Field-induced dielectric properties of laser ablated antiferroelectric $(Pb_{0.99}Nb_{0.02})(Zr_{0.57}Sn_{0.38}Ti_{0.05})_{0.98}O_3$ thin films

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Niobium-modified lead zirconate stannate titanate antiferroelectric thin films with the chemical composition of $(Pb_{0.99}Nb_{0.02})(Zr_{0.57}Sn_{0.38}Ti_{0.05})_{0.98}O_3$ were deposited by pulsed excimer laser ablation technique on Pt-coated Si substrates. Field-induced phase transition from antiferroelectric to ferroelectric properties was studied at different fields as a function of temperature. The field forced ferroelectric phase transition was elucidated by the presence of double-polarization hysteresis and double-butterfly characteristics from polarization versus applied electric field and capacitance and voltage measurements, respectively. The measured forward and reverse switching fields were 25 kV/cm and 77 kV/cm, respectively. The measured dielectric constant and dissipation factor were 540 and 0.001 at 100 kHz, respectively, at room temperature.

Field-induced ferroelectric phase switching in antiferroelectric Nb-modified lead zirconium stannate titanate materials was studied for transducer and high charge storage device applications by Berlincourt and Jaffe.[1,2] An antiferroelectric is characterized by rows of dipoles with the dipole moment of adjacent rows equal but antiparallel[3,4] and can be regarded as two interpenetrating sublattices of equal and opposite polarization with no net spontaneous polarization. The antiferroelectrics can be switched into ferroelectric phase by application of a suitable electric field due to the small free energy difference between the antiferroelectric and ferroelectric phases. The transition between antiferroelectric and ferroelectric phases can also occur spontaneously with temperature change, increase in electric field, or change in stress configuration. The electric field enforced antiferroelectric to ferroelectric phase transition may be used for conversion of electrical to mechanical energy by virtue of the geometrical change of the primitive unit cell. Since the transition occurs also with temperature change, thermoelectric and thermomechanical energy conversions are also possible. Removal of the applied external electric field, from field induced ferroelectric state reverses the antiferroelectric phase and during such a backward switching process, i.e., ferroelectric from antiferroelectric phase, all the stored polarization charge can be released in nanosecond order and hence these materials can be utilized for charge storage devices.[5,6] Ferroelectric phase transitions in perovskite oxides cause an expansion of specific volume. On the other hand, antiferroelectric crystals generally contract in volume at the phase transition, as explained by the electrostrictive phenomenology proposed by Uchino and co-workers.[7] Hence, the field-induced transition from an antiferroelectric to ferroelectric one is much larger than that associated with ferroelectric polarization reversal.

The electric field-induced ferroelectric phase switching was demonstrated first in $PbZrO_3$ by Shirane and co-workers,[8] in a narrow temperature region near the Curie point (~232 °C). Later Jaffe and co-workers found that the free energy could be minimized between polar and antipolar phases over a much wider temperature range by substantial substitution of Sn^{4+} and Ti^{4+} for Zr^{4+} in antiferroelectric compositions.[9] Most of the antiferroelectric crystalline materials would break down before switching this way, and hence thin films of these compositions are interesting for applications in microelectromechanical systems (MEMs), due to higher breakdown strengths. Preparation of antiferroelectric PZ thin films was reported earlier by many research groups with different processing techniques.[10,11] Deposition of antiferroelectric thin films compositions such as lead zirconate stannate titanate modified by La and Nb were reported earlier by Cross and co-workers, as well as Payne and co-workers, using chemical route sol–gel deposition technique.[12,13] Few reports of processing of Nb-modified lead zirconate stannate titanate antiferroelectric thin films exist in the literature *via* physical vapor deposition techniques. Pulsed excimer laser ablation is one of the most versatile techniques to deposit stoichiometric multicomponent oxide thin films with a wide range of operable parameters to control the microstructure of the thin films. In this study, processing of room temperature antiferroelectric thin films of $(Pb_{0.99}Nb_{0.02})(Zr_{0.57}Sn_{0.38}Ti_{0.05})_{0.98}O_3$ (denoted as PNZST in the rest of the article), by KrF excimer laser ablation technique, field induced ferroelectric phase switching, and dielectric studies are presented.

Dense ceramic targets of PNZST, prepared via conventional solid state reaction route, were used for the deposition of thin films on Pt- coated Si substrates. An excess of 10% PbO was taken in the ceramic target in order to prevent the Pb-losses in the films during laser ablation process. Thin film depositions were carried out in an ultrapure 100% oxygen environment with a partial pressure of 5–10 mTorr. Films of various thicknesses were deposited on the Pt- coated Si substrates at a substrate temperature of 300 °C. The rapid thermal annealing (RTA) procedure was adopted at temperatures between 650–725 °C keeping the annealing time for 60–90 s

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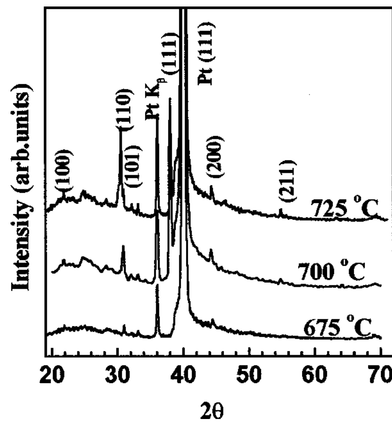

FIG. 1. X-ray diffraction patterns of the PNZST thin films as a function of RTA temperature.

using a quartz infrared image furnace (ULVAC SINKU-RINKU MILA 3000). The structures of the films were confirmed by an x-ray (Cu $K\alpha$ radiation) diffraction technique (Scintag) and a scanning electron microscopy (Cambridge) was utilized for microstructural analysis. Stoichiometric compositional analysis on the deposited films was carried out by energy disperse x-ray analysis to establish the required composition and its reproducibility. Circular gold electrodes with 600 nm diameter onto the films were deposited by an evaporation technique in order to study the electrical and dielectric properties of the films in metal–insulator–metal configuration. Field enforced ferroelectric phase switching in antiferroelectric PNZST thin films was studied with polarization versus field response using a Radiant Technologies Ferroelectric Test System (RT-66A). Capacitance versus voltage characterization was carried out to confirm the field force ferroelectric phase switching in these films using a combination of automated Keithley LCZ 3330 meter in conjunction with a Keithley source measure unit (Model: 236). The dielectric measurements were done in the frequency range of 0.1–100 kHz over a temperature range of 30–250 °C using an Keithley LCZ meter and a Keithley digital multimeter (Model: 2000).

As-grown films were found amorphous in nature and the crystallization with perovskite phase formation was observed

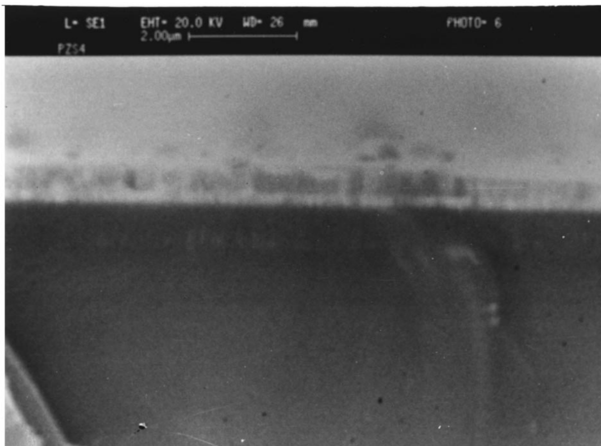

FIG. 2. SEM cross sectional view of PNZST thin film, deposited at 300 °C and annealed rapid thermally at 725 °C for 60 s. Films exhibited columnar fibrous grain structure.

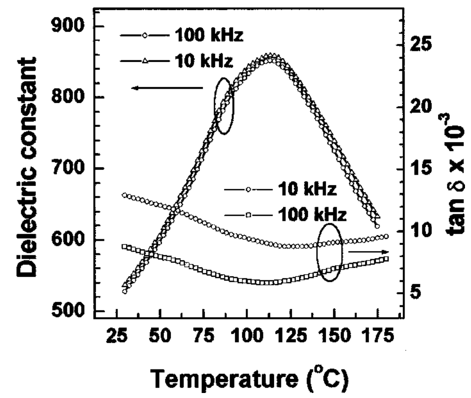

FIG. 3. Dielectric constant and dissipation factor as a function of temperature.

at and above 675 °C. Figure 1 shows the x-ray patterns of PNZST thin films deposited at 300 °C as a function of RTA temperature. At an annealing temperature of 675 °C for 60 s, films showed preferred orientation along (111) direction with a small intensity perovskite peak of (110). Increasing the annealing temperature gradually to 700 °C, films showed polycrystalline structure, and at an annealing temperature of 725 °C a tetragonal splitting in (110) perovskite peaks were exhibited along with the (111) peak, indicating the completion of the crystallization process. The films exhibited a columnar microstructure as was confirmed from the cross sectional analysis of scanning electron microscopy (SEM) studies, shown in the Fig. 2.

Frequency dependence of low field dielectric characterization of the films were done with an oscillating level of 50 mV, and the room temperature measured dielectric constant and the associated dissipation factor were 540 and 0.001 at 100 kHz frequency, respectively. Figure 3 shows the variation of the dielectric constant as a function of temperature over a range 25–200 °C during free cooling process. The dielectric constant exhibited a peak value around 123 °C followed by a gradual decrease and was in close agreement with the Curie temperature of PNZST films (150 °C) processed by sol–gel route.[14] The minor variation in the Curie temperature, between the former composition and present set of films, was anticipated due to the slight variation of Zr/Sn ratio and titanium contents present in the films.[1]

The field-enforced ferroelectric phase switching in antiferroelectric PNZST thin films at room temperature, showed

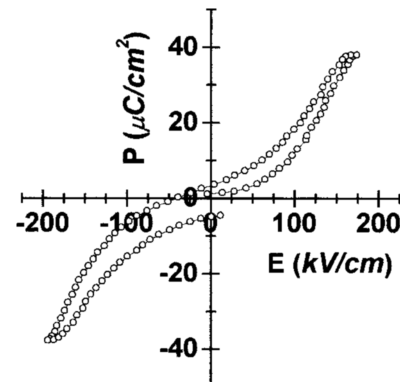

FIG. 4. Polarization hysteresis behavior in PNZST thin films. Thin films of this particular composition exhibited slanted double hysteresis loop.

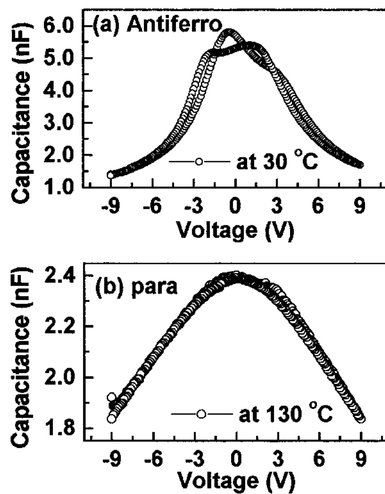

FIG. 5. $C-V$ characteristics of PNZST thin films at two different sample temperatures (a) 30 °C and (b) 130 °C.

a slanted double hysteresis loop with a maximum polarization of 36 μC/cm^2 with a zero remanence and is shown in the Fig. 4. Figures 5(a) and 5(b) show the $C-V$ characteristics of the PNZST thin films at room temperature and 130 °C. The forward and reverse switching field values of this particular composition were confirmed from $C-V$ analysis at room temperature. The measured forward and reverse switching fields were 25 kV/cm and 77.5 kV/cm, respectively. The presence of double-butterfly characteristics in the $C-V$ repose at room temperature confirmed, once again, the antiferroelectric nature of these thin films, whereas the inverted parabolic $C-V$ response was a confirmation of paraelectric nature beyond the phase transition temperature (123 °C). The slanted shape of the polarization hysteresis loop could make this particular composition for digital microactuator application which needs precise accuracy in positioning and quick response speeds. Whereas, Zr-rich compositions with square hysteresis loops, large maximum polarization, and high phase switching fields are promising candidates for high-energy storage devices such as charge decoupling capacitors in high-speed multichip modules. Efforts are underway in developing the Nb- modified lead zirconium stannate titanate thin films with various Zr/Sn ratios and will be reported elsewhere with the necessary electrical and structural characterization.

In conclusion, antiferroelectric PNZST thin films were deposited by an excimer laser ablation technique. The field-induced ferroelectric phase switching and dielectric properties were studied in these PNZST thin films which are very attractive for the development of MEMS.

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