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Processing and Dielectric Properties of Sol-Gel Derived PMN-PT (68:32) Thin Films

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Abstract. PMN-PT thin films near MPB were prepared using sol-gel technique. A transparent solution of the ceramic was prepared by using lead acetate trihydrate, magnesium ethoxide, niobium ethoxide and titanium isopropoxide as precursors along with 2methoxyethanol as solvent and acetic acid as catalyst. Thin films of the ceramic were prepared on Pt/Si and on ITO coated glass substrates. X-ray diffraction (XRD) studies show the formation of perovskite phase of the films with less than (5%) pyrochlore phase. Scanning electron microscopy (SEM) study of the films on different substrates show well developed grains of sub-micron size. Dielectric constant measurement at different temperature was carried out. Room temperature value of dielectric constant and dielectric loss at 1 kHz of the ceramic thin films on ITO coated glass and Pt/Si substrates were found to be 500, 0.03 and 415, 0.01 respectively. Dielectric measurements for different thicknesses of the films have also been carried out. P-E loop and I-V studies of the films were also carried out.

Keywords: PMN-PT, sol-gel, ferroelectric films, relaxors, MPB

Introduction

Piezoelectric thin films have attracted considerable attention as one of the essential materials in microfabricated devices, such as microsensors and microactuators [1]. The piezoelectric response in ferroelectric thin films with superior properties has generated interest in ferroelectric materials. PMN-PT (Lead Magnesium Niobate-Lead Titanate) near morphotropic phase boundary (MPB) has attracted the utmost attention because of the excellent dielectric and electromechanical properties [2]. High dielectric constant of this material is suitable for miniature capacitors, storing high charge density and for dynamic random access memory (DRAM) applications. In spite of attractive properties of PMN-PT, pure phase formation of this material remains a problem. The main concern in PMN-PT system is the occurrence of parasitic pyrochlore phase with perovskite phase, which results in the degradation of physical characteristics significantly [3]. This pyrochlore phase formation in the PMN-PT system can be minimized by appropriate selection of annealing temperature. Among several thin film deposition techniques, sol-gel process offers simple and low cost processing of thin films. This process is also compatible with other device processing steps [4]. In this article, we report the development of perovskite phase as a function of annealing temperature and the electrical properties of sol-gel derived PMN-PT (68:32) thin films on different substrates.

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Experimental Procedure

Lead acetate trihydrate, $Pb(C_2H_5O_2)_2{\cdot}3H_2O$, magnesium ethoxide, $Mg(OC_2H_5)_2$, niobium ethoxide $Nb(OC_2H_5)_5$ and titanium isopropoxide, $Ti(OCH(CH_3)_2)_4$ (all Aldrich) were used as starting materials with 2methoxyethanol ($CH_3OCH_2CH_2OH$) and acetic acid (CH_3COOH) as solvent and catalyst. A transparent solution of PMN-PT (68:32) stoichiometric composition with 15 mole% excess lead (to

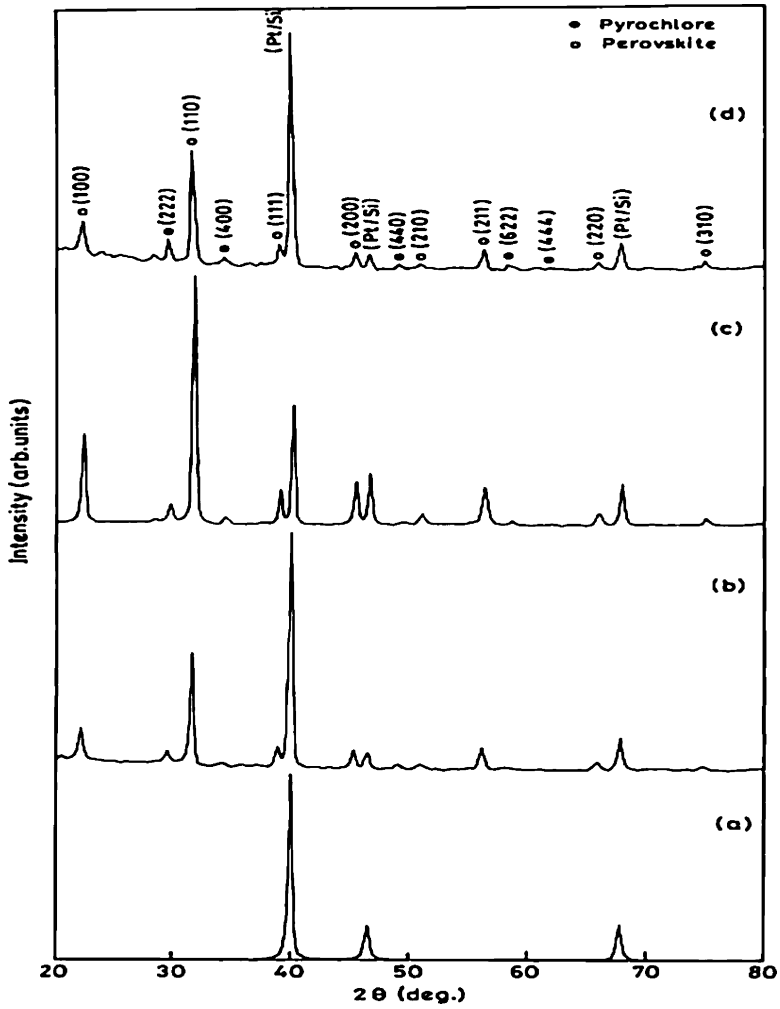

Fig. 1. XRD patterns of (a) Pt/Si substrate and PMN-PT (68:32) thin films on PT/Si substrate annealed at (b) 550°C, (c) 600°C, (d) 650°C.

compensate lead loss during annealing) was prepared using a route reported earlier [5]. Lead acetate trihydrate was dissolved and dehydrated in acetic acid. Magnesium ethoxide and niobium ethoxide were separately dissolved in 2methoxyethanol. Lead alkoxide solution was mixed with Mg-Nb complexed ethoxide and stirred at 80°C for 4 hrs. Finally, tiatanium isopropoxide, along with acetyl acetone as a stabilizing agent, was mixed in the Pb-Mg-Nb alkoxide solution at 60°C and stirred for 2 hrs to get the transparent PMN-PT (68:32) solution. Pt/Si and ITO coated glass substrates were ultrasonically cleaned, first in methanol then in trychloroethylene and finally in acetone. First, two layers of PT (Lead Titanate) were spin coated on both the substrates for better lattice match [6]. PMN-PT (68:32) thin films were coated using a spin coater at 3000 rpm for 20 seconds. The films were heat treated at 250°C in air for 2 minutes after each coating and annealed at 550°C, 600°C and 650°C for 20 minutes after each two coatings. The final firing of the films was done at 650°C for 2 hrs in air. The structure and morphology of the films were characterized using XRD (PW 3020 Philips CuKα radiation, $\lambda = 1.5405°$) and SEM (Cambridge Stereo scan 360 scanning electron microscope) techniques. Bottom electrodes were created by etching the films in 5% HF solution. Thicknesses of the films were measured by using a tale-step method. For electrical

measurements, gold electrodes of 1mm diameter were deposited by rf sputtering. Dielectric constant at 1 kHz as a function of temperature was measured by an impedance analyzer (Model 4192A HP) with an oscillation level of 100 mV. Polarisations versus electric field properties were characterized using a Radiant Technology RT66A ferroelectric test system. Current versus voltage (I-V) measurements were measured using 610°C (Keithley) electrometer.

Results and Discussion

PMN-PT (68:32) thin films were heat treated at 250°C for 2 minutes after each coating for solvent removal and at 550°C, 600°C and 650°C for 20 minutes after each two coatings for perovskite phase formation. Figures 1 and 2 show the XRD patterns of the films annealed at different temperatures along with substrates XRD respectively. These diffraction lines were indexed in different crystal systems and unit cell configurations using a computer program package 'Powdmult'.

Structures of the films on Pt/Si and ITO coated glass substrates were found to be tetragonal and rhombhohederal on the basis of minimum $\Sigma\ \Delta d\ (= d_{obs} - d_{cal})$, where 'd' is interplaner spacing. The lattice parameters of the unit cells were refined using least square fit method. The c/a ratio for the thin films of tetragonal structure is 1.0036 with lattice parameters $a = 3.9920$ and $c = 4.0065$ while $a = 4.0025$ and $\alpha = 90.17^{\circ}$ for the films with rhombhohederal structure. Pyrochlore phase formation of the films,

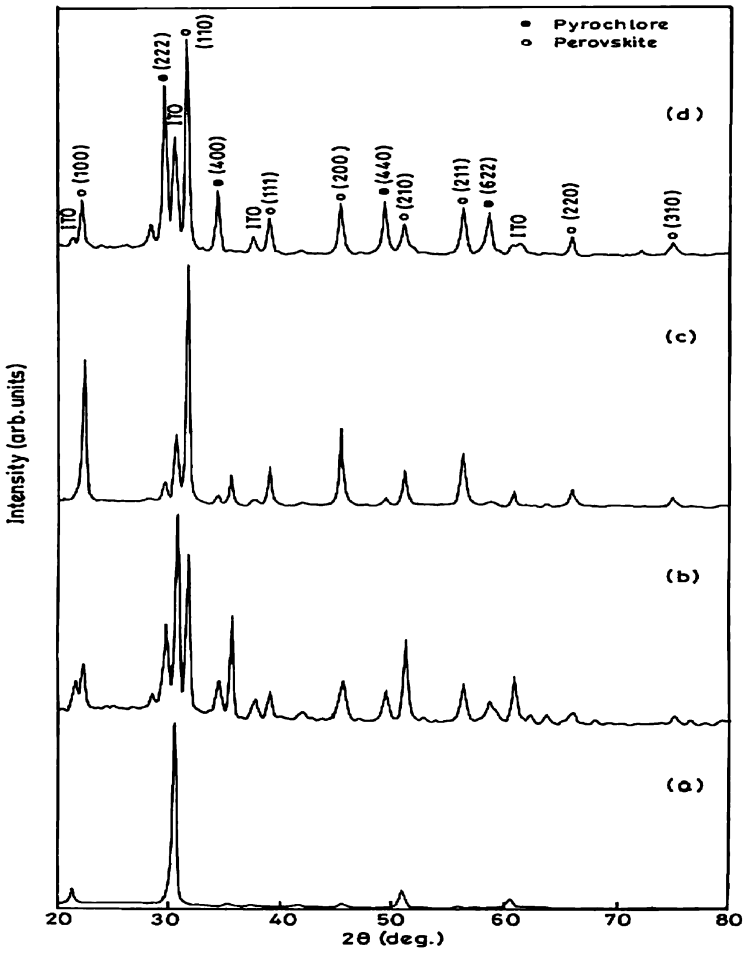

Fig. 2. XRD patterns of (a) ITO coated glass substrate and PMN-PT (68:32) thin films on ITO substrate annealed at (b) 550°C, (c) 600°C, (d) 650°C.

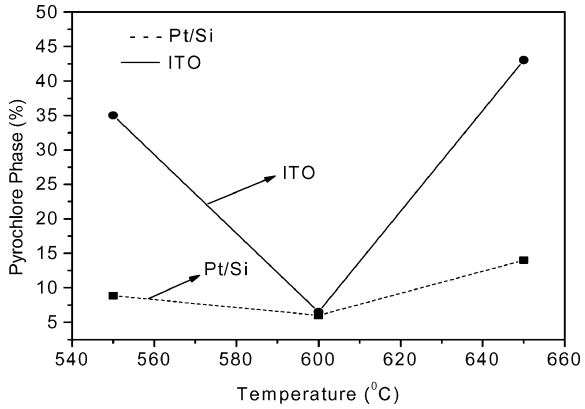

Fig. 3. Variation of pyrochlore phase with the annealing temperature.

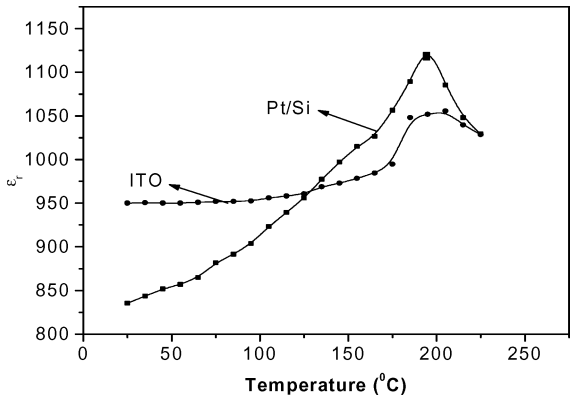

Fig. 4. Dielectric constant variation with temperature of PMN-PT (68:32) thin films on Pt/Si and ITO coated glass substrates.

deposited on two substrates and heat treated at 550°C, 600°C and 650°C is shown in Fig. 3. Pyrochlore phase (%) was calculated using the relation [7]

$$\textit{Pyrochlore phase}\,(\%) = I_{\text{pyro}}/(I_{\text{perov}} + I_{\text{pyro}}) \times 100;$$

and pyrochlore phase (%) was found to be minimum (∼5%) in the films heat treated at 600°C on both the substrates. At other annealing temperatures the films on ITO coated glass substrate show more pyrochlore phase (%). This can be attributed to the large lattice mismatch of PT base layers with the ITO glass substrate. The SEM micrographs reveal that the films are crack-free and with dense and smaller grain size of the films on ITO coated glass substrate.

Dielectric constant (ε_r) of the films was found to vary with the thickness of the films. Values of ε_r of 0.3 μm thick films at room temperature on ITO coated glass/Platinized Silicon substrates are 500/415 and of 0.8 μm thick films are 950/835 respectively. Variation of ε_r of 0.8 μm thick films on both the substrates at 1 kHz as a function of temperature is shown in Fig. 4. Values of ε_r of the films varies from 835 to 1110 on Pt/Si and from 950 to 1055 on ITO coated glass substrates respectively with broad diffuse phase transition ∼190°C. The diffuse phase transition of the films can be due to ultra fine particle size of the films [8] and applications of different stress to different grains and variations in local stress [9]. Room temperature value of the dielectric loss for the films on both the substrate was found to be ∼0.03.

The ferroelectric hysteresis loops of the two films are shown in Fig. 5. The value of remanent polarization

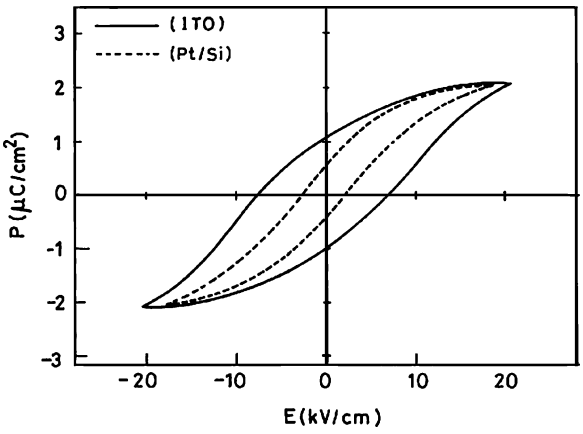

Fig. 5. P-E Hysteresis loops of PMN-PT (68:32) films on Pt/Si and ITO coated glass substrates.

(P_r) and coercive field (E_c) of the films on ITO coated glass substrate are ∼1.1 μC/cm^2 and ∼7.7 kV/cm while on Pt/Si are ∼0.55 μC/cm^2 and ∼3 kV/cm respectively. The value of P_r of the films on Pt/Si substrate is less than that on ITO coated glass substrate and this may be due to more pinning centers in the films on Pt/Si substrate [9]. The high value of E_c of the films on ITO coated glass substrate may be due to smaller grain size of the films as observed by SEM [10]. Leakage current characteristics of the PMN-PT (68:32) thin films on Pt/Si and ITO coated glass substrates are shown in Fig. 6. The current increases linearly with external field in the low electric field region, which suggests ohmic conduction [11]. At higher voltages, it follows square law dependence and this bears a striking resemblance to one carrier space charge limited (SCL) injection current

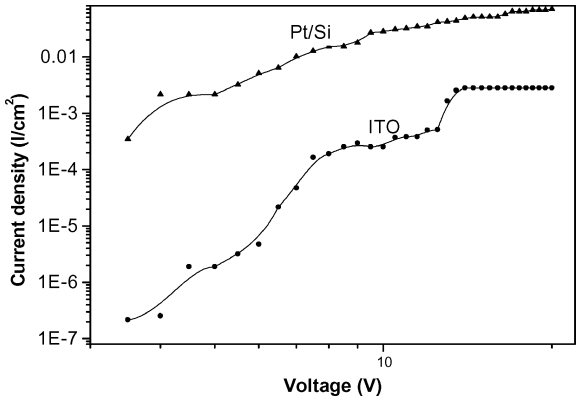

Fig. 6. I-V characteristics of PMN-PT (68:32) thin films on Pt/Si and ITO coated glass substrates.

[12]. The leakage current of the Au/PMN-PT/ITO capacitor is lower than Au/PMN-PT/Pt/Si capacitor. This may be due to densely packed grains of the films on ITO coated glass substrate [13].

Conclusions

Phase formation of PMN-PT (68:32) thin films as a function of annealing temperature was studied. Films annealed at 600°C show minimum pyrochlore phase (%). Grains of the films on ITO coated glass substrate were smaller and densely packed. Phase transition was diffuse with Curie temperature ∼190°C. P-E hysteresis loops of the films show the ferroelectricc nature of the films. The leakage current of the Au/PMN-PT/ITO capacitor is lower than Au/PMN-PT/Pt/Si capacitor.

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