



Temperature dependence of oriented growth of $\text{Pb}[\text{Yb}_{1/2}\text{Nb}_{1/2}]\text{O}_3\text{--PbTiO}_3$ thin films deposited on LNO/Si substrates

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ABSTRACT

$(1-x)\text{Pb}[\text{Yb}_{1/2}\text{Nb}_{1/2}]\text{O}_3\text{--}x\text{PbTiO}_3$ (PYbN–PT, $x=0.5$) (001) oriented thin films were deposited onto LaNiO_3 (LNO)/Si (001) substrates by sol–gel processing. The crystallographic texture of the films was controlled by the annealing temperature and heating rate. Highly (001) oriented LNO thin films were prepared by a simple metal organic decomposition technique, and the samples were annealed at 700 °C and 750 °C using a rapid thermal annealing process and furnace, respectively. X-ray diffraction analysis revealed that the films of PYbN–PT were highly (001) oriented along LNO/Si substrates. The degree of PYbN–PT orientation is dependent on the heating rate and annealing temperature. Annealing heating rate of 10 °C/s and high annealing temperature near 750 °C produce the greatest degree of (001) orientation, which gives rise to improved dielectric properties.

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1. Introduction

Piezoelectric thin films have attracted much attention in the past several years due to their possible applications in a wide range of microelectromechanical systems (MEMS), including high frequency ultrasonic transducers, accelerometers, pumps, and motors [1–3]. $\text{Pb}(\text{Zr}_{1-x}\text{Ti}_x\text{O}_3)$ (PZT) films at the morphotropic phase boundary have been chosen for many of these applications due to the high available piezoelectric response [1]. As noted in these studies, improved the temperature stability and enhanced piezoelectric properties of thin films are still needed for lower voltage piezoelectrically-driven MEMS devices. Recently, very large piezoelectric responses have been reported in single crystal solid solutions in the relaxor ferroelectric– PbTiO_3 family, such as $(1-x)\text{Pb}[\text{Mg}_{1/3}\text{Nb}_{2/3}]\text{O}_3\text{--}x\text{PbTiO}_3$ (PMN–PT) and $(1-x)\text{Pb}[\text{Zn}_{1/3}\text{Nb}_{2/3}]\text{O}_3\text{--}x\text{PbTiO}_3$ (PZN–PT) [4–7]. In rhombohedral crystals of PZN–PT, Park and Shrout reported that a d_{33} piezoelectric coefficient as high as 2600 pC/N can be obtained along the pseudocubic (001) single planes [8]. For this orientation, no driving force exists for non-180° domain wall motion, consequently, the response should be largely intrinsic. Maria et al. have also reported d_{33} piezoelectric coefficients of PMN–PT thin films having values as high as ~ 180 pC/N [9]; these were obtained in (001) epitaxial films on $\text{SrRuO}_3/(001)\text{LaAlO}_3$ substrates. Similarly, Bai et al. report e_{31f} values up to ~ 25 C/m² in thick PMN–PT films [5]. However, PMN–PT single crystals near the morphotropic phase boundary (MPB) composition exhibit a low Curie temperature (T_c) < 160 °C which may limit their implementation. Thus, there is an interest in exploring materials with good piezoelectric properties and higher Curie temperatures

(>300 °C) [10–12]. Bornand et al. and Yoshimura et al. grew $(1-x)\text{Pb}[\text{Yb}_{1/2}\text{Nb}_{1/2}]\text{O}_3\text{--}x\text{PbTiO}_3$ (PYbN–PT) (111) and (001) epitaxial films by pulsed laser deposition (PLD) and characterized their structure and electrical properties [13,14]. Effective transverse piezoelectric coefficients (e_{31f}) of ~ 14 and ~ 19 C/m² were reported for 1 and 3 μm thick (001) epitaxial films, respectively. Of the known relaxor ferroelectric– PbTiO_3 solid solutions, PYbN–PT has the highest transition temperature (~ 360 °C) at the MPB composition ($x=0.5$) [15]. A chemical solution deposition process for (111) and (001) oriented films on Pt/Si substrate were recently reported [17]. It was observed that (001) oriented thin films have better piezoelectric properties (e_{31f} coefficients of ~ 8.2 C/m²) than (111) oriented PYbN–PT thin films (e_{31f} coefficients of ~ 4.8 C/m²). In our previous work, using (001) oriented LaNiO_3 (LNO) oxide thin films [18], which are structurally compatible with ferroelectric thin films as bottom electrodes, to grow (001) PYbN–PT thin films would be an effective way to enhance ferroelectric properties and to match the acoustic impedance of thin films.

In this work, the growth of (001) oriented 0.5PYbN–0.5PT thin films deposited onto (001) LNO/Si substrate by sol–gel processing is reported. The orientation and textures of the films are monitored as a function of heating rate and annealing temperature. The degree of orientation is estimated by Lotgering's method, and the dielectric properties of the films are examined.

2. Experimental processing

LNO thin films were deposited on the silicon substrate by metal organic decomposition technique (see Fig. 1). In this process, lanthanum nitrate $\text{La}(\text{NO}_3)_3$ and nickel acetate $\text{Ni}(\text{Ac})_2$ were used as starting materials, and acetic acid (HAc) plus water were used as the solvents. Nickel

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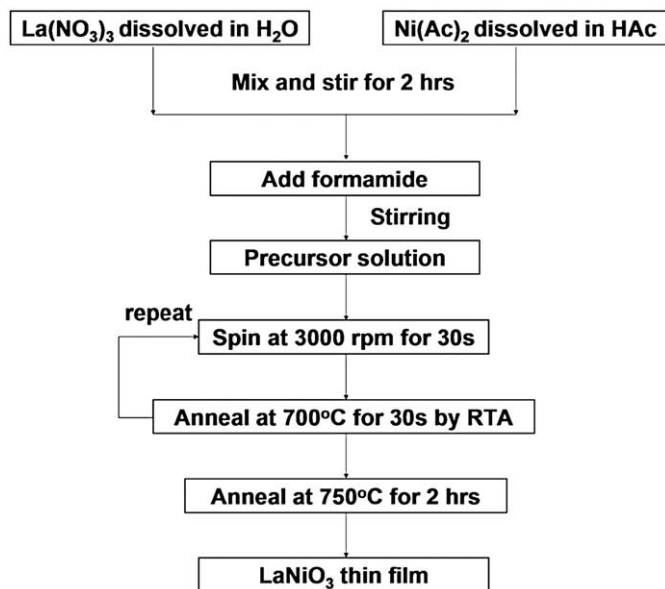


Fig. 1. Flow chart showing the processing of LNO precursor solution.

acetate was initially dissolved in acetic acid at room temperature. Then, the appropriate quantity of lanthanum nitrate was dissolved in water. The solutions above were mixed under constant stirring at 45 °C. A 5% (wt) formamide was added into the solution for stabilization. The concentration of the solution was adjusted to 0.30 M for the preparation uniform films. The solutions were spin-coated on a Si (001) substrate that had been cleaned with hydrofluoric acid and de-ionized water and then spun at 3000 rpm for 30 s using a photoresist spinner. After deposition, each layer was annealed at 300 °C for 2 min to drive out the solvent and decompose organic compounds, and annealed at 700 °C for 60 s using rapid thermal annealing (RTA). This procedure was repeated to achieve the desired thickness of about 300 nm. Finally, the LNO film was furnace-fired at 750 °C for 2 h to enhance conductivity.

The precursor solutions of PYbN-PT films were synthesized using lead acetate trihydrate, $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot 3\text{H}_2\text{O}$, ytterbium isopropoxide, $\text{Yb}(\text{OC}_3\text{H}_7)_3$, niobium ethoxide, $\text{Nb}(\text{OC}_2\text{H}_5)_5$, and titanium isopropoxide $\text{Ti}(\text{OC}_3\text{H}_7)_4$. 2-methoxyethanol (2-MOE) was used as the solvent. Firstly, Yb-isopropoxide and Nb ethoxide were dissolved in 2-MOE and refluxed at 120 °C for 3 h under a dry argon atmosphere. Then the solution was cooled to 80 °C. A stoichiometric amount of Ti-isopropoxide was added slowly to the solution while stirring, and the mixture was refluxed at 120 °C for 4 h under a dry argon atmosphere. The Yb–Nb–Ti complex solution was then cooled to room temperature. In the meantime, Pb-acetate trihydrate (20 mol% in excess of stoichiometry) was dissolved in 2-MOE, and dehydrated at 115 °C with stirring under vacuum. This was mixed with the above complex solution and refluxed at 120 °C for 4 h under an argon atmosphere. Following the refluxing step, the solution was vacuum distilled at 120 °C. 2-MOE was added to achieve a final PYbN-PT complex solution concentration of 0.40 M. PYbN-PT films were deposited onto LNO/Si(001) substrate. The solution was deposited onto the substrate by spin coating at 3000 rpm for 30 s. The substrate was then placed on a hot plate at 250 °C to 350 °C to evaporate the solvent and pyrolyze organics. A 1 min rapid thermal anneal (RTA) at the desired temperature with different annealing rates was performed to crystallize the layer. The process was repeated to achieve the desired thickness up to 2.5 μm .

The crystalline structure of the thin films was examined by a Rigaku X-ray diffractometer using $\text{Cu-K}\alpha$ radiation with monochromatic source. The X-ray diffraction (XRD) patterns were recorded in the 2θ range of 20°–60°. Film thicknesses were measured using a surface profiler (Tencor Instruments), and their morphology was observed using a scanning electron microscope (SEM) (Hitachi, S-3500N, Tokyo,

Japan) operated at 15 kV. To characterize the electrical properties of the films, 0.6–1.0 mm-diameter circular Au top electrodes were sputtered onto the film through a shadow mask. The dielectric permittivity was measured using an impedance analyzer (HP4192A, Hewlett-Packard) with oscillation amplitude of 30 mV.

3. Results and discussion

LNO is a very attractive candidate for electrodes in integrated ferroelectric MEMS devices with silicon semiconductor technology. The pseudocubic lattice parameter is 0.384 nm, and a match with most ferroelectric perovskites would be expected. Fig. 2 shows the XRD pattern of the LNO thin films deposited on Si (001) substrate annealed at 750 °C for 2 h. High intensity peaks at (001) and (002) orientation were observed, and a small (110) peak and broad peak of Si substrate also appeared (see Fig. 2). No other peaks were observed, which indicates the LNO layer does not react with silicon substrate after it is sintered at 750 °C. The degree of (001) orientation, F , was estimated using the Lotgering's method [18],

$$F = (P - P_0) / (1 - P_0) \quad (1)$$

where $P = I(h00)/I(hkl)$ and $P_0 = I_0(h00)/I_0(hkl)$ and I is the sum of the XRD peak intensities for the thin films, and I_0 is the sum of peak intensities in the powder diffraction pattern. Diffraction peaks between $2\theta = 20^\circ$ and 60° were used for the calculation. All the results were expressed in the pseudocubic notation for Miller indices. Using Eq. (1), Fig. 2 and a reference XRD of LNO powder [19], the degrees (F) of (001) orientation of the LNO film is about 85%. The result indicates that LNO thin films has a highly (001) orientation.

Fig. 3 (a) shows the XRD patterns of 0.5 μm -thick PYbN-PT thin films deposited onto (001) LNO/Si substrates annealed at 750 °C for 60 s with heating rate of 10 °C/s. The main peaks of XRD, excepting one peak due to the substrate, were indexed on the basis of PYbN-PT and LNO perovskite peaks. It shows that the PYbN-PT films has a highly (001) orientation along LNO/Si substrate. Using Eq. (1), data of Fig. 3(a) and a reference XRD of PYbN-PT powder [13], the degrees (F) of the (001) orientation parameter of PYbN-PT films is found to be about 93%. The orientation degree (F) of the films is much better than that of (001) PYbN-PT thin films deposited onto Pt/Ti/SiO₂/Si substrate (55%) [16]. Fig. 3 (b) and (c) show the XRD patterns of the films using different heating rates such as 50 °C/s and 100 °C/s. It can be seen from Fig. 3(a)–(c) that the degree of (001) orientation in the PYbN-PT films decreases with higher heating rates. The degrees (F) of (001) orientation of these films are about 90% and 65%, when the heating rates are

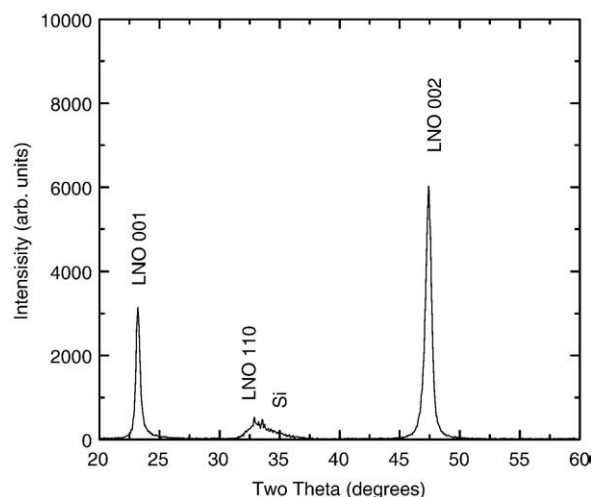


Fig. 2. XRD patterns for the LNO thin films deposited on a Si substrate and annealed at 750 °C for 2 h.

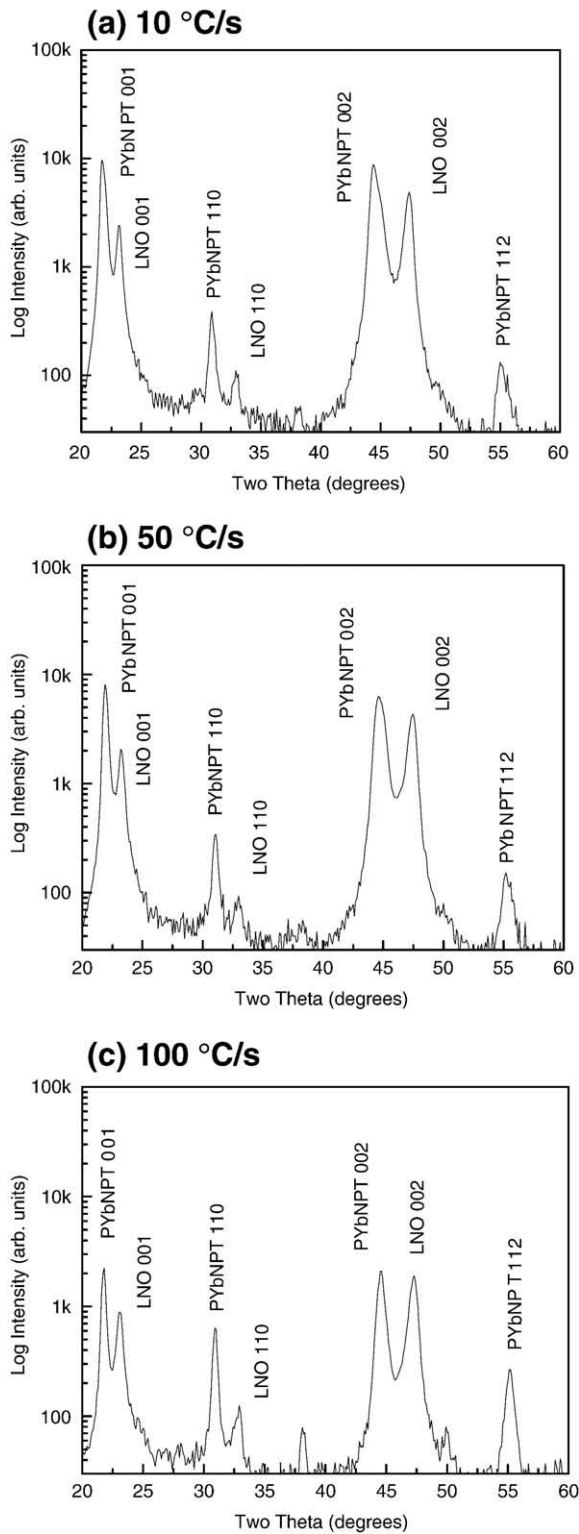


Fig. 3. XRD patterns of 0.5 μm -thick PYbN-PT thin films deposited onto (001) LNO/Si substrates and annealed at 750 $^{\circ}\text{C}$ as a function of heating rate: (a) 10 $^{\circ}\text{C/s}$, (b) 50 $^{\circ}\text{C/s}$ and (c) 100 $^{\circ}\text{C/s}$. Starred peaks come from substrate.

50 and 100 $^{\circ}\text{C/s}$, respectively. Results from Fig. 3(a–c) show that the annealing rates affect evidently the orientation of thin films.

Fig. 4 shows the XRD patterns of 200 nm-thick thin films deposited onto (001)LNO/Si substrates and annealed at a heating rate of 10 $^{\circ}\text{C/s}$ at 650, 700 and 750 $^{\circ}\text{C}$, respectively. It is seen that the films are crystallized with (001) orientation by 650 $^{\circ}\text{C}$ (see Fig. 4(a)), and that

the intensity of the PYbN-PT (001) peak increases significantly with increasing temperature (see Fig. 4 (b) and (c)) because of better crystallization. There is no strong correlation between the degree of orientation and the crystallization temperature, the degree of (001) orientation being about 75% for all samples. Comparing Figs. 3(a) and 4(c) for films of different thickness annealed at same condition, it

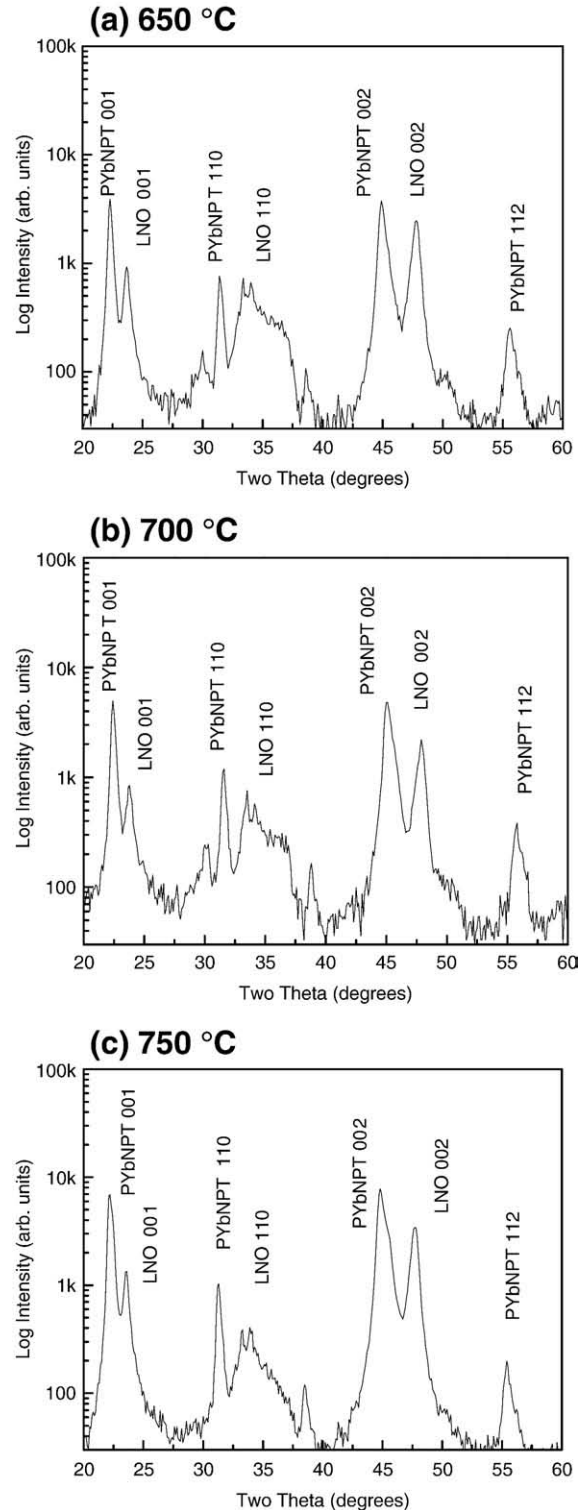


Fig. 4. XRD patterns of 0.2 μm PYbN-PT thin films deposited onto (001) LNO/Si substrates as a function of heating temperature (heating rate is 10 $^{\circ}\text{C/s}$): (a) 650 $^{\circ}\text{C}$, (b) 700 $^{\circ}\text{C}$ and (c) 750 $^{\circ}\text{C}$. Peak identified with a “*” may come from pyrochlore phase.

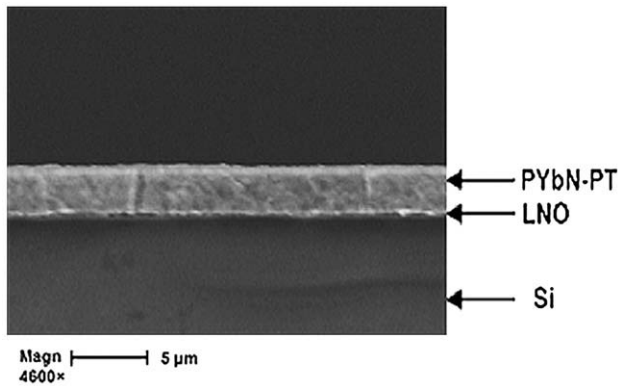


Fig. 5. SEM cross-sectional photographs of the PYbN-PT film on LNO/Si substrate (heating rate is 10 °C/s).

appears that the degree of orientation along (001) increases from 75% to 93% when the thickness increases from 200 to 500 nm, respectively. It is suggested that the heating rates below 10 °C/s promote nucleation at the surface [20].

Fig. 5 presents the SEM cross-sectional micrograph of a 2.5-μm thick PYbN-PT film on LNO/Si substrate (heating rate was 10 °C/s) annealed at 750 °C. Fig. 6 shows that the relative dielectric constant (ϵ_r) of the 0.5-μm-thick PYbN-PT thin films annealed at 750 °C for 60 s with annealing rate of 10 °C/s. The values of ϵ_r and $\tan \delta$ of the film at 1 kHz are 1050 and 0.032, respectively. The value of ϵ_r for this film is larger than that of corresponding values (~900) for PLD-derived (001) PYbN-PT films [14]. Results show that the sol-gel derived (001) oriented PYbN-PT thin films above on LNO/Si substrate exhibit better electrical properties.

4. Conclusion

In this study, (001) oriented LNO thin films on Si substrate were obtained by the MOD technique. It was found that LNO films annealed at 750 °C exhibit good conductivity at room temperature, and can be used as both bottom electrode and buffer layer to inhibit the reaction between thin film and Si substrate for device application. The degree of (001) orientation of 0.5PYbN–0.5PT thin films grown by the sol-gel process on LNO-coated (001) silicon substrates was determined as a function of annealing heating rate and temperature. For sample annealed at 750 °C, the XRD patterns revealed that the highest oriented PYbN-PT (001) films (93%) are obtained using low heating rates (10 °C/s). The degree of orientation of the films also increased with increasing film thickness. The relative dielectric permittivity and dielectric loss of thin films annealed at 750 °C at 1 kHz were 1050 and 0.032, respectively. The (001) oriented films exhibit good electrical properties. Because of their good electrical properties and higher Curie temperature, highly oriented

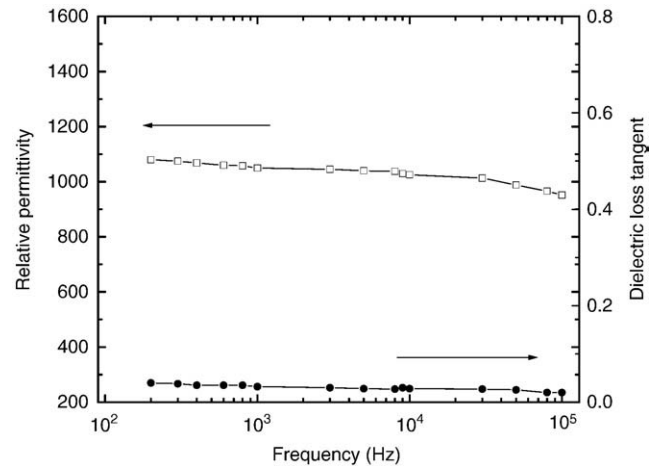


Fig. 6. Frequency dependence of dielectric permittivity and loss of (001) PYbN-PT thin films on LNO/Si substrate annealed at 750 °C.

(001) PYbN-PT thin films have a potential application in the fabrication of high frequency MEMS ultrasound transducers.

Acknowledgments

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