$LiNbO_3$-based ferroelectric heterostructures

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Abstract

We report the growth of $LiNbO_3$ thin films onto In_2O_3:Sn-coated <111>-Si substrates by standard radio-frequency sputtering. Multi-layer procedures, up to 4 successive deposits, have been developed that can subsequently improve the structural and macroscopic ferroelectric properties of such as-grown composite structures. The enhancement of polarization, as high as 40 $\mu C.cm^{-2}$ in 4 stacked layers, is attributed to *c*-oriented seed-layer-induced crystallization (self-polarization) and interfacial (migratory) polarization.

1. Introduction

In the past few years, ferroelectric thin films and superlattices have become the subject of increasing importance in order to develop new active materials, adaptive structures and self-organized architectures for the new generation of ferroelectric random access memories (FRAM) or surface acoustic wave (SAW) thin film devices. No doubt that what may be called "the nanoscale century" will follow this trend, thus leading to a new technical and technological revolution, particularly in terms of thin film processing and materials.

$LiNbO_3$ (LN) is expected to be an ideal alternative for small-scale systems. In an attempt to both develop novel integrated electro-optical systems and offer new functionality for future LN-based devices, the stacked-layer growth of LN thin films onto In_2O_3:Sn (ITO)-coated <111>-Si substrates has been investigated by radio-frequency (r.f.) sputtering. Breakthroughs in material processing and LN capabilities are the driving idea behind the choice of such an underlying template. Indeed, with both its low refractive index and good electrical conductivity for low SnO_2 content (<10%), ITO appears as an efficient material for transparent electrodes in contemporary and emerging thin films[1]. A possibility to enhance the *c*-oriented growth and modulate the polarization response consists in performing multi-step procedures and imposing stacked-layer configuration by interrupting the growth and recovering ambient temperature and pressure conditions between different deposits[2]. Up to 4 stacked LN layers were successively and successfully deposited onto ITO/Si substrates. In the present work, structural and macroscopic ferroelectric properties of 2-step and 4-step grown systems are compared and discussed on the basis of correlated nucleation and polarization effect. These experiments can potentially contribute to the better understanding of the mechanisms responsible for orientation selection onto ITO/Si and illustrate the crucial role of space-charge like defects on polarization in ferroelectric thin-film capacitors.

2. Experimental

Mono- and multi-layered LN films were deposited by r.f. sputtering through home-made Li-enriched ceramic powder onto commercial 250nm-thick ITO (10% Sn)-coated <111>-Si substrates. Details of the deposition procedures are listed in Table 1[2]. In all cases, the last deposition hours were performed at 600°C to favor the crystallization of the material. Whatever the deposition process, and after a total deposition time of 6h, the resultant stacked layers exhibit dense, columnar microstructures with a total thickness of 300nm as revealed by scanning electron microscopy. Phase analysis of the films has been performed at room temperature by X-ray diffraction (XRD) using a Cu Kα radiation. To study the ferroelectric properties, circular platinum (Pt) electrodes of 0.2 mm^2 area have been sputtered ex-situ on the film through a shadow mask. Pulsed hysteresis loops have been measured at room temperature with a computer-controlled standardized ferroelectric test system (Precision Workstation, Radiant Technology).

3. Results and discussion

3.1. Selective orientation

Due to the lack of atomic registry and lattice match between LN (rhombohedral, R3c) and ITO (cubic, Ia3), polycrystalline structures are observed on LN mono-layers directly grown onto ITO[2,3]. One way to promote oriented growths lies in multi-step procedures, with the first-sputtered LN layer as thin as possible to prevent both grain growth and heterogeneous nucleation. As previously reported, LN bi-layers corresponding to 1h (first deposit) and 5h (second deposit) deposition times, at 600°C, can exhibit degrees of orientation along the *c*-axis as high as 50%[2]. This thin LN homo-template appears as a suitable seed-layer for the next nucleation-growth process, thus resulting in oriented materials (Fig. 1a). The deposition of 4 successive thin layers can further improve this texturation, with degrees of orientation, estimated through the factor of Lotgering *f*(006), as high as 94% (Fig. 1b).

To explain this spontaneous orientation, different mechanisms can be considered, such as (1) space-charge field, (2) self-polarization, or (3) collective nucleation, re-crystallization and polarization effect. Beyond its ferroelectric nature, $LiNbO_3$ is a well-known ionic conductor[4].

Due to the easy diffusion of low-sized low-charged Li ions, a gradient of Li vacancies can be formed in the LN films near the interface(s), which can induce a space charge field (SCF) in the direction perpendicular to the substrate[5]. Even if the boundaries of this interdiffusion region seems to be quite narrow as revealed by depth profile analysis by secondary ion mass spectroscopy[2], this SCF may promote the formation of *c*-oriented crystallites. The higher the number of layers, the stronger the built-in-field, the greater the self-orientation effect (Fig. 1). In the same way, the different dynamical properties of the electrons and ions in the plasma can induce a superimposed electric field near the surface, all the more important since the selected ambient is rich in oxygen (Ar:O_2 = 40:60). Consequently, the electrostatic coupling of the growing columns of material with this built-in electric field could favor a preferential orientation parallel to this field, *i.e.* perpendicular to the substrate Since the polar direction is along the <001> crystallographic axis in $LiNbO_3$, (00*h*) crystalline planes are preferentially set parallel to the substrate. The strong variation of the film orientation according to the thermal history during a same deposit is a qualitative proof of this coupling with the plasma self-polarization. An example is given in figure 2 for bi-layered systems. By progressively increasing the temperature during the second deposit, one can strongly affect the characteristics of the plasma near the heated surface and the resulting crystalline texture of the film. This results in the shift of the preferential orientation from (00*h*) to (0*hh*). Note that working at lower temperatures during both the first deposit and the first hours of the second deposit can also limit interdiffusion phenomena at the film/substrate interface (Fig. 2b), thus reducing the associated ionic defects. Finally, structural considerations can provide an additional explanation for the observed selective orientation. Re-crystallization process during the successive deposits can favor a *c*-oriented, (006) planes possessing one of the fastest growth rate of the LN structure[6]. The complexity of the phenomena results form the close interplay between these different scenarios.

3.2. Polarization effects

The degree of polarization is known to be determined by both crystal orientation and degree of texturation along a same direction. Un-polarized films with non-polar <011>-preferential orientation exhibit poor ferroelectric capabilities. On the contrary, the higher the degree of orientation along the *c*-polar direction, the higher the remanent polarization P_r (Fig. 3). Moreover, increasing the number of interfaces in 4-layer systems leads to a further intensity enhancement of P_r, evidencing once again the important role played by space-charge induced built-in-field effect. The recorded macroscopic polarization in multi-layered materials is certainly the result of a collective effect combining natural polarization and what may be called "migratory" polarization[7]. One can assume the inclusion of a contribution to polarization arising from the transfer of charges across the successive interfaces in addition to its internal self-polarization resulting from the *c*-preferred orientation[8,9]. The charged defects accumulated at the interfaces – real capacitive phases in parallel to the ferroelectric capacitor - may create a local electric field under the externally applied potential, thus generating a cooperative movement (Fig. 4). The result is an enhancement of the overall macroscopic P_r-E characteristics and an elongation of the hysteresis loops to show higher P_r. The fact that the value of the coercitive field is almost identical in 2-step and 4-step *c*-oriented layers tends to validate such a scheme. Localized charges create local electric fields which stimulate the occurrence of self-oriented micro-clusters at the layer boundaries with local polarization.

4. Conclusions

The multi-layer process is one of the effective approaches to enhance both the selective orientation and macroscopic polarization of ferroelectric heterostructures. Highly *c*-oriented 4-layered LN films could be sputtered onto ITO/Si, that exhibit P_r as high as 40 µC.cm^{-2}. However, the complexity of phenomena in such systems is provided by the interplay between bulk ferroelectric polarization, domain motion and space-charge effects at the interfaces. Careful investigation of the mechanisms of formation of the built-in electric field(s) in such stacked layers appears of primary importance in understanding their macroscopic ferroelectric properties and, ultimately, commenting on both the technical challenges of such multi-layer approaches and the technological reliability of as-deposited systems.

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Table 1 Deposition conditions of r.f. sputtered $LiNbO_3$ thin films

Figure 1 X-ray diffraction patterns of $LiNbO_3$ thin films sputtered onto ITO-covered <111>-Si substrates and annealed in air at 750°C for 1h **(a)** 1h/600°C + 5h/600°C **(c)** four steps, 3*1h30/300°C + 1*1h30/600°C The relative intensity of LN (006) peak increases for multi-layered structures. Parasitic phases can be suppressed in as-deposited composite systems.
❍→LN; ▼→ITO; ▲→<111>-Si; ✳→parasitic phase

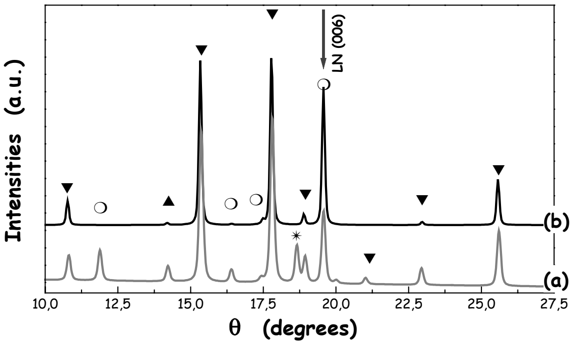
Figure 2 X-ray diffraction patterns of two-step (1h+5h) deposited $LiNbO_3$ thin films sputtered onto ITO-covered <111>-Si substrates and annealed in air at 750°C for 1h **(a)** 1h/600°C + 5h/600°C **(b)** 1h/300°C + 5h/300°C(3h)+600°C(2h). Variations of plasma properties during sputtering, induced by changes of substrate temperature during deposition, can shift the preferential orientation from (h00) to (hh0).
❍→LN; ▼→ITO; ▲→<111>-Si; ✳→parasitic phase

Figure 3 Hysteresis loops versus film orientation and deposition procedure of $LiNbO_3$ thin films sputtered onto ITO-covered <111>-Si. Films of Figures 1 and 2.
Applied field (E_a): 120 kV.mm^{-1}; 100Hz

Figure 4 Schematic representation of a 4-layered LN film deposited onto ITO-covered <111>-Si.

Table 1 Deposition conditions of r.f. sputtered $LiNbO_3$ thin films

Target	Li-enriched ceramic (Li:Nb=1.4)
$d_{\text{substrate-target}}$	45 mm
Input Power	100 W (↔ 6.2 W.cm^{-2})
Pressure	60 mTorr
Oxygen content	60%
Time	Total: 6h
Annealing	750°C / 1h in air



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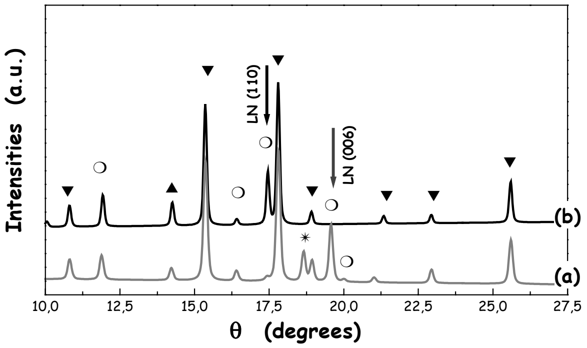

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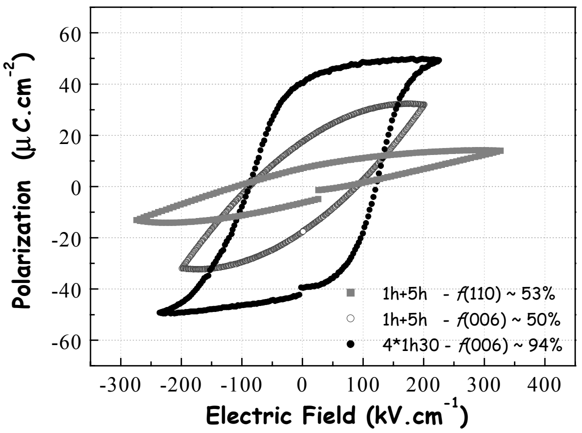

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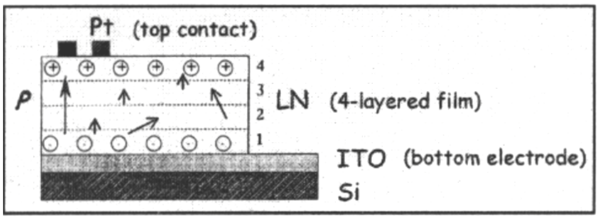

Figure 4 Schematic representation of a 4-layered LN film deposited onto ITO-covered <111>-Si.