

Structure and piezoelectric properties of sol-gel-derived 0.5 Pb[Yb_{1/2}Nb_{1/2}]O₃-0.5 PbTiO₃ thin films

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0.5 Pb[Yb_{1/2}Nb_{1/2}]O₃-0.5 PbTiO₃ thin films were deposited on (111) Pt/Ti/SiO₂/Si substrates by sol-gel processing using a thin Pb(Zr_{0.52}Ti_{0.48})O₃ seed layer. X-ray diffraction analysis and scanning electron microscopy revealed that the films were strongly (111) oriented, mimicking the orientation of the (111) Pt/Ti/SiO₂/Si substrate. No pyrochlore phase was observed by x-ray diffraction and the films had a uniform grain size of about 50–60 nm. The dielectric permittivity and loss factor varied only slightly with frequency in the range of 100–10 000 Hz. At 1 kHz, the dielectric permittivity was 1025 and dielectric loss was 0.028. The films exhibited good ferroelectric and piezoelectric properties. The remanent polarization (P_r) was 30 $\mu\text{C}/\text{cm}^2$. The effective transverse piezoelectric $e_{31,f}$ coefficient ($-4.8 \text{ C}/\text{m}^2$) of the films was measured using a modified wafer flexure method. © 2002 American Institute of Physics. [DOI: 10.1063/1.1472476]

Piezoelectric thin films such as PbZr_{1-x}Ti_xO₃ (PZT) are highly attractive for microelectromechanical systems (MEMS) device applications^{1,2} and there has been a growing interest in the development of new materials with better piezoelectric properties. Since Park *et al.*³ and Yamashita *et al.*⁴ reported that single-crystal relaxor ferroelectric-PbTiO₃ solid solutions such as (1-x)Pb[Mg_{1/3}Nb_{2/3}]O₃-xPbTiO₃ (PMN-PT) and (1-x)Pb[Zn_{1/3}Nb_{2/3}]O₃-xPbTiO₃ exhibited very large piezoelectric coefficients, many epitaxial relaxor ferroelectric films have been investigated.⁵⁻⁸ For example, Maria *et al.*⁹ reported epitaxial PMN-PT films with d_{31} coefficients as high as $-180 \text{ pC}/\text{N}$, which are larger than those of PZT. Bornand *et al.*¹⁰ and Yoshimura *et al.*¹¹ fabricated (1-x)Pb[Yb_{1/2}Nb_{1/2}]O₃-xPbTiO₃ (PYbN-PT) (111) and (001) epitaxial films by pulsed laser deposition and characterized their structure and electrical properties. Good piezoelectric properties were reported for these films. Of the known relaxor ferroelectric-PbTiO₃ solid solutions, PYbN-PT has the highest transition temperature ($\sim 360^\circ\text{C}$) at the morphotropic phase boundary composition ($x=0.5$).¹² This should improve the temperature stability of piezoelectrically driven MEMS devices fabricated with relaxor-PT solid solutions.

It is known that sol-gel processing produces high quality and large area thin films and these characteristics make them desirable for MEMS device applications. There have been no inadequate reports in the literature on the fabrication of PYbN-PT films by sol-gel processing. In this letter, the fabrication of (111)-oriented 0.5 PYbN-0.5 PT thin films by sol-gel processing is reported and their structure and ferroelectric and piezoelectric properties are described.

The precursor solutions were synthesized using lead ac-

etate trihydrate, ytterbium isopropoxide, niobium ethoxide, and titanium isopropoxide. 2-methoxyethanol (2-MOE) was used as the solvent. First, ytterbium isopropoxide and niobium ethoxide were mixed in 2-MOE and refluxed at 120 °C for 3 h under a dry Ar atmosphere. The solution was cooled to 90 °C and a stoichiometric amount of titanium isopropoxide was slowly added to the solution while stirring. The mixture was then refluxed at 120 °C for 5 h and the resulting Yb-Nb-Ti complex solution was cooled to room temperature. In the meantime, lead acetate trihydrate (20 mol % in excess of stoichiometry) was dissolved in 2-MOE, and dehydrated at 125 °C. This was mixed with the Yb-Nb-Ti complex solution and refluxed at 120 °C for 5 h in an Ar atmosphere. Following the refluxing step, the solution was vacuum distilled at 120 °C. Finally, 3 ml acetic acid was added during refluxing in order to control the viscosity of the solution. 2-MOE was added to achieve a final PYbN-PT complex solution concentration of 0.45 M.

In this work, PYbN-PT films were deposited on (111)Pt/Ti/SiO₂/Si substrates. Solutions were filtered through a 0.2 μm filter and deposited onto the substrate by spin coating at 3000 rpm for 30 s. A thin layer (50 nm) of Pb(Zr_{0.52}Ti_{0.48})O₃ annealed at 700 °C was first deposited onto the substrate as a seed layer. The wafer was then placed on a hot plate at 200 °C to evaporate the solvent. A rapid thermal anneal at 750 °C for 1 min was performed to crystallize the layer. The process was repeated to achieve the desired thickness.

The crystalline structure of the thin films was examined using a Scintag x-ray diffractometer with Ni filtered Cu $K\alpha$ radiation. The x-ray diffraction (XRD) patterns were recorded at a rate of 1°/min in the 2θ range of 20°–60°. Film thicknesses were measured using a surface profiler (Tencor Instruments). The morphology of the films was observed using a scanning electron microscope [(SEM) Hitachi, S-3500N]. To characterize the electrical properties, 0.5 mm-

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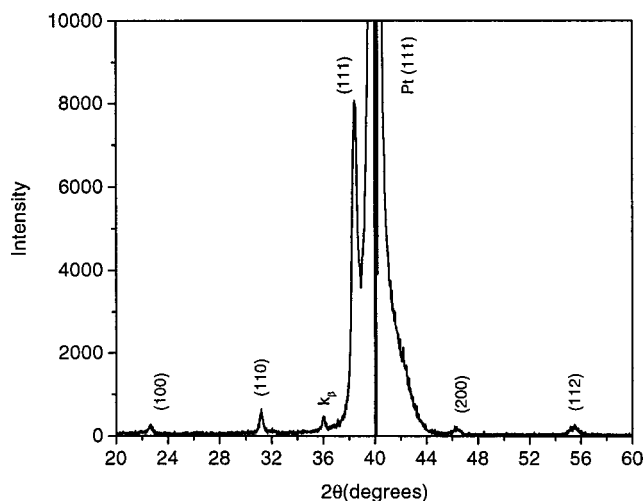


FIG. 1. XRD pattern of a 0.5 μm -thick 0.5 PYbN-0.5 PT thin film deposited on PZT/(111)Pt/Ti/SiO₂/Si.

diameter circular Pt top electrodes were sputtered on the surface of film through a shadow mask. The dielectric permittivity was measured using an impedance analyzer (HP4192A, Hewlett-Packard) with an oscillation amplitude of 30 mV. The high field hysteresis properties were characterized using a RT66A (Radiant Technology, Albuquerque, NM) ferroelectric test system. The effective transverse piezoelectric ($e_{31,f}$) coefficients of the films were characterized using a modification of the wafer flexure method described previously.^{13,14}

Figure 1 shows the XRD pattern of a 0.5 μm -thick 0.5 PYbN-0.5 PT thin film deposited on a (111) Pt substrate with a thin PZT seed layer, and crystallized at 750 °C for 60 s. All peaks are indexed on the basis of the pseudocubic perovskite cell. It can be seen that PYbN-PT thin films were crystallized into the perovskite phase with a pronounced (111)-preferred orientation and there was no detectable pyrochlore phase. Bornand¹⁰ found that avoiding the appearance of pyrochlore phases is very difficult in pulsed-laser deposition (PLD)-deposited PYbN-PT films because the nucleation energies of the pyrochlore and perovskite phases are very close during crystallization of PYbN-PT thin films. This high nucleation energy barrier can be reduced using seed or buffer layers with good lattice constant and structure matches. Park *et al.*⁶ reported that using a PT seeding layer reduced the nucleation temperature of PMN-PT films and adjusted their texture development. In our experiments, a thin PZT buffer layer produced highly (111)-oriented PYbN-PT thin films.

A SEM micrograph of the film surface is shown in Fig. 2. It is seen that the PYbN-PT films are dense and crack free, and that the grain size of the films is uniform (about 50–60 nm).

The dielectric permittivity, ϵ_r , and the dielectric loss tangent, $\tan \delta$, were evaluated using an HP4192A impedance analyzer. ϵ_r and $\tan \delta$ versus frequency are shown in Fig. 3. It can be seen that ϵ_r and $\tan \delta$ vary slightly with frequency from 100 to 10 000 Hz. The values of ϵ_r and $\tan \delta$ of the film at 1 kHz are 1025 and 0.028, respectively. The value of ϵ_r for this film was lower than the corresponding values (~ 1300) for PLD derived (111) PYbN-PT films.¹¹ This

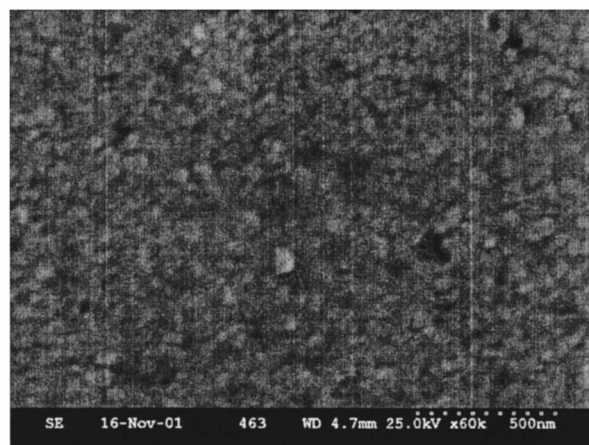


FIG. 2. SEM micrograph of the surface of a (111)-oriented 0.5 PYbN-0.5 PT thin film.

might be due to the smaller grain size and a different film thickness.

The high field hysteresis behavior of PYbN-PT films at room temperature was measured using a RT66A ferroelectric test system. Figure 4 shows a polarization hysteresis ($P-E$) loop of a (111)-oriented PYbN-PT thin film. The loop exhibits better symmetry than PLD-deposited films.^{10,11} It can be seen that the remanent polarization (P_r) and coercive field (E_c) are 30 $\mu\text{C}/\text{cm}^2$ and 68 kV/cm, respectively. The maximum polarization (P_{max}) is over 70 $\mu\text{C}/\text{cm}^2$. These high values are consistent with the high transition temperature in this compound.¹²

As the film is clamped to the substrate, a modified wafer flexure method was used to measure the effective transverse piezoelectric coefficient, $e_{31,f}$, of the film.¹³ $e_{31,f}$ = charge/strain, was calculated from the measured data. A small piece of sample was glued on a 3 in.-silicon wafer and suspended over a cylindrical cavity. By controlling the air pressure in the cavity using the output of an audio speaker (which provided a reference signal of 0.5 V_{rms} at 4 Hz), a periodic strain in the film produces current. A lock-in amplifier was used to detect this current. KFG-IN-120-C1-11L3M3R prewired strain gages (Omega Engineering, Inc.,

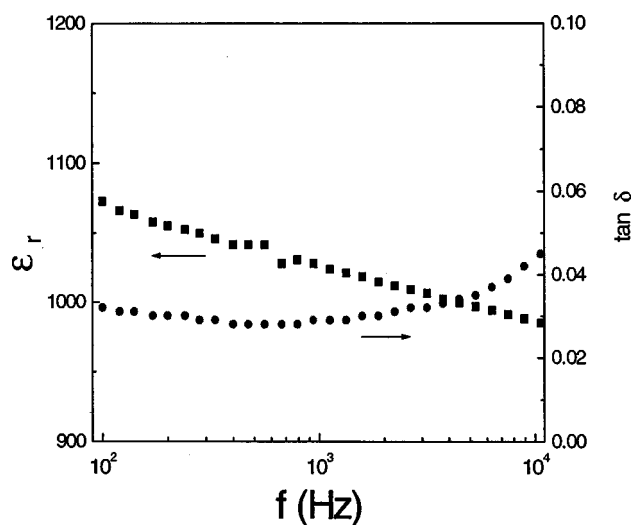


FIG. 3. Frequency dependence of the dielectric permittivity and loss of a (111)-oriented 0.5 PYbN-0.5 PT thin film.

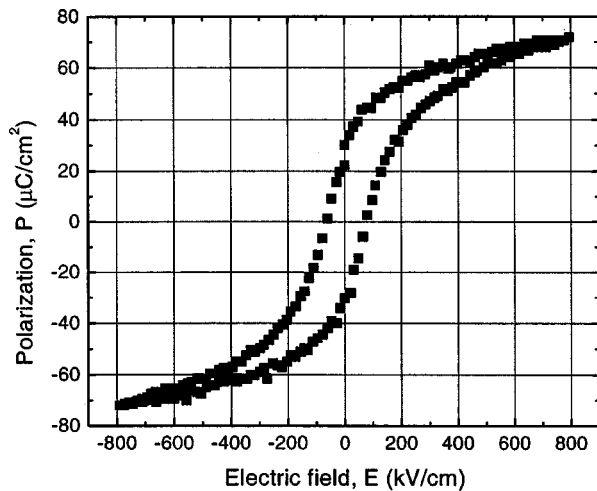


FIG. 4. Polarization–electric field hysteresis loop of a (111)-oriented 0.5 PYbN–0.5 PT thin film.

Stamford, CT) were used to measure the strain produced in the film. Prior to the measurement, films were poled for 15 min at room temperature. Figure 5 shows the variation of the $e_{31,f}$ coefficient as a function of the poling electric field. It is

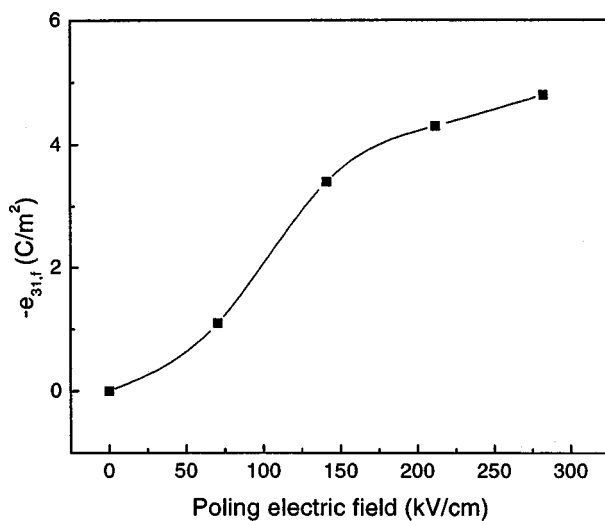


FIG. 5. $e_{31,f}$ coefficient of a (111)-oriented 0.5 PYbN–0.5 PT thin film as function of poling electric field.

seen that $e_{31,f}$ increases with increasing poling field and the maximum $e_{31,f}$ value of -4.8 C/m^2 was obtained with a poling field of 280 kV/cm at room temperature. This $e_{31,f}$ value is larger than PLD-deposited (111) epitaxial PYbN–PT films ($-2.5\text{--}3.3 \text{ C/m}^2$).¹¹ The higher value may result from the incomplete (111) texturing, differences in the grain size, or film stress state.

In summary, pure perovskite phase (111)-oriented 0.5 PYbN–0.5 PT thin films have been prepared by sol–gel processing. The films are dense and crack free with a large dielectric permittivity ($\epsilon_r \sim 1025$) and low dielectric loss ($\tan \delta < 3\%$). The films also exhibit good ferroelectric and piezoelectric properties. The remanent polarization P_r ($=30 \mu\text{C/cm}^2$) and piezoelectric $e_{31(\text{eff})}$ coefficient (-4.8 C/m^2) are large. Results suggest that sol–gel derived PYbN–PT thin films have potential application in MEMS devices. Further, fabrication of sol–gel derived (100)-oriented PYbN–PT thin films is in progress, and these are expected to exhibit even better piezoelectric properties.¹⁵

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