Compositionally Modulated $Pb(Mg_{1/3}Nb_{2/3})O_3$-$PbTiO_3$ Relaxor Thin Films Deposited by Pulsed Excimer Laser Ablation Technique

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Abstract- Thin films of (1-x)$Pb(Mg_{1/3}Nb_{2/3})O_3$ – x$PbTiO_3$ (x = 0.1 to 0.3) (PMN-PT) were deposited on the platinum coated silicon substrate by pulsed excimer laser ablation technique. A template layer of $LaSr_{0.5}Co_{0.5}O_3$ (LSCO) was deposited on platinum substrate prior to the deposition of PMN-PT thin films. The composition and the structure of the films were modulated via proper variation of the deposition parameter such as substrate temperature, laser fluence and thickness of the template layers. We observed the impact of the thickness of LSCO template layer on the orientation of the films. A room temperature dielectric constant varying from 2000 to 4500 was noted for different composition of the films. The dielectric properties of the films were studied over the frequency range of 100 Hz - 100 kHz over a wide range of temperatures. The films exhibited the relaxor- type behavior that was characterized by the frequency dispersion of the temperature of dielectric constant maxima (T_m) and also diffuse phase transition.

INTRODUCTION

Modern age microelectronic and microelectromechanical (MEMS) devices require integration of high performance electrostrictive materials on to silicon-based devices in sub-micron form. Electrostriction is an electric field-induced strain proportional to the square of applied electric field, which is very small in magnitude. However, the discovery of giant electrostriction in $Pb(Mg_{1/3}Nb_{2/3})O_3$ (PMN) based ceramic has provoked a tremendous thrust on fundamental and applied research of these materials. $Pb(Mg_{1/3}Nb_{2/3})O_3$ and its solid solution with $PbTiO_3$ (PMN-PT) are the most well known relaxor ferroelectric materials, which exhibit very high dielectric constant, high electrostrictive coefficient and diffuse phase transition [1, 2]. These relaxor materials have recently received great attention for their potential application in thin film capacitors, which are being used in mechanical actuators, transducers and dynamic random access memories (DRAMs). Through a proper variation of the processing parameters such as substrate temperature, oxygen partial pressure and energy fluence of the laser beam during thin films deposition we were successfully able to produce 100 % pyrochlore free perovskite phase in PMN-PT thin films on commercially available platinum coated silicon substrate. This imparts knowledge regarding the process of phase formation on Pt substrates and the technical challenge to grow good quality PMN-PT thin films on the relatively cheaper Pt/Si substrates. The use of a thin $La_{0.5}Sr_{0.5}CoO_3$ (LSCO) template layer on Pt substrate has been found to have great impact on perovskite phase formation as well as the orientation of the films. PMN-PT thin films with different orientation were grown on same Pt substrate. The dielectric properties of the films were studied over the frequency range of 100 Hz - 100 kHz over a wide range of temperatures. The room temperature dielectric constant was varied from 6000 to 4000 with 10 to 30 atomic percentage of PT concentration in PMN thin films at a frequency of 1 kHz. The films exhibited the relaxor- type behavior, which was characterized by the frequency dispersion of the temperature (T_m) at which the dielectric constant (ε) exhibits maximum value and also diffuse phase transition. The films showed a gradual shift of relaxor behavior to normal ferroelectric with increase in PT content.

EXPERIMENTAL

A pulsed laser ablation technique has been used for the deposition of the $Pb(Mg_{1/3}Nb_{2/3})O_3$-$PbTiO_3$ (PMN-PT) thin films from highly stoichiometric crystalline targets. The ceramic targets were prepared using columbite process to obtain pure perovskite phase. A KrF pulsed-laser (wavelength 248nm) operating at a frequency of 8 Hz and 2.5 J/cm^2 energy fluence was incident on the rotating target. The deposition chamber was initially evacuated to a pressure of $1x10^{-5}$ Torr and then flushed with high purity oxygen to the required pressure in the range of 150-350 mTorr. The substrate temperature during deposition of PMN-PT thin films was varied from 600 °C to 700 °C to obtain the proper crystallization. The template layers of LSCO of thickness varying from 20 nm to 200 nm were grown on highly oriented Pt (111) substrate using pulsed laser ablation technique at 650 °C under 100 mTorr oxygen partial pressure. Subsequently the PMN-PT thin films were deposited under 200 mTorr

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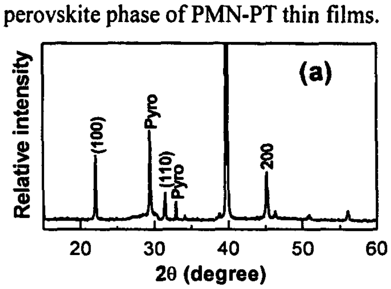
oxygen partial pressure (P_{O2}). The thickness PMN-PT thin film was 8000 A. The phase of the deposited film was checked using X-ray diffraction ($CuK_{\alpha} \sim 1.54$ Å) (Scintag diffractometer). Information regarding the composition of the films was obtained from energy dispersive x-ray analysis (EDX) using scanning electron microscopy, which was also used to obtain the microstructural informations. For electrical measurements Au dots of 1.96×10^{-3} cm^2 area were deposited on the top surface of the films through a shadow mask and thermal evaporation technique. The Pt substrate was used as the bottom electrode for measurements. A Keithley 3330 LCZ meter has been used for the measurement of dielectric constant and loss tangent as a function of frequency in the range of 100Hz to 100kHz at different temperatures. The polarization hysteresis behavior of ferroelectric PMN-PT thin film capacitors was measured using Radiant Technologies RT66A ferroelectric test system.

RESULTS AND DISCUSSION

Structure and composition

The formation of the perovskite phase together with the control on orientation of the PMN-PT thin films deposited on the same Pt/ Si substrates is the most important part in the present work. There are several advantages in using the Pt/Si wafers over single crystal oxide substrate for most ferroelectric materials. Platinized silicon substrates as obtained commercially are found to be mostly (111) oriented, leading to a very strong reflection of the substrate in the obtained X-ray diffraction patterns. The problems in perovskite phase formation of PMN-PT relaxor on Pt coated silicon substrate are not well understood. The lattice mismatch between PMN-PT layer of perovskite phase (3.98 Å) and Pt layer (4.029 Å) is 2.7% only. So, there is no clear reason, which can apparently affect the perovskite phase formation. According to Tantigate et. al.[3] the texture of substrate surface has an impact on perovskite phase formation of PMN-PT thin films. It has also been observed that the Pt substrate acts as a good nucleating agent for pyrochlore phase comparatively at lower temperature. To avoid these problems, a thin layer of LSCO was grown on Pt/Si substrate prior to the deposition of PMN-PT thin films. This resulted 100% pyrochlore free perovskite phase in the films grown at similar ambient conditions. Figure 1(a) and (b) show the impact of the LSCO template layer on perovskite phase of PMN-PT thin films.



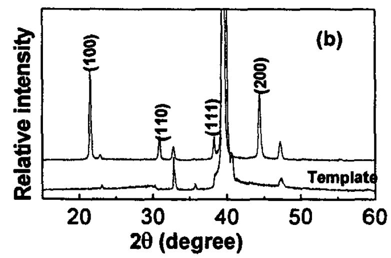
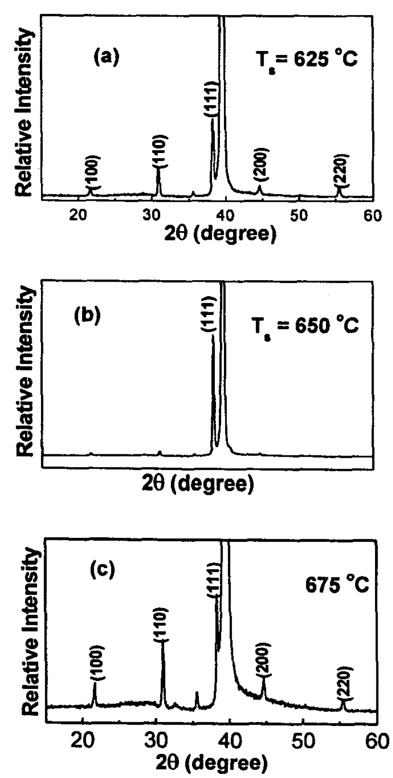


Figure 1 X-ray diffraction pattern of 0.8PMN – 0.2PT thin films (a) without and (b) with template layer.

It is clearly evident that 100 % pyrochlore phase (222) was formed on bare Pt substrate for the films deposited at similar condition. This result led to conclude that the platinum grains act as nucleating center for pyrochlore phase while by changing the nucleating center (grains of LSCO) in later case. Figure 2 shows the perovskite phase formation for the 0.9PMN-0.1PT films deposited at different substrate temperatures.

Excellent improvement in the perovskite phase formation was observed. The effect of the substrate temperature (T_s) was also found to have impact on perovskite phase of PMN-PT thin films. The following figures depict how the substrate temperature affects the crystallinity of films. The figures demonstrate that as the substrate temperature



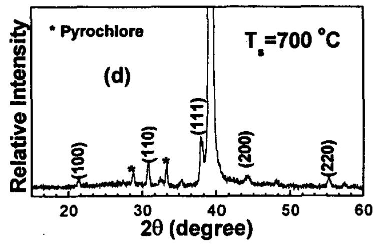
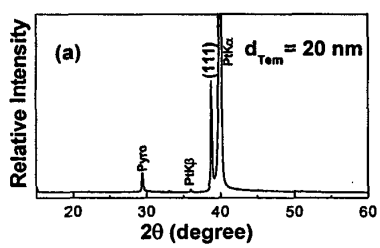
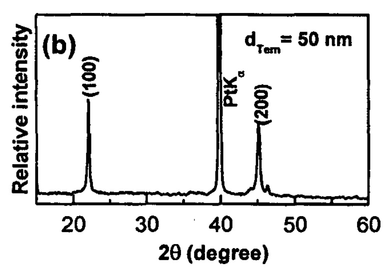
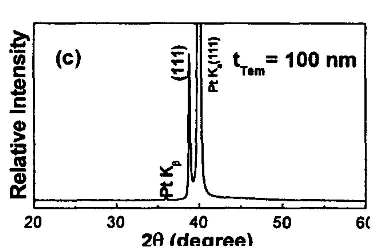


Figure 2 X-ray diffraction patterns of 0.9PMN-0.1PT thin films deposited at (a) 625 °C, (b) 650 °C, (c) 675 °C, and (d) 700 °C, respectively.

is increased crystallinity of the films change from polycrystalline (T_s = 625 °C) to highly oriented (111) perovskite phase (T_s = 650 °C). At T_s =675 °C the films show again polycrystalline in nature and finally at very high temperature (700 °C) the pyrochlore phase starts appearing in films. This could be due the non-stoichiomentry in the composition because of the Pb evaporation at higher temperature. This shows the possibility of controlling the orientation of PMN-PT thin films deposited at Pt coated Si substrate. Inspite of the different surface texture of Pt layer, high quality perovskite PMN-PT thin films of various orientations were successfully deposited on (111) Pt substrate. Figure 3 (a), (b) and (c) show the impact of the template layer thickness on x-ray diffraction pattern for films deposited at 650 °C.







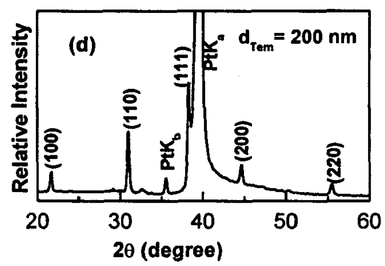


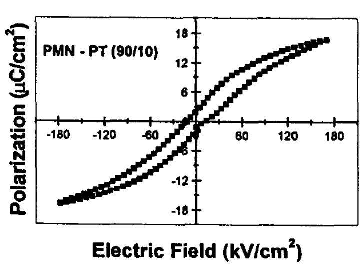
Figure 3 X-ray diffraction patterns of 0.7PMN-0.3PT thin films as a function of template layer thickness. Thicknesses of template layers are (a) 20 nm, (b) 50 nm, (c) 100 nm and (d) 200 nm. All the films are deposited at 650 °C under oxygen partial pressure of 200 mTorr

A gradual change in the crystalline quality and crystallographic orientation is observed as the thickness of the template layer is increased. It is evident from the figure that an optimum thickness of the template layer is required to obtain pyrochlore free thin films. The effect of substrate texture is minimized with increase in the template layer thickness. In case thicker template layer (d_{Tem}=100 nm), platinum substrate effect is totally minimized and films become polycrystalline since LSCO template layer shows polycrystalline in nature (shown in Fig. 1).

ELECTRICAL PROPERTIES

Ferroelectric Hysteresis

The ferroelectric nature of PMN-PT thin a film was verified from the polarization-hysteresis behavior. Figure 7 (a), (b) and (c) show the Polarization-Electric field *(P-E)* loop measured at room temperature for the films different composition. The films up to 20 % of PT content exhibited good ferroelectric nature that is characterized by higher value of remanent polarization. 0.7PMN – 0.3PT films show good hysteresis property with remanent and saturation polarization of 10 and 20 μC/cm², respectively, at room temperature with a coercive field of 30 kV/cm.



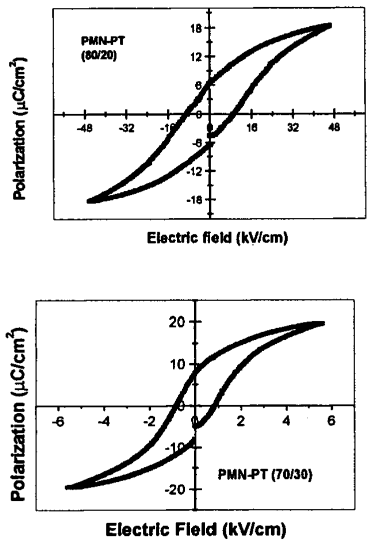


Figure 4 Room temperature polarization hysteresis behavior of PMN – PT thin films with three different compositions

Gradual decrease of remnant polarization with decrease in PT content shows that the films undergo from ferroelectric (tetragonal) to paraelectric (cubic) phase.

Dielectric properties

The diffuse nature of the phase transition temperature of PMN - PT thin films with different compositions is shown in Fig.5. One can observe that both case temperature of maximum dielectric constant (T_m) are shifted to towards the higher temperatures as the measuring frequency is increased. Such behavior confirms the relaxor nature of the PMN-PT thin films. Several theoretical models [4] have been proposed to describe the behavior of relaxor ferroelectrics, which exhibit a broad phase transition along with a strong dispersion in the frequency spectrum. One of the well-known relations employed to

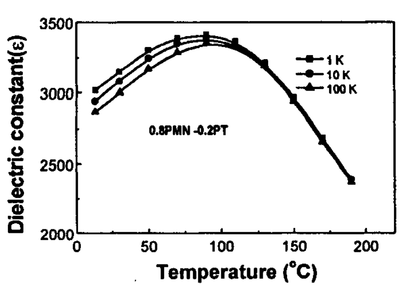


Figure 5(a) Temperature dependence of dielectric constant of PMN-PT (80/20), showing the frequency dispersion of the temperature of dielectric constant maxima.

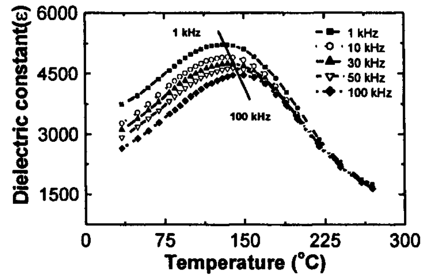


Figure 5(b) Frequency dispersion of the temperature of dielectric constant maxiama showing the relaxor behavior of PMN-PT (70/30) thin films.

describe the frequency dispersion of transition temperature of relaxor materials is Vogel-Fulcher (V-F) relation [5]. It describes the freezing of the dipoles with decrease in temperature. This was observed in the present case, where the relaxation time of the dipole was found to increase exponentially with decrease in temperature.

CONCLUSION

In summary, structural and dielectric properties of PMN-PT have been studied for various compositions. The use of LSCO template layers on Pt (111) substrates facilitates the perovskite grain growth of PMN-PT films grown at higher temperatures. No pyrochlore phase was observed in the films grown on LSCO/Pt/Ti/SiO2/Si substrate temperature within 600 to 675 °C under the oxygen partial pressure of 200 mTorr. The films exhibited a systematic variation of dielectric and ferroelectric properties as function of compositions. The relaxor type behavior in PMN-PT thin films is confirmed from the diffused phase transition along with the frequency dispersion of the temperature of dielectric constant maximum

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