

Direct Observation of Ferroelectric Domains in LiTaO₃ Using Environmental Scanning Electron Microscopy

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Direct observation of ferroelectric domain structures in LiTaO₃ crystal, without etching or surface coating, has been realized by using environmental scanning electron microscopy in secondary electron emission mode. The new method can nondestructively provide domain contrast image at submicron resolution, and the domain contrast image is very stable. Conditions for best domain contrast of LiTaO₃ crystals have been established. [S0031-9007(97)04101-X]

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In recent years, scanning electron microscopy (SEM) has found applications in the study of ferroelectric domain structures [1–4]. Using low accelerating voltage a contrast between antiparallel ferroelectric domains can be imaged on an unmetalized polar crystal surface in secondary electron emission mode. The technique does not need special treatment of the sample surface and is nondestructive. It has been successfully used to study domain structures of several ferroelectric crystals [5–7].

In the SEM method, the key is to avoid surface charge accumulation onto an insulating crystal. The experimental conditions are very strict; particularly, the choice of probe current and accelerating voltage is very critical, and no contrast can be found if the parameters are not properly chosen. Moreover, the contrast image is short lived; i.e., it disappears under the influence of electron beam after a few seconds to a few minutes. The observation time for the contrast shortens with the increase of accelerating voltage and magnification. Consequently, it is not possible to obtain a stable contrast image with high resolution and magnification [1,2].

In this Letter we report a new secondary electron image (SEI) technique of observing ferroelectric domains by using environmental scanning electron microscopy (ESEM). Because the ESEM [8,9] can operate at pressures 10 000 times higher than that of standard SEM, the free ions which are created by collisions between moving electrons and neutral gas molecules can be used to provide a conducting path for beam-deposited surface charges, which allows one to examine unprepared, uncoated insulating samples. The results show that one can obtain *stable* domain contrast under relatively high accelerating voltage, large beam current, and slow scan rate using ESEM. Because higher accelerating voltage can be used, higher resolution than the conventional SEM is expected. The technique has been applied to a LiTaO₃ crystal with uncoated surface. A clear stable secondary electron image of the domain structures was obtained.

The spontaneous polarization P_s of LiTaO₃ can be reversed by a pulse electric field at room temperature [10]. Using different electrode pattern LiTaO₃ crystals can be

poled into periodic and quasiperiodic domain structures which have been widely used in acoustics [11], nonlinear optics, and solid state laser devices [12–16]. Preliminary examination of the domain structure in a poled LiTaO₃ sample was made by optical microscopy on an etched surface. The destructive method of etching often affects further experiments on the sample. Therefore, it is desirable to develop new convenient nondestructive methods for the observation of domain patterns on an unprepared surface of a poled LiTaO₃ crystal.

In this work we used *c*-cut LiTaO₃ crystal wafers. The domain structures in the wafers were engineered by field poling method at room temperature. Two kinds of aluminum electrodes were fabricated: one is periodic and the other is uniform plane. During pulse poling using the above two kinds of electrodes two types of domain morphology, stripe and triangular shape, were produced.

The domain observations were performed using an ESEM (ElectroScan Model E-3, Wilmination, MA) in secondary electron emission mode. Figure 1 is a schematic diagram of the experimental arrangement and crystal orientation. A periodically poled sample was etched in a solution containing 2 parts HNO₃ and 1 part HF for 15 h at room temperature, and was attached to an aluminum sample mount using double faced tape for observation. The sample mount was grounded. The electric potential of the detector was set at +0.5 kV. Water vapor was chosen as the imaging gas. Under normal observation condition of wet mode, chamber pressure 3–3.5 Torr, accelerating voltage 15 kV, condenser 40, scan rate 8–30 sec/frame, and aperture size 30 μ m, we got a topographic image of the periodic domain pattern on the +*c* surface, which is [001] orientation, as shown in Fig. 2(a). In the image the surfaces of negative domains are lower than those of positive domains. The formation of the surface steps is due to different etching rates of positive and negative domains in the acid. A wider stripe and some island domains shown in the figure are attributed to imperfect poling. One can see that the contrast only appears in domain boundaries which are brighter than the interior of domains, reflecting the fact

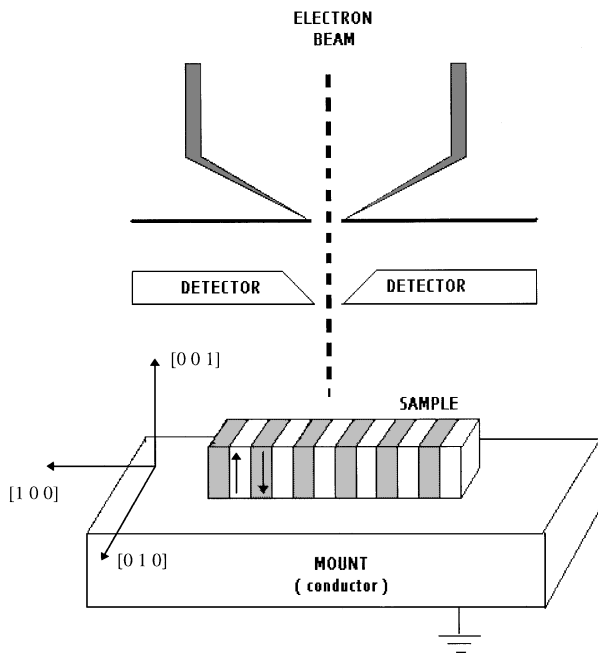


FIG. 1. Schematic diagram of the experimental arrangement.

that more secondary electrons are emitted at the edges of the etching steps. No contrast was revealed between the positive and negative domains due to the screening of the polarization P_s by the probing current. In other words, the positive and negative domains have nearly equal secondary electron emission rate.

After the first observation, the etched sample was taken out of the chamber and the [001] surface was polished. When the polished sample was reexamined using ESEM under the same condition, nothing interesting was seen except some polishing scratches on the surface. However, after the experiment parameters were changed by decreasing the chamber pressure, increasing the probe current by decreasing the condenser current and increasing the aperture, and increasing the accelerating voltage, contrast stripes began to appear [shown in Fig. 2(b)]. The locations and shapes of the contrast patterns in Fig. 2(b) exactly match the etched patterns in Fig. 2(a). This confirms that the contrast stripes originated from the antiparallel domains.

Optimum contrast was obtained under the following conditions: accelerating voltage, 30 kV; chamber pressure, 2 Torr; aperture size, 50 μm (maximum for the E-3 system); condenser, 10 (lowest of the E-3 system); and scan rate, 17–30 sec/frame. The positive domains were sufficiently brighter than the negative domains, indicating that the secondary electron emission from positive domains exceeds that from negative ones. The contrast is very stable in time, no change was observed over a period of 4 h which was the longest observation time used in our experiments. This is a marked advance from the conventional SEM method in which the contrast can only be kept for a few seconds to a few minutes [1,2].

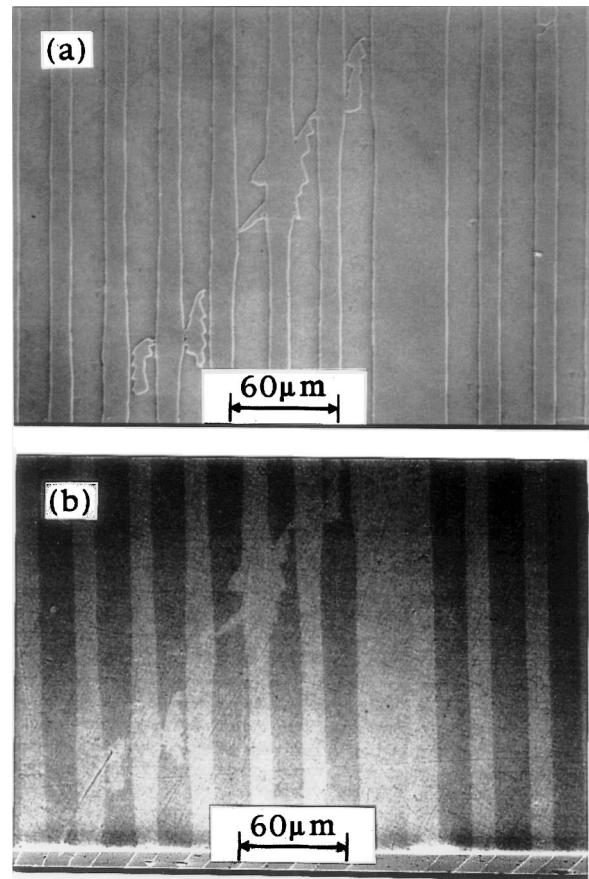


FIG. 2. Comparison of ESEM images of a surface portion in a *c*-cut LiTaO₃ with antiparallel domains. (a) Etched surface: voltage = 15 kV, condenser = 40, pressure = 3.0 Torr, and aperture = 30 μm . (b) Polished surface: voltage = 30 kV, condenser = 10, pressure = 2.0 Torr, and aperture = 50 μm .

With a slight tilt of the sample, we could simultaneously observe the previously etched patterns of the periodic domain structure on the [010] surface of the sample which was not polished [see the bottom of Fig. 2(b)]. The image patterns on the two adjacent [001] and [010] faces are consistent. However, if we tilt the sample to the $[0\bar{1}0]$ surface which was polished, no contrast stripes were found. This means that only the polar surfaces can show the domain contrast images.

We found that although higher contrast domain images could be obtained under the optimum conditions mentioned above, the experimental conditions are not very critical. With an aperture of 50 μm , domain contrast could appear in the range of accelerating voltages from 20–30 kV, condenser current setting from 10–30, scan rates from 4–60 sec/frame, and chamber pressure from 1.0–3.0 Torr. In all cases the positive domains were always brighter than the negative ones.

The visualization of domain contrast is also independent of surface roughness. We could clearly observe the contrast image of domains on a crack surface with appropriate conditions as shown in Fig. 3. The sample in

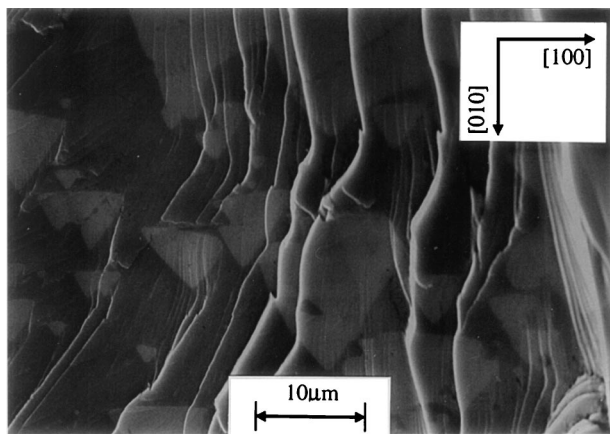


FIG. 3. ESEM image of a crack surface of LiTaO_3 crystal with nearly $[00\bar{1}]$ orientation. The sample was partially poled by a poling field of $E = 21$ kV/cm. The triangular antiparallel domains with positive polarity are shown as brighter regions on the darker background. Image conditions: voltage = 30 kV, condenser = 10, pressure = 2.0 Torr, and aperture = 50 μm .

Fig. 3 was partially poled under a pair of plane aluminum electrodes. After poling, the electrodes were removed in NaOH solution which only resolves the aluminum but not the LiTaO_3 crystal. In Fig. 3 some triangular domains with positive polarity are shown as lighter regions on the dark background of negative polarity. Generally speaking, the morphology of the inverted domains depends on the symmetry of the crystal as well as the intensity of the poling field. The polarization direction of LiTaO_3 is parallel to its triad axis. Using a moderate field of $E = 21$ kV/mm, the triangular shape inverted domains can be formed under plane electrode in a partial poling process. The sides of the triangle corresponding to domain walls are parallel to crystallographic x directions. Domains grow by gradually extending the domain walls along crystallographic y directions during poling. This is a typical growth morphology of the antiparallel domains of LiTaO_3 in a quasiequilibrium process through two-dimensional nucleation [17]. The domains in Fig. 3 have different sizes, which reveals that the polarization reversal in the crystal is through multisite nucleation and growth; i.e., a large number of inverted domains are nucleated first, then they grow and coalesce to complete the switching process.

The domain contrast in Fig. 3 is better than that in Fig. 2(b) which has to be contrast enhanced by computer. This is because a depolarization layer is produced on the polished surface, while the cracked surface has much less mechanical artifact; thus a better contrast image can be obtained. This phenomenon is also found in the domain contrast image observation using conventional SEM [1,2].

Le Bihan [1] proposed a theoretical model to explain the domain contrast of triglycine sulfate (TGS) crystal using conventional SEM under low voltage condition. It was assumed that the contrast of ferroelectric domains is

caused by polarization charges, hence the surface of positive domain should be darker than that of a negative domain. However, this is in contradiction with our results here. Generally speaking, for an insulating sample, surface electric charge equilibrium is the fundamental principle for producing these contrast images. In conventional SEM technique, the charge neutralization relies on the exact balance of surface input and output currents. The samples need to be slightly conductive or coated with a conducting layer in order to accomplish this task under vacuum. For the ESEM this charge balance is achieved by neutralizing surface electron buildup with positive ions under finite vapor pressure.

The secondary electron emission rate depends on the level of interaction between the electron beam and the surface layer of ferroelectric crystal. Although it is not clear if the probing current is sufficient to instantly screen the charge on the sample surface at each frame, there is definitely a charge balance after a short period of time. Therefore, the polarization charges cannot be the main cause of contrast due to the large amount of ionic composition under finite vapor pressure. Because the technique is new, the exact mechanism for the image formation is still under investigation.

In conclusion, for the first time we have successfully observed *stable contrast image* of antiparallel domains in poled LiTaO_3 crystals using ESEM technique. This technique is very promising since it allows us to directly observe antiparallel domains in an unetched and uncoated insulating sample surface. The condition for obtaining the contrast image is not very strict and the domain image for LiTaO_3 crystal is stable for several hours. From our experience, better image can be produced with higher voltage, lower condenser current, and larger aperture (more electrons). Because the ions produce a conducting path to neutralize the surface charge accumulation, the technique allows the use of higher accelerating voltage with higher magnification; therefore, submicron resolution can be obtained.

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