Journal of Electroceramics, 13, 293–297, 2004

Pyroelectric Electron Emission Behaviors of Congruent and Stoichiometric Lithium Niobate Single Crystals

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Submitted February 12, 2003; Revised March 3, 2004; Accepted April 30, 2004

Abstract. Pyroelectric electron emission current measurements and current distribution collecting were performed on congruent and stoichiometric lithium niobate single crystals. Electron emission behaviors were found to be gap distance (crystal-detector) dependent. For small gaps, in both crystal compositions, emission was accompanied by a partial superficial domain inversion, triggered by surface plasma ignition. For large gaps (>2 mm) in congruent single crystals the emission was activated by a true pyroelectric effect.

Keywords: pyroelectric, electron emission, plasma, lithium niobate

1. Introduction

The use of ferroelectric materials appears to be an easy way to generate electrons without need of external high voltages or any special surface preparation. Due to its simplicity, ferroelectric electron emission has been investigated for about 30 years and several applications have been suggested: displays, x-ray generators, and sensors [1]. Most of them rely on electron emission generated by polarization switching, and several mechanisms have been proposed to explain the interesting phenomena [2]. Less attention has been paid to the pyroelectrically induced electron emission, and the underlying physics is still not fully understood.

We investigated pyroelectric electron emission (PEE) behaviors of lithium niobate (LN) single crystals. The PEE current and its distribution were influenced significantly by varying the gap between the crystal surface and the detector. Moreover, an electrical discharge occurred and a partial domain inversion was observed on crystal surface after emission.

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2. Experimental

We used polished monodomain Z-cut plates of congruent lithium niobate (CLN) single crystals 1 mm thick (Crystal Technology Inc.) and stoichiometric lithium niobate (SLN) single crystals 0.5 mm thick (Oxide Corporation); $[Li_2O]$:$[Nb_2O_5]$ mole ratio of the former is 48.4:51.6 and that of the latter is 49.9:50.1. The lithium-deficient 'congruent' composition has a much higher coercive field, about 22 kV/mm than that of the stoichiometric one, less than 4 kV/mm [3, 4]. We heated the crystals up to 140°C at a heating rate of 10°C/min in a high-vacuum chamber. The chamber was equipped with a turbo-molecular pump system with a base pressure of less than 10^{-6} Torr. We varied the gap distance between the sample surfaces and the electron detectors from 90 μm to 4.5 mm. After electron emission, we examined the surface of crystals by wet etching in hydrofluoric acid (HF 50%) for 100 min. Such an etching can reveal domain patterns, since $-$Z oriented domains have a much faster etching rate than +Z ones [5, 6].

A Si p-n junction photodiode (AXUV-100, International Radiation Detectors, Inc.) was used as a detector for emission currents and resulting currents were measured by an electrometer (Model 6514, Keithely

Instruments, Inc.). Responsivity of the photodiode (PD) is about 0.2 A/W for electrons with energy in the range of 1 keV to 40 keV. Electrons produced by LN crystals during heating have a large energy up to 100 keV, and hence the PD amplification factor of the emission current is about 10^4 [7]. Receptive electron-beam resist (ZEP-520, Nippon Zeon Co., Ltd.) was used to study the spatial distribution of the emission current. ZEP-520 E-beam resist is known to have sensitivities of $\sim$1 μC/cm^2 for positive tone area exposures to 1 keV electrons [8]. It was very simple to use resist-coated wafers as detectors and the high sensitivity enabled us to observe current distribution of PEE.

3. Results

Figure 1 shows the PEE current evolution with temperature during the first heating run of as-received CLN samples at different gaps between the crystal surface and the PD detector. Current signal from a small gap of 0.5 mm demonstrates an abrupt decrease during heating. The current peak is nearly the same when the gap was varied from 0.5 mm to 4.5 mm.

After PEE current measurements the crystals were etched with HF acid solution (50%), then their surfaces were observed by using an optical microscope. Figure 2 shows +Z-face surfaces of CLN crystals from which electrons were emitted for different gaps. Linear patterned striations was revealed on the +Z surface after etching. Magnified view of the striation lines shows a tree-like pattern which is probably a signature of electrical discharge during PEE current measurements. The density of striations decreases as the gap is increased. Striations practically disappeared when the gap was 2.5 mm and up.

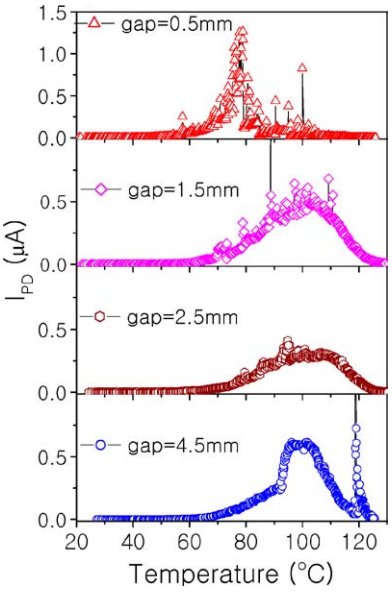

Fig. 1. Emission current evolution with temperature from +Z-face of CLN crystals at different gap variations: 0.5, 1.5, 2.5 and 4.5 mm.

We also carried out PEE current measurements from +Z-face of SLN crystals at different gaps (Fig. 3), no abrupt current decrease was observed in the studied gap range. As is shown in Fig. 4, etched +Z surfaces of the SLN crystals revealed a linear striation for a small gap (90 μm) and a large dispersed spots for a large gap (0.5 to 4 mm). High magnification shows that the patterning on crystal surface has a regular shape (hexagonal geometric) which is a tangible sign of inverted domains. Thus, the striations observed on the CLN crystals are in fact superficial domain-inversion traces.

The density of the domain inversion region on the SLN crystal was higher than on the CLN one. Moreover, superficial domain inversion did not disappear for a gap up to 4 mm. The difference could be due to the small coercive field of the SLN crystal.

Figure 5 shows the spatial current distribution on the receptive E-beam resist surface for different gaps. In small gaps (90 μm to 0.5 mm), the emission impact was manifested in regular crossed and elongated lines. The line density increased with decreasing gap distance. The geometrical configuration of these lines was analogue to the superficial domain inversion traces observed on crystal surfaces. Such correspondence elucidates that the PEE was accompanied by a superficial polarization reversal.

4. Discussion

The optical microscopic analysis of emitter LN crystal and E-beam resist surfaces after PEE tests show that the emission from the +Z-face is controlled by two different processes depending on the emitter-collector gap distance: emissions with and without domain inversion.

For small gaps, the emission could be attributed to domain inversion associated with an electrical breakdown. Indeed, the high electric field magnitude induced in the gap by pyroelectric effect ($\sim 10^6$ V/cm), and according to Paschen's laws in which the electric field threshold for breakdown decreases as the gap

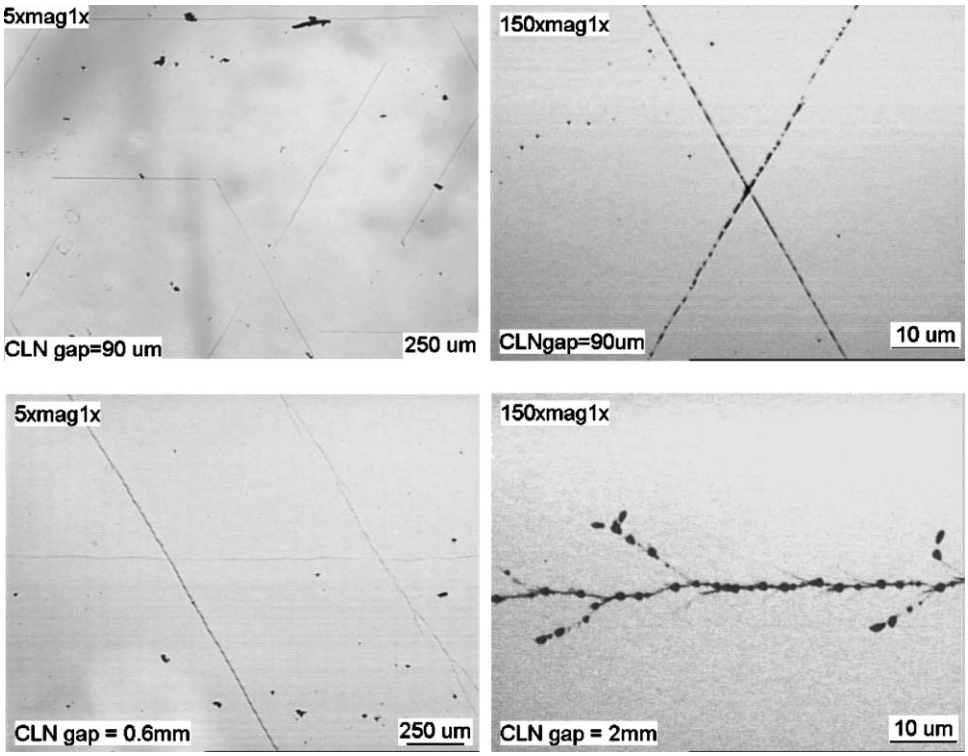

Fig. 2. Variation of superficial domain inversion density on the +Z-surface of CLN crystals for different gaps.

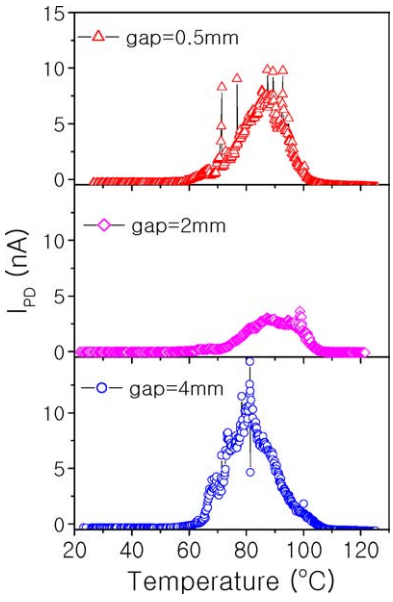

Fig. 3. Emission current evolution with temperature from +Z-face of SLN crystals at different gap variations: 0.5, 2 and 4 mm.

decreases, all these parameters are favorable for an electrical discharge triggering and, thereby, the treeing shape of linear striations on the crystal surface could be explained. The electrical discharge, which is the consequence of the ionized molecule gases persisting in the vacuum, compensates the unscreened charges subsisting on the crystal surface while heating and consequently causes a drop in the emission current. This also could explain the intermittent emission current seen in a small gap by the CLN crystal (Fig. 1).

The manifestation of domain inversion in elongated and crossed striations on +Z-face crystal and their corresponding electron emission impact on the E-beam resist with the same pattern (elongated and crossed lines) suggest that such geometrical configuration could be attributed to a special uncompensated negative charge distribution on crystal surface which is relative to the hexagonal crystalline lattice structure of lithium niobate. From these locales of uncompensated charge accumulation the electrical discharge is preferentially primed and the emission is supplied. Thus in a small emitter-collector gap, according to the above

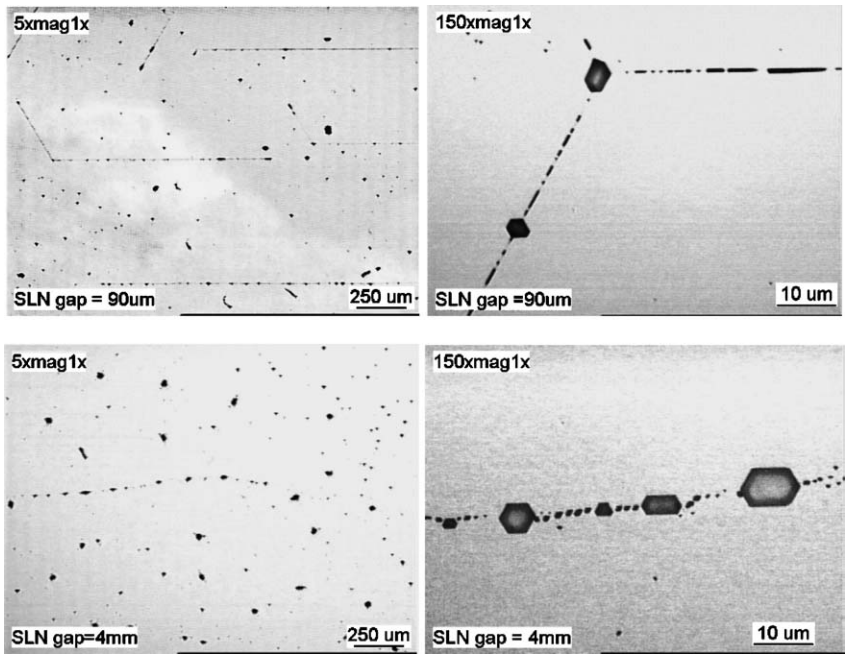

Fig. 4. Variation of superficial domain inversion density on the +Z-surface of SLN crystals for different gaps.

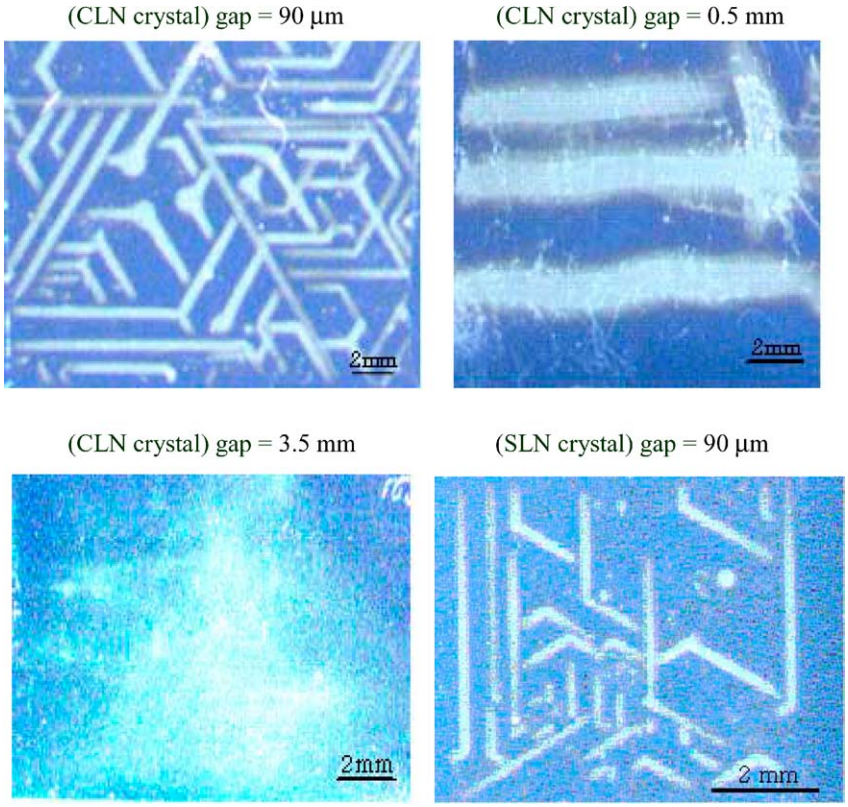

Fig. 5. Emission current impact on the receptive E-beam resist from +Z-face of CLN and SLN crystals at different gaps.

statements, the emission current is triggered by a surface plasma ignition.

In a large gap ($\geq$2.5 mm) the electron emission from CLN crystal +Z-face did not show any domain inversion on the crystal surface, likewise, the emission current did not manifest any decrease with gaps as large as 4.5 mm. Such behavior suggests that the emission is controlled by a field emission without any plasma formation. In other words, the electron emission was simply activated by a true pyroelectric effect.

5. Conclusion

PEE measurements were performed on CLN and SLC single crystals with varying gap distances between the crystal surfaces and the detector. The emission current curve characteristics, the electron impact on the E-bam resist and the morphological domain patterning on the crystal surface allow us to conclude that for small gaps the emission is assisted by a plasma discharge effect, differently to large gaps where the emission is activated by a pure pyroelectric effect.

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