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Ferroelectric films and micro devices

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Abstract

The study of microelectromechanical systems (MEMS) has of late opened up significant new opportunities for miniaturized mechanical devices based on thin film materials and silicon technology. Their functionality can be increased by joining many elements on a small space. Infrared detector arrays, high-frequency ultrasonic imaging arrays and cantilever arrays for mass storage applications are examples of such improvement. An important family of functional materials is ferroelectrics, or more generally polar materials. Their piezoelectricity can be used in sensors, actuators and transducers, while pyroelectricity is used in infrared detectors. This paper deals with the preparation and characterization of ferroelectric thin films for MEMS applications. Emphasis is laid on lead zirconate titanate (PZT) and lead calcium titanate (PCT).

Sol–gel technique for ferroelectric film deposition is considered in detail. Thin films of $(Pb,La)(Zr,Ti)O_3$ have been deposited by sol–gel method on a variety of substrates. Attempts have been made to crystallize the thin films at as low a processing temperature as possible. The properties studied include dielectric measurements and hysteresis. Thin films of calcium-modified lead titanate (PCT) were also prepared by the sol–gel technique and their pyroelectric characteristics were studied for use in infrared detectors.

Keywords: Ferrelectrics, sol–gel, MEMS, self-assembled monolayer.

1. Introduction

The unique properties of ferroelectric materials, piezoelectricity and pyroelectricity, combined with design flexibility and miniaturization offered by thin film geometry and also developments in integrated circuitry and electrooptic technologies, have fuelled great interest in ferroelectric thin films. Thin films of ferroelectric devices are being considered for application in numerous electronic and electro-optic devices such as nonvolatile semiconductor memories, optical waveguide devices, spatial light modulators, switching capacitors for integrated circuitry, SAW devices, pyroelectric devices and imaging sensors.[1–3] Another potential application is micropositioning and actuation, with recent developments in micromotors and other microelectromechanical systems (MEMS).

The exploitation of ferroelectric thin films for electronic and electromechanical applications has been restricted due to limitations in deposition processes for device-quality ferroelectric thin films. However, recent advances in thin film deposition technology, especially in the areas of sol–gel technology and metal organic chemical vapour deposition, have generated significant excitement within the electronic ceramics community. For thin ferroelectric applications, lead-

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based perovskite oxides such as PT, PZT and PLZT have been the major materials of interest and the primary objective in fabricating thin films has been to reproduce the polar properties of the bulk materials. Usually, a cubic pyrochlore phase is also obtained in PZT and PLZT thin films which is otherwise perovskite, leading to degradation in the ferroelectric properties of the film. Also, most reported methods require a sintering temperature of $\geq$ 600°C. There is a need to reduce this temperature to $\sim$500°C for integration of the films with silicon technology.

The substrate–film interface plays an important role in the growth and subsequent properties of the film. A number of studies[4–10] have been carried out to investigate and optimize the deposition parameters of ferroelectric thin films. However, a coherent view of the relative importance of the factors that control the structural and electrical properties of PLZT thin films is still lacking.

The past 20 years has seen the emergence of self-assembled monolayer (SAM) technology as an important tool for nanoscale control of interfacial chemistry and to effect controlled surface modification.[11] The use of functionalized SAMs[12] as organic templates for the controlled formation (at reduced temperatures) of thin films from aqueous and/or alcoholic solutions has been demonstrated.[13] In a reasonable extension of this concept, it is expected that an organic surface would be able to accommodate some lattice mismatch because of its high compliance and this may result in stabilizing the properties of electroactive thin films.

The studies reported herein are a systematic record of the effect of parameters like sintering temperature, heating cycle, substrate and the material composition on the film characteristics. The influence of SAM-coated substrate on the phase formation of PLZT films has also been reported.

2. Experimental

2.1. *Preparation of SAM templates*

The substrate used for the work reported herein was ITO-coated quartz. Coating the substrate with 16-trichlorosilylhexadecylthioacetate created SAM templates. The preparation of this silane, its coating on to glass, quartz, and silicon substrates, and its oxidation to a sulfonate-bearing surface have been reported earlier.[14,15]

2.2. *Ceramic film preparation*

PLZT sol was prepared using lead acetate trihydrate, lanthanum acetate hydrate, zirconium acetyl acetonate and titanium isopropoxide (Aldrich, USA) as precursors, along with 2-methoxyethanol as solvent and acetic acid as catalyst. The sol was prepared as described earlier.[9–10] Filtered sols were dispensed from a syringe using a 0.2-μ syringe filter and spin-coated at a speed of 3000 rpm for 30 s on sulfonate-SAM-modified ITO-coated quartz substrates. For comparison, films were also deposited on clean ITO quartz substrates (no SAM). Multiple coatings were deposited to get optimal film thickness. After each coating, the films were heat-treated at 150°C to remove volatile organics. The multilayer films were then heated (temperature increase at 1°C/min) to 400°C and maintained at that temperature for 1 h to expel residual organic material. The films were then heated rapidly to temperatures ranging from 500°C to 600°C and maintained at the desired temperature for 1 h, followed by furnace cooling. The crystallinity and phases of the sintered films were examined after heat-treatment using X-ray diffraction (Rigaku, Cu Kα radiation, $\lambda = 1.5405$Å). Microstructual studies of the sintered films were carried out using a scanning electron microscope (JEOL, Japan). The film thickness was determined using a tele-step method. Aluminium electrodes were vacuum-deposited for dielectric and charge field hysteresis studies. Hysteresis studies were done using a Sawyer–Tower circuit. Dielectric properties of the films at various frequencies were measured using an impedance analyzer (HP 4192 A).

Thin films of calcium-modified lead titanate (PCT) with compositional formula $P_{.76}C_{24}$ TiO_3were also prepared by sol–gel technique. The sol was prepared by dissolving lead acetate and calcium nitrate in acetic acid. The solution was refluxed for an hour at 80°C after adding ethylene glycol in it. Alcoholic solution of titanium iso-propoxide was added to this solution to prepare the final sol of PCT. Thin films were deposited on ITO-coated substrates using the sol prepared by spray pyrolsis on substrate kept at 450°C. No further heat-treatment was carried out. The pyroelectric current was measured after corona poling samples.

3. Results and discussion

When as-deposited amorphous PLZT films are heat-treated they pass through an intermediate cubic pyrochlore phase before finally transforming to a ferroelectric perovskite phase. Figure 1 shows X-ray diffractograms of the films, with and without SAM templates. All the films are polycrystalline. Figure 1a shows PLZT films sintered at 550°C on substrates without SAM templates. Both perovskite and pyrochlore phases are present in these films. However, in films sintered at 600°C (Fig.1b) the pyrochlore phase is gone. In PLZT films deposited on substrates modified with SAM templates and sintered at 550°C, only the perovskite phase is obtained (Fig.1c). The lower crystallization temperature for films deposited on SAM templates may be due to the fact that SAM provides sulfonate (-SO_3^-) sites for controlled nucleation of the cationic complex of PLZT, analogous to previously reported work with oxide precipitation on to sulfonate-bearing surfaces.[14]

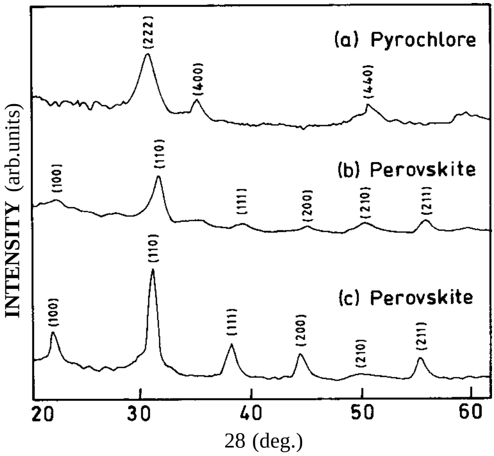
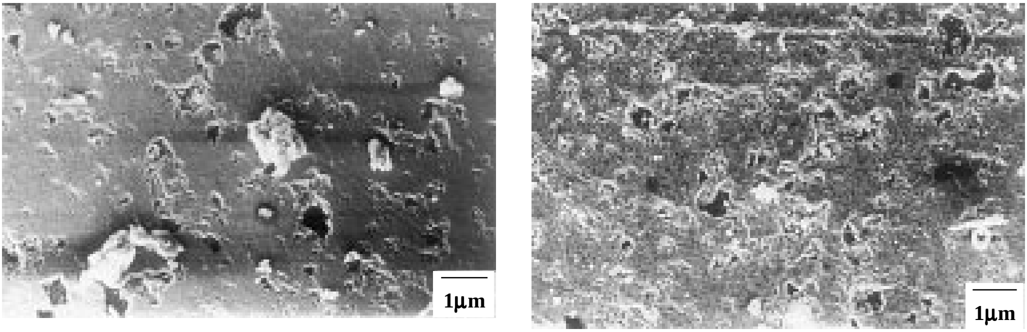


FIG. 1. X-ray diffractograms of (a) PLZT films on substrates without SAM templates, sintered at 550°C, b) the same films, sintered at 600°C, and c) PLZT films on substrates modified with sulfonate SAM templates, sintered at 550°C.



(a) (b)

FIG. 2. SEM micrographs of PLZT films deposited on substrates with (a) SAM templates and (b) without sulfonate SAM templates.

Figure 2 shows SEM micrographs of films deposited on substrates with and without SAM templates, respectively. As can be observed, there are considerably less pits and cracks in the PLZT films deposited on the SAM templates. The slow heating schedule gives sufficient time for any organics (including the small amount of materials from SAM) to evaporate. Moreover, the grains are also well formed with negligible porosity. This may be attributed to the fact that SAM presents a more uniform and complete array of polar sites that act as nucleation sites for cationic complexes, promoting better adherence and dense films. We have reported similar results for TiO_2 and ZrO_2 films deposited from solution on to SAM templates.[14, 15]

The dielectric properties of PLZT films deposited on ITO-coated quartz substrates and heat-treated at 600°C are reported. Films created without the benefit of the sulfonate SAM template and annealed at<600°C were difficult to characterize for electrical properties as substantial amount of micro pores were present and these films had cracks which were electrically shorted during measurements. However, films deposited on SAM templates (annealed at 550°C) showed good dielectric properties. Figure 3a shows the frequency dependence of PLZT dielectric constant. The dielectric constant decreases and the loss factor increases with increase in frequency. The room-temperature value of the dielectric constant for films deposited on unmodified substrates was found to be 650 and exhibits extremely low dispersion, while the tan δ value is 0.027. The dielectric constant value in the case of films deposited on SAM-modified substrates was $\cong$ 850, while tan δ is 0.01. The temperature-dependence of dielectric constant at 1 kHz shows typical

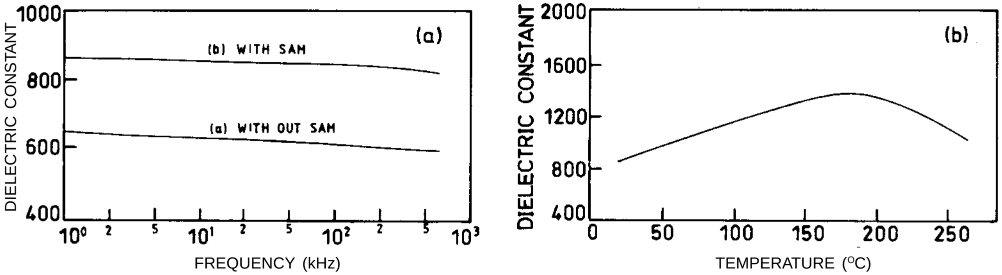


FIG. 3 (a). The frequency and (b) temperature dependence of the dielectric constant at 1 kHz.

Table I
Figures of merit of PCT and PZT

	PCT	PZT
1. Dielectric constant (ε')	100	400
2. Loss tangent (ε")	0.03	0.05
3. Pyro coefficient: (μC/m^2/°K)	50	175
4. F_i (Current): ($\times 10^{-11}$Cm/J)	5.0	5.8
5. F_v (Voltage): ($\times 10^{-2}$m^2/C)	5.6	1.6
6. F_d (Noise): ($\times 10^{-6}$m^3/J)$^{1/2}$	5.6	3.6

dipolar behavior as shown in Fig. 3b. There is a broad Curie peak associated with the ferroelectric–paraelectric transition. The higher value of the dielectric constant in the case of films deposited on SAM-modified substrates is likely due to improved microstructure and low porosity. Also, the reduced sintering temperature may decrease the PbO loss from the samples. It is known that lead volatility leads to oxygen vacancies which results in domain pinning.[17]

Figure 4 shows the charge-field hysteresis loop for films deposited on the SAM templates and heat-treated at 550°C. The results are compared with those obtained for films of the same composition deposited on unmodified substrates (but heat-treated at 600°C as this is the lowest temperature at which we could obtain pure perovskite films). An improvement in the saturation polarization (from 25 μC/cm^2 to 30 μC/cm^2) for films on SAM templates is observed. This improvement as well can be attributed to the improved microstructure of the films and their lower processing temperature. Figure 5 shows the pyroelectric coefficient of PZT and PCT films. It can be seen from this figure that the pyrocoefficient of PCT is almost constant in the measured temperature range. This is a useful characteristic to calibrate and integrate pyrosensor with the electronics. The figures of merit of these films are given in Table I. As can be noticed, lower dielectric constant of PCT leads to higher voltage sensitivity.

It is important to note that while there is precedence for using SAM layers under spin-coated sol–gel processed ceramics, in previously reported examples, SAM (typically hydrophobic) is

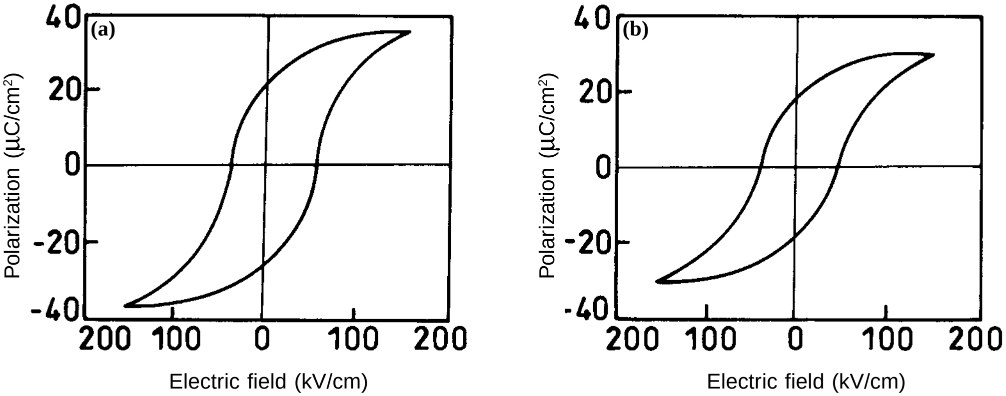


FIG. 4. Hysteresis loop for films deposited, (a) on the SAM templates and heat-treated at 550°C and (b) on unmodified substrates, heated at 600°C.

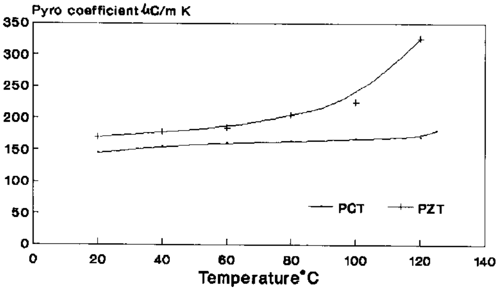


FIG. 5. Temperature-dependence of the pyroelectric coefficients of PCT and PZT.

used to reduce adhesion of the sol and prevent ceramic film attachment.[17] In our work, functionalized SAM enhances film growth, uniformity and performance. In general, however, our work seems to be the first demonstration of functionalized SAMs adding a new control element to the crystallization of sol–gel processed ceramics. With further experimentation in terms of processing conditions and SAM structure and chemistry, it is likely that functionalized monolayer surfaces can lead to further improvements in ceramic film processing and properties. It is clear from the results obtained on PCT films that these films can find useful application in pyroelectric devices due to higher voltage sensitivity (F_v).

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