectric $LiNbO_3$ crystal with regular domain structure. By applying the pyroelectric effect, it was possible to form voltage contrast images of domain structures because the neighboring domains had opposite directions of the pyroelectric polar axis Z and opposite signs of the surface charges, respectively.

Materials and Methods

These experiments have been performed at the Centre National de la Recherche Scientifique, Grenoble, using a JEOL JSM-840 SEM. In the secondary electron emission mode, the SEM permits visualization of the electric potential distribution in a regular domain structure on the $LiNbO_3$ crystal surface, since the low energy secondary electrons (1-50 eV) are sensitive to surface charges. The ferroelectric crystal surface was visible at an accelerating voltage $E_o = 2$ kV and a probe current $I_o = 6 \cdot 10^{-10}$ A. The use of higher accelerating voltages (> 3 kV) was not possible, because the insulating ferroelectric substrate became highly charged and led to a distortion of the image due to the deflection of electron trajectories [3].

For our investigations, we used ZY-cut of a $LiNbO_3$ crystal with a regular domain structure. In this case, the polar pyroelectric axis Z is normal to the crystal surface. The regular domain structure with a domain width of ~ 55 μm was formed in the $LiNbO_3$ crystal by the method of the thermo-electrical treatment after growth near the Curie temperature (T_c ~ 1100 °C) at the conditions of the temperature gradient and gradient of the electric field [1]. The neighboring domains in the regular domain structure have the opposite directions of the polar pyroelectric axis Z and opposite directions of the spontaneous polarization, $\vec{P}$, respectively. The pyroelectric effect was used to form the charges on the surface of the ZY-cut of a $LiNbO_3$ crystal. A semiconductor microrefrigerator Peltier was placed in the SEM to excite the pyroelectric effect in the $LiNbO_3$ crystal by thermal cooling and heating (ΔT). The $LiNbO_3$ crystal with a regular domain structure was placed on the surface of the semiconductor microrefrigerator Peltier.

Experimental Results and Discussion

Figure 1 demonstrates the experimental scheme, and Figure 2 shows the scanning electron photomicrographs [obtained at an accelerating voltage $E_o = 2$ kV and a probe current $I_o = 6 \cdot 10^{-10}$ A without (a) and with excitation of the pyroelectric effect (b, c)] of the ZY-cut of a $LiNbO_3$ crystal with regular domain structure. The domain width was 55 ~ μm. Figure 2a demonstrates that under normal conditions ($\Delta T = 0$°C), the voltage contrast image of the regular domain structure is absent. Figures 2b and 2c show images of the same surface obtained with thermal cooling (b) and heating (c) of the sample by the semiconductor microrefrigerator Peltier effect. The ferroelectric $LiNbO_3$ crystal is a pyroelectric crystal. A pyroelectric solid exhibits a change in spontaneous polarization as a function of temperature.

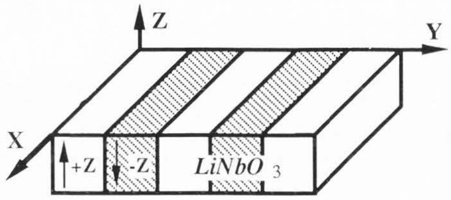


Figure 1. Experimental scheme showing the ZY-cut of a $LiNbO_3$ crystal with regular domain structure.

The relationship between the change in temperature, ΔT, and the change in spontaneous polarization, $\Delta\vec{P}$, is linear and can be written as $\Delta\vec{P} = \vec{\gamma}\Delta T$ where $\vec{\gamma}$ is the pyroelectric tensor. In tensor component form, this may be written as $\Delta P_i = \gamma_i \Delta T$. In the $LiNbO_3$ crystal, the pyroelectric effect is due to the movement of the lithium and niobium ions relative to the oxygen layers. Since the Li and Nb ions move only in a direction parallel to the polar axis Z, the pyroelectric tensor is of the form,

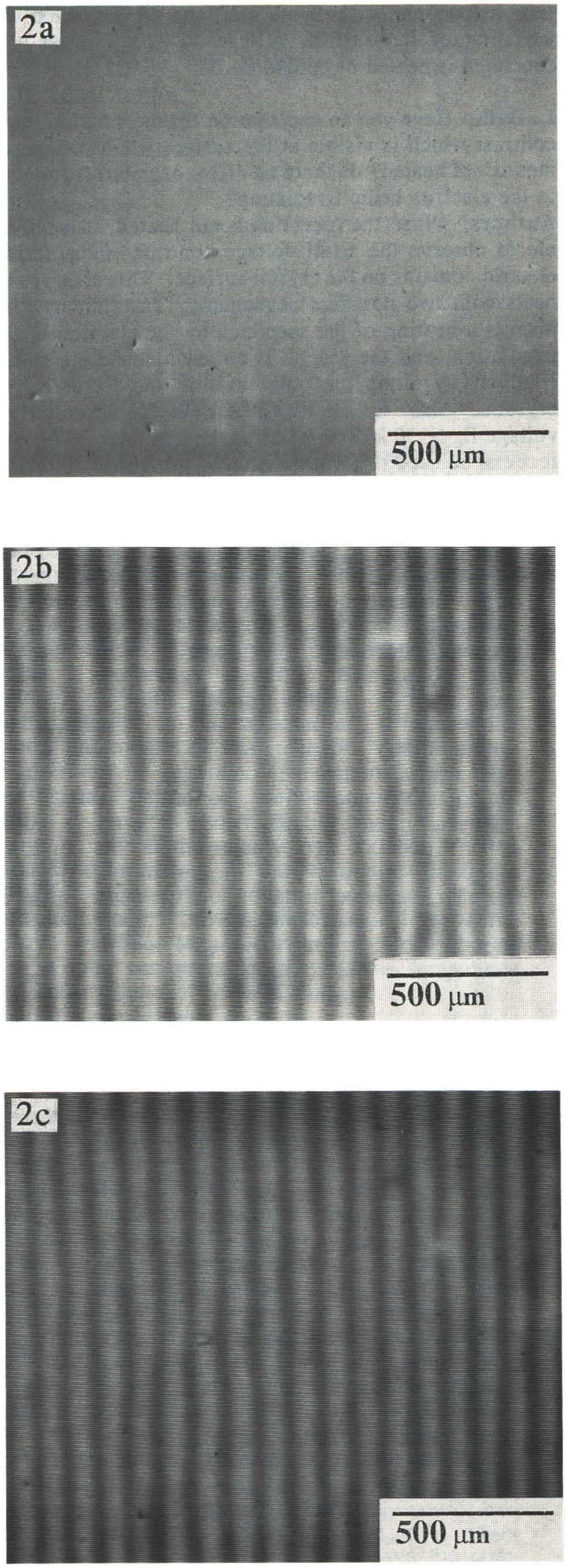
$$\gamma_i = \begin{bmatrix} 0 \\ 0 \\ \gamma_3 \end{bmatrix},$$

where $\gamma_3 = -4 \cdot 10^{-5}$ C/(K·m^2) [10]. Thermal cooling of the sample by $\Delta T = -5$°C (Fig. 2b) leads to form the positive charge on the Z-plane in one domain with value $\Delta P_3 = 2 \cdot 10^{-4}$ C/m^2 and negative charge in the neighboring domain with value $\Delta P_3 = -2 \cdot 10^{-4}$ C/m^2, because the neighboring domains have the opposite directions of the polar pyroelectric axis Z and opposite directions of the spontaneous polarization $\vec{P}$ along this axis, respectively. The positive charge (positive potential) decreases the number of detected secondary electrons from the crystal surface and has dark contrast, while negative charge (negative potential) increases the number of detected secondary electrons and has bright contrast. The negative value of pyroelectric coefficient γ_3 indicates, that upon thermal cooling, the +Z crystal face will became more positively charged (Fig. 2b, domains with dark contrast). Thermal heating of the $LiNbO_3$ crystal by $\Delta T = 5$°C (Fig. 2c) inverts the voltage contrast image of the regular domain structure by inversion of the signs of the surface charges in the neighboring domains (positive to negative, and negative to positive, respectively). Therefore, the formation of the voltage contrast image by pyroelectric effect is very useful to observe the domain structures in ferroelectric crystals and to determine the direction of the pyroelectric polar axis Z (plus or minus).

Conclusions

This paper demonstrates the formation of the SEM voltage contrast image of the ferroelectric $LiNbO_3$ crystal with a regular domain structure. We have shown the possibility to use the pyroelectric effect for voltage

Figure 2 (at right). Scanning electron photomicrographs of the ZY-cut of a $LiNbO_3$ crystal with a regular domain structure obtained with different temperature conditions: (**a**) $\Delta T = 0°C$; (**b**) cooling, $\Delta T = -5°C$; (**c**) heating, $\Delta T = 5°C$.



contrast observation of the ferroelectric domain structures in SEM. This non-destructive method is very useful to control the domain structures and to determine the directions of the polar axis in ferroelectric and pyroelectric crystals.

References

1. Antipov W, Blistanov AA, Sorokin NG, Chizhikov CI (1985) Formation of regular domain structure in ferroelectric $LiNbO_3$ and $LiTaO_3$ near the phase transition. Sov. Phys. Crystallogr. **30**, 428-430.

2. Burfoot JC, Taylor GW (eds.) (1979) Polar dielectrics and their applications. The MacMillan Press Ltd., U.K., 229-231.

3. Goldstein JI, Yakowitz H (eds.) (1975) Practical Scanning Electron Microscopy: Electron and Ion Microprobe Analysis. Plenum Press, 212-216, 253-254.

4 Kuz'minov YS (1987) Electro-optical and nonlinear optical lithium niobate crystal. Nauka, Moscow 16-17.

5. Lu Y, Mao L, Cheng S, Ming N, Lu Y (1991) Second-harmonic generation of blue light in $LiNbO_3$ crystal with periodic ferroelectric domain structures. Appl. Phys. Lett. **59**, 516-518.

6. Mizuuchi K, Yamamoto K, Taniuchi T (1991) Second-harmonic generation of blue light in a $LiTaO_3$ waveguide. Appl. Phys. Lett. **58**, 2732-2734.

7. Naiben M, Youngyuan Z, Duan F (1990) Ferroelectric crystals with periodic laminar domains as the micron superlattices for optic acoustic processes. Ferroelectrics **106**, 99-104.

8. Nutt ACG, Gopalan V, Gupta MC (1992) Domain inversion in $LiNbO_3$ using direct electron-beam writing. Appl. Phys. Lett. **60**, 2828-2830.

9. Roshchupkin DV, Fournier Th, Brunel M, Plotitsyna OA, Sorokin NG (1992) Scanning electron microscopy observation of excitation of the surface acoustic waves by the regular domain structures in the $LiNbO_3$ crystals. Appl. Phys. Lett. **60**, 2330-2331.

10. Weis RS, Gaylord TK (1985) Lithium Niobate: summary of physical properties and crystal structure. Appl. Phys. **A37**, 191-203.

Discussion with Reviewers

L. Balk: Have you an estimation of the variation of the surface voltage when the specimen is heated or cooled?
Authors: The variation of the surface voltage is a function of the surface charge and thickness of the specimen, $\Delta U = (\gamma_3 \Delta T d)/(\varepsilon_{33}\varepsilon_0)$, where: d is the thickness of the specimen, and $\varepsilon_{33} = 99.5$ is the dielectric constant in the direction of the polar axis Z. In our experiment, we

used a specimen with d = 1 mm, and we estimated the variation of the surface voltage as 227 V when the specimen is heated or cooled by ΔT = 5°C.

L. Balk: Have you an explanation for the small voltage contrast which is visible at the surface when the specimen is not heated? Is there an effect of polarization due to the electron beam irradiation?
Authors: When the specimen is not heated, it is possible to observe the small voltage contrast of the ferroelectric domains on the crystal surface. This effect connects with two possible mechanism. The first mechanism is a heating of the specimen by the electron beam irradiation, and the second is an asymmetric electrical conductivity along the polar axis in the ferroelectric crystals. Also, the electron beam with an accelerating voltage $E_0 > 10$ kV can polarize the specimen. This effect can be used to form the domain structures in ferroelectric crystals.

D. Chan: How would charging on the crystal due to the beam affect the formation of the voltage contrast image? What steps did you take to ensure that these effects were negligible?
Authors: The small voltage contrast of the domain structure, which is due to the beam affect, disappear very fast. In this case, it is difficult to obtain scanning electron photomicrographs of the ferroelectric domain structure.

D. Chan: What is the resolution of the method used for imaging the domains?
Authors: In our experiment we used the regular domain structure with domain ~ 55 μm, but we think that it is possible to observe the domain structure with domain width ~ 1 μm.