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Development of Ferroelectric Thin Films and Composite Materials by Sol-Gel Process

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Abstract

Sol-gel processing provides an interesting alternative for the fabrication of ferroelectric thin films and composite materials which are both use ful in various electronic applications. Lead zirconate titanate (PZT) thin films with a Zr/Ti ratio of 52/48 were fabricated by spin-coating solutions of polymeric complex Pb, Zr, Ti-methoxyethoxide onto Pt-coated Si substrates. A technique of adding excess Pb in the solution was used in order to reduce an intermediate or second phase formation which usually became a problem for PZT film formation. This technique led to a complete transformation of the intermediate phase to the desired perovskite phase. In addition, the exploration of annealing conditions was also considered.

The sol-gel derived PZT films containing 10 mole% excess Pb showed good ferroelectric and dielectric properties at the annealing condition of 700°C, 30 minutes. The remanent polarization was 19.2 $\mu C/cm^2$ for 7 volts applied voltage. The coercive field was 46.4 kV/cm for films with thickness 3000 Å. The relatively reasonable value of dielectric constant of 940 was found. The good quality films could be due to the nearly complete crystallization to the single perovskite phase. The results from electrical properties corresponded to the uniform and dense microstructure which was observed by field-emission scanning electron microscope (FE-SEM). A printable thick film paste of sol-gel based composite could be produced by dispersing 75% by weight PZT powders into 0.88M PZT sol-gel solution.

1. Introduction

Lead oxide based ferroelectric films were investigated for a variety of device applications including electro-optic devices [1], non-volatile Random Access Memories (RAMs) [2], pyroelectric detectors [3] and microelectromechanical systems (MEMS) [4]. Lead zirconate titanate (PZT) composition of the morphotropic phase boundary, PZT(52/48), (Pb $(Zr_{0.52}Ti_{0.48})O_3$), is a candidate material for these applications because it exhibits superior dielectric, ferroelectric and piezoelectric properties. In the preparation of PZT thin film by solution deposition or sol-gel processing, metallo-organic starting reagents such as metal alkoxides are employed. Sol-gel processing offers several potential advantages for forming thin films and composite materials such as high purity, chemical homogeneity, low crystallization temperature and its ease of fabrication.

However, previous investigations [5-6] reported that it was difficult prepare phase-pure perovskite PZT thin films. Regarding to sol-gel derived PZT, it first crystallized upon heating to an intermediate phase (identified as either a fluorite-structured compound or a pyrochlore phase) at low temperature before transforming to the perovskite structure. Small volume percentages of residual non-ferroelectric intermediate phase can be especially detrimental for PZT thin film quality. Therefore, device performance depends on the presence of this intermediate phase [7].

Moreover, understanding the evolution of microstructure and transformation of the intermediate phase to the perovskite phase is very important for preparing high quality films. Since the crystal structure of pyrochlore is considered a Pb-deficient structure, an addition of excess Pb in solution technique is therefore used to reduce the pyrochlore formation. The excess Pb is added to compensate for lead-loss on heat treatment. This technique leads to crystallization of dense perovskite microstructure. Experimental parameters included not only the study of different precursor chemistry, but also the exploration of annealing conditions. However, film thickness in a conventional sol-gel system is generally limited to 50 to 500 nm because of the increase in tendency of cracking as film thickness approaches 1 μm [8].

In recent years, thick film technology such as sol-gel composite materials could be made by dispersing PZT particles into a PZT sol-gel matrix [9]. The resulting solution could be spin-, dip- or spray deposited onto a substrate. Deposited film was annealed in the same manner as regular sol-gel films. With this new method, it is possible to fabricate sol-gel thick films which had thickness up to 60 μm on various substrates such as Pt-coated silicon, stainless steel or aluminum . The screen printing process was a good deposition technique which was precise and efficient for the fabrication of composite materials having a specific image [10].

2. Materials and Methods

2.1 Sol-gel Process and Thin Film Preparation

In this study, a stock solution was prepared following the previous studies [6, 11-13]. Figure 1 shows the schematic chart of preparation method for the PZT thin film. In order to compensate for lead loss on heat treatment during sintering state, excess Pb was added in the solution in the range of 0 to 10 mole%. 5 layers of solution were deposited onto the substrates in order to achieve film thickness approximately 3000 Å. Then, films were annealed at 600°C to 700°C for 30 to 60 minutes in an electric box furnace at 5°C/minute ramp rate.

2.2 Thick Film Preparation

The thick PZT films were fabricated by preparing sol-gel based composites which were composed of PZT powders and PZT sol-gel solution. PZT powders were fabricated by mixed oxides or conventional method. The weighed oxides were homogenized by wet-ball milling for 24 hours. After that, the dried powders were calcined at 800°C for 4 hours and then the calcined powders were milled by attrition at 600 rpm for 3 hours. The particle size distribution of PZT powders was characterized by laser light scattering technique (Mastersizer S Ver. 2.11, Malven Instruments Ltd.,UK). To produce sol-gel based composites, PZT powders were dispersed in PZT sol-gel which acted as an organic vehicle. After that, the mixture was milled for 24 hours. The resulting paste could be printed onto Pt-coated Si substrate using a screen printing method.

3. Results and Discussion

3.1 PZT Thin Film Study

3.1.1 Structural Characterization

The structure of PZT powders and PZT films were identified using room temperature X-ray diffractometer (JEOL: JDX-3530) with monochromatic CuK$_\alpha$ radiation (λ = 1.5418 Å). Glancing angle of 5° between incidence and sample surface was also used in this study in order to obtain a better resolution of thin film x-ray peaks without interference from those of the high intensity substrate.

XRD patterns of PZT films prepared from solution without adding excess Pb are shown in Figure 2. From the XRD patterns of the as-deposited film after pyrolysis at 300 °C on the hot plate, only strong peaks from the substrate can be shown in Figure 2(a). It can be confirmed that the film was still in amorphous stage. In other word, the crystallization had not occured at 300°C. Figure 2(b), (c), (d), (e) and (f) show XRD patterns of the annealed films, after such an annealing process at 550 to 700°C for 30 minutes. By applying a glancing angle, it is clear that XRD patterns show the coexistence of pyrochlore-like phase and perovskite PZT phase. It can be seen that the highest intensity peak of pyrochlore-like phase is between 28.4

and 30° which covers a very broad area. It is believed that the broad peak is due to the small grains in nanometer size range which is a characteristic of the intermediate phase or second phase which in this case is pyrochlore [14].

The amount of the intermediate phase in the vicinity of $2\theta = 30°$ seemed to be reduced after annealing at 700°C for 30 minutes as seen in Figure 2(f). The perovskite PZT phase in this study showed nearly random orientation. The intermediate phase or pyrochlore-like structure, $Pb_2(Zr_{1-x}Ti_x)_2O_6$, was assumed that Zr partially replaced the position of Ti in $Pb_2Ti_2O_6$. This implied that Pb volatiled during annealing process resulted in the formation of Pb-deficient phase which was known as pyrochlore-like or fluorite-type structure and the transformation from intermediate to perovskite phase was not completed. Therefore, an addition of excess Pb in the stock solution was required to compensate for Pb-loss.

Figure 3 shows XRD patterns of PZT films with an addition of 5 mole% of excess Pb annealed at three different conditions. As studied by glancing angle, it can be seen that a broad peak of pyrochlore-like phase was still observed after 650°C annealing. Even though annealing time increased, the pyrochlore-like phase was unable to transform completely to the pure perovskite phase. XRD patterns of PZT film annealed at 700°C for 30 minutes showed the broad peak of pyrochlore-like phase. However, it could be possible that adding more excess Pb would be required in order to complete the transformation. Figure 4 shows XRD patterns of PZT films with an addition of 10 mole% excess Pb at three different annealing conditions. XRD patterns of PZT film with 10 mole% excess Pb solution showed that the preferred (100) and (111) oriented films were obtained. There was no indication of an intermediate phase after heat treatment at 700°C for 30 minutes. This observation confirmed that an addition of excess Pb content and annealing temperature was somehow necessary to complete the transformation.

Therefore, it is reasonable to summarize from these results that the films which were pyrolyzed at 300°C showed amorphous structure. During annealing process, an intermediate or metastable pyrochlore phase first formed and then transformed to the perovskite phase at higher annealing temperature. However, the pyrochlore phase left in films was due to Pb-loss during heat treatment. To compensate this loss, therefore, the amount of excess Pb was incorporated into stock solution. This technique enhanced the formation of pure-phase perovskite for a given annealing time and/or temperature which was required for the phase conversion.

3.1.2 Microstructural Characterization

Since the primary grain size and cluster of sol-gel PZT thin films in previous studies showed the size range in nanometer scale [6]. A field-emission scanning electron microscope (FESEM) using the JEOL (JSM 6301F) was employed. The SEM micrograph of 5-layer-deposited PZT films on Pt-coated Si substrates appeared in Figure 5. The film thickness was about 0.3 μm. It can be confirmed that single-layer thickness of an annealed film was approximately 600 Å. It was also shown that the PZT thin film grown on Pt-coated Si substrate and Pt layer was about 1 μm in thickness.

Figure 6 shows the microstructure of PZT thin films made from the solutions with excess Pb additions ranging from 0 to 10 mol %. These films were annealed at a rate of 5°C/minute at 650°C 30 minutes. It can be observed from the contrast of the micrograph that there were 2 phases of PZT thin films which were made from the solutions with 0 and 5 mole% excess Pb. They consisted of large perovskite rosettes or spherulites embedded in a nanometer grain size pyrochlore matrix. Because of the higher density, the perovskite phase had a higher secondary electron emission yield and appeared brighter in the SEM micrographs. The microstructures of PZT thin films in this study were similar to those of the previous studies [12,15]. This spherulite crystallite originated from a center, in other words, it nucleated radially from nanocrystalline pyrochlore matrix. Figure 6(a) depicted that films with no excess Pb had a perovskite content less than films prepared from solution with excess Pb. When excess Pb content increased, more spherulites nucleated and coalesced one another at the expense of nanocrystalline pyrochlore matrix.

In 10 mole % Pb excess films, the SEM micrographs presented that the size of perovskite phase was much smaller than those of films prepared from solution with lessPb. In addition, the area of nanocrystalline pyrochlore matrix was very small. The pyrochlore phase had existed but it had not been detected by 2θ-θ mode of x-ray diffraction.

The microstructures of films annealed at 650°C for 60 minutes shown in Figure 7 were quite similar to films annealed at 650°C for 30 minutes. The SEM demonstrated that there was no strong effect on the annealing times of the amount of perovskite phase. The microstruture of films prepared from solution with 0 and 5 mole% Pb excess as shown in Figure 8(a)-(b) were also similar to those of films annealed at 650°C for 30 minutes. In film with 10 mole% Pb excess, when the annealing temperature was increased, more dense PZT films were obtained. The cluster size of sol-gel PZT thin films was approximately 1 μm. The SEM micrograph demonstrated that an addition of 10 mol% Pb excess was beneficial in maintaining the stoichiometry of the PZT films during annealing. Moreover, the intermediate or pyrochlore-like phase could completely transform to perovskite phase after being heated to 700°C for 30 minutes.

3.1.3 Electrical Characterization

Hysteresis measurements were done using RT66A standardized ferroelectric test system at a frequency of 60 Hz and applied voltage of 7 volts under the virtual ground mode. To measure the capacitance and dielectric loss of the films at room temperature, a Hewlett Packard multi-frequency LCR meter (HP 4192A Impedance analyzer) was used at 1 kHz.

An electrical characterization of the PZT thin films was performed to determine the film quality.The film thickness in this characterization was approximately 0.3 μm. Figure 9 shows the hysteresis loops of sol-gel PZT thin films. The polarization of PZT films with excess Pb additions ranging from 0 to 10 mole% was measured as a function of electric field. The remanent and saturated polarization (P_r and P_s) increased as the percent of excess Pb increased. These results indicated that the amount of excess Pb strongly affected ferroelectric properties. When the annealing temperature rose P_s and P_r of films with 10 mole% Pb excess increased significantly since an addition of Pb excess was enough to compensate Pb oss at higher temperature during heat treatment. Consequently, the intermediate phase could transform almost completely to the desirable perovskite phase. Figure 10 shows the hysteresis loops of PZT films with 10 mole% Pb excess at different annealing conditions. Films annealed at 700°C for 30 minutes significantly had ferroelectric preperties better than films annealed at 650°C for 30 and 60 minutes. However, only slight property improvement was obtained by increasing annealing time.

In this study, PZT films containing 10 mole% Pb excess showed good ferroelectric and dielectric properties at the annealing condition of 700°C for 30 minutes. The remanent polarization was 19.2 μC/cm^2 for an applied voltage of 7 volts. The coercive field was 46.4 kV/cm for films with thickness of 3000 Å. The relatively high dielectric constant was 940 which is comparable to other thin film studies [14-18]. The dielectric loss was about 0.070. The good quality films could be due to nearly complete crystallization to a single perovskite phase. These electrical properties corresponded to the uniform and dense microstructure as previously discussed in microstructural study section.

3.2 PZT Thick Film Study

Figure 11 shows XRD patterns of PZT powders fired at 800°C for 4 hours. It can be seen that the XRD patterns showed the coexistence of the two perovskite phases (tetragonal and rhombohedral phases). The coexistence of tetragonal and rhombohedral phases always occured in $Pb(Zr_xTi_{1-x})O_3$ near the morphotropic phase boundary composition ($0.52 \leq x \leq 0.55$) when prepared by solid-solid reaction among the constituent oxides [14]. The PSD of PZT powders, which were analyzed by relative distribution of volume of particles in the range of particle diameters, showed 90% by volume of PZT powder was less than 0.9 μm in size. These powders were believed to be suitable for preparation of sol-gel PZT based composite for use as ink paste in screen printing.

In this study, the paste composition of thick film was composed of sol-gel PZT solution and PZT powders. The sol-gel PZT solution at a concentration of 0.88M served as an organic vehicle. Ink paste rheology of thick film should exhibit pseudoplastic or thixotropic property in which viscosity is an inversion function of shear rate. Therefore, viscosity of paste which strongly affected the print ability was controlled by wt% solid in the paste. In addition, more vol% solid yielded high density fired films. When %solid loading was more than 75% by weight, the mixture was not able to be ball milled effectively to a homogeneous paste. Therefore, % solid was varied from 70 to 75% by weight. Figure 12 shows the relationship between the shear stress and shear rate of pastes at different %solid loading. These results indicated that this paste was pseudoplastic. A summary of print ability of three compositions of paste is shown in Table 1.

Table 1 A summary of printability of three different pastes.

%solid loading	The range of shear rate (sec^{-1})	The range of viscosity (Pa*sec)	Printability and surface
70	0.102-0.340	18.6-23.5	unable to print, viscosity was too low
72.5	0.017-0.102	58.6-118	printable, not smooth pattern
75	0.017-0.102	35.0-172	printable, better smoothness on surface

4. Conclusions and Future Work

The sol-gel PZT thin films with good electrical properties were successfully fabricated by the addition of 10 mole% excess Pb into polymeric complex Pb,Zr,Ti-methoxyethoxide solution and then annealed at 700°C for 30 minutes. The microstructure evolution was examined using a FE-SEM. The SEM micrograph showed nearly a single perovskite phase and dense microstructure. The results were in good agreement with the XRD data. In addition, the reasonable electrical properties indicated that controlling the microstructure evolution and the phase development by exploration of annealing conditions and the amount of excess Pb were very important for the optimization of electrical properties. Besides, Thick film fabrication was accomplished by dispersing 75%by weight of PZT powders in 0.88M PZT sol-gel solution. Pseudoplastic pastes showed no signs of any difficulty for screen-printing.

5. Acknowledgement

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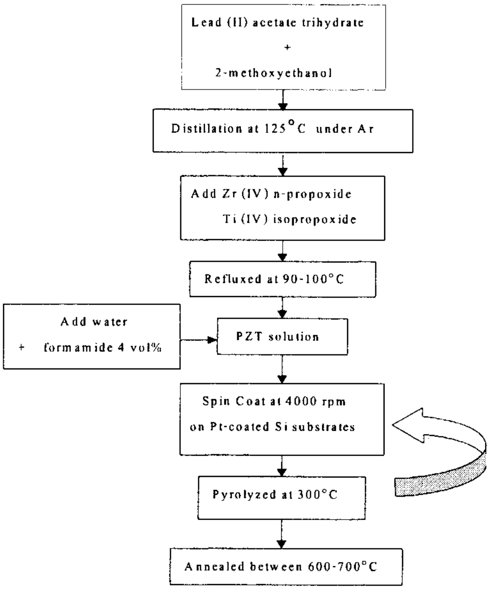


Figure 1 A schematic chart of sol-gel processing and the PZT thin film preparation.

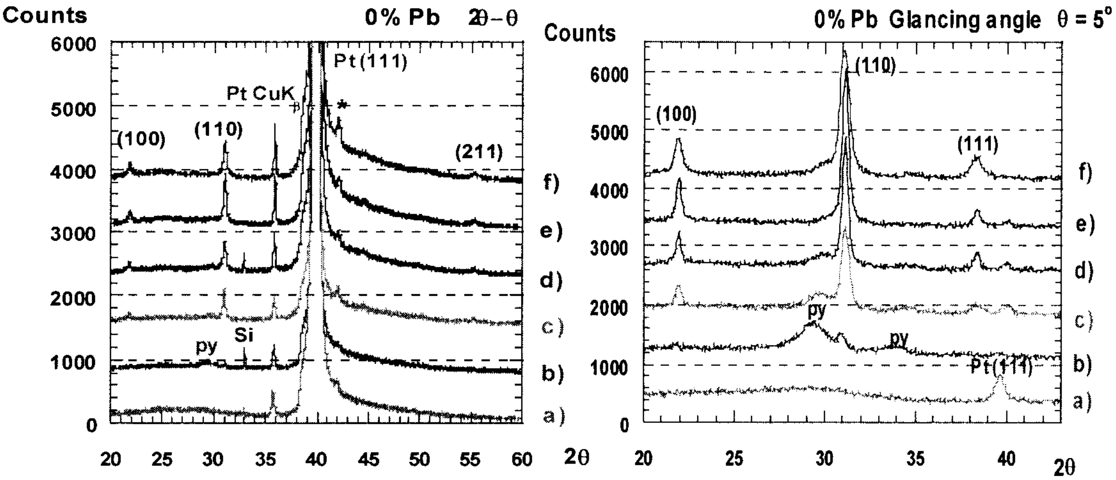


Figure 2 XRD patterns of PZT films with an addition of 0 mole% excess Pb made from different annealing conditions: (a) as-deposited film, (b) the PZT film annealed at 550°C for 30 minutes, (c) 600°C for 30 minutes (d) 650°C for 30 minutes, (e) 650°C for 60 minutes and (f) 700°C for 30 minutes.

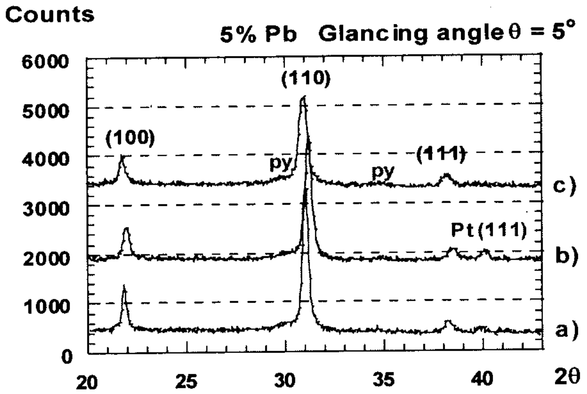


Figure 3 XRD patterns of PZT films with an addition of 5 mole% excess Pb made from different annealing conditions: (a) films annealed at 650°C for 30 minutes, (b) 650°C for 60 minutes and (c) 700°C for 30 minutes

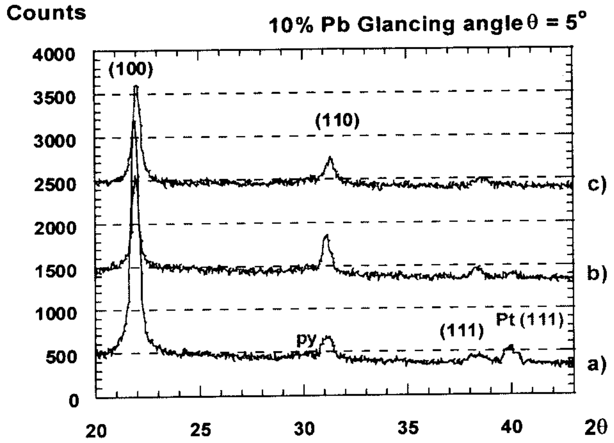


Figure 4 XRD patterns of PZT films with an addition of 10 mole% excess Pb made from different annealing conditions: (a) films annealed at 650°C for 30 minutes, (b) 650°C for 60 minutes (c) 700°C for 30 minutes

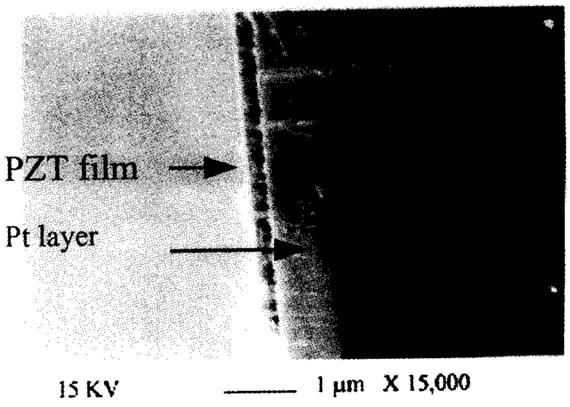


Figure 5 SEM micrograph of 5-layer-deposited PZT films on Pt-coated silicon substrate

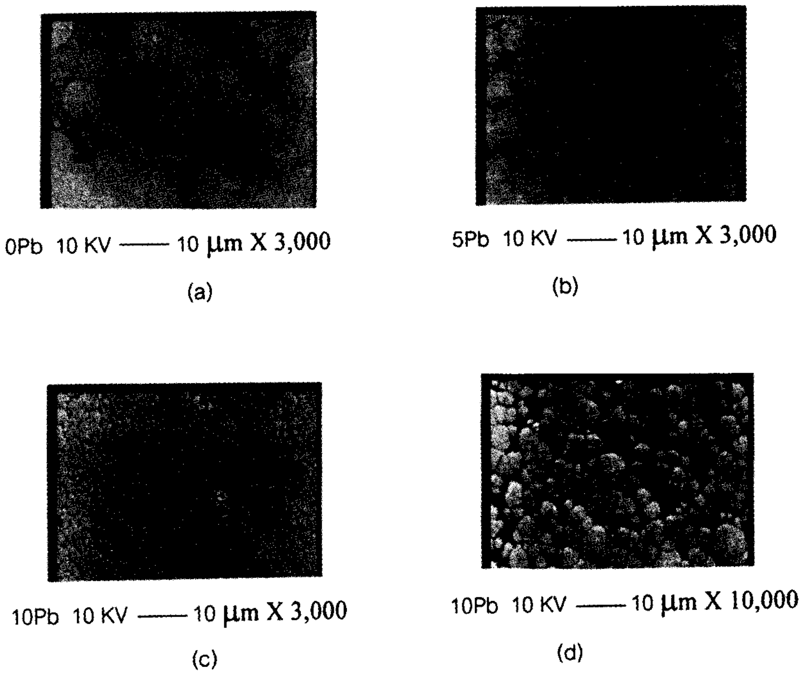


Figure 6 Micrographs of PZT thin films annealed at 650°C for 30 minutes: (a) 0 mole%, (b) 5 mole%, (c) and (d) 10 mole% excess Pb

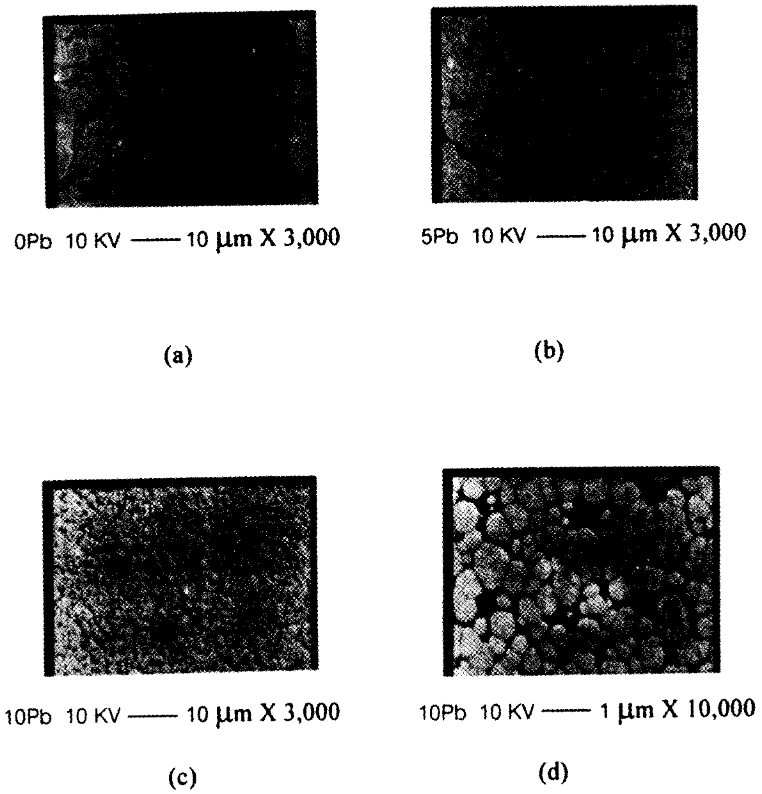
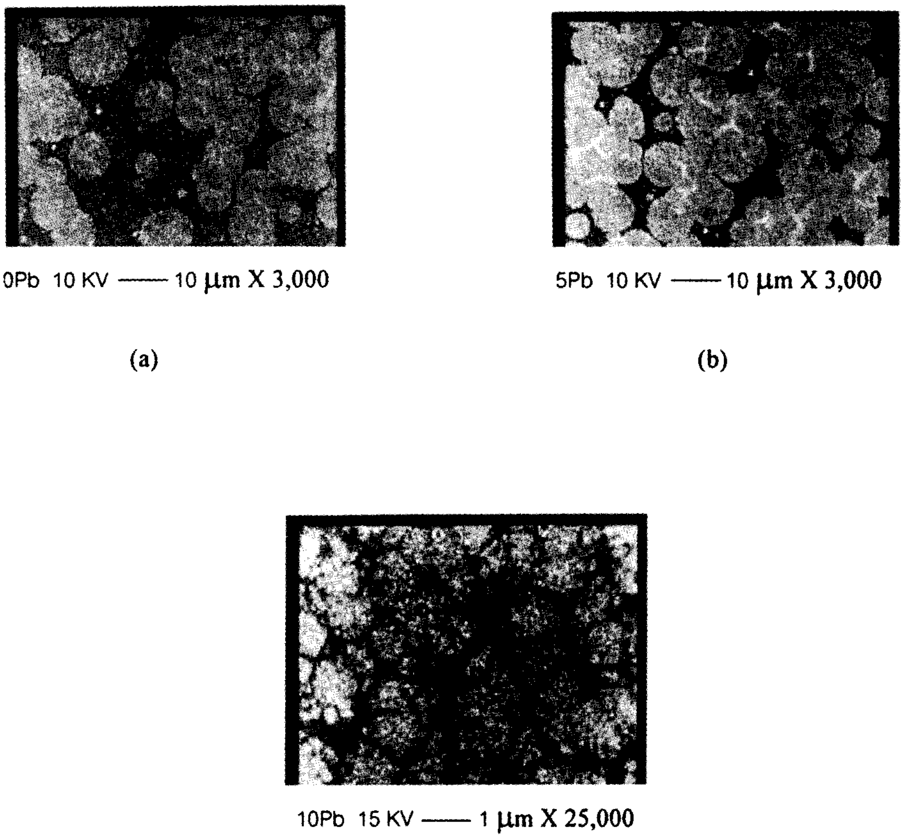


Figure 7 Micrographs of PZT thin films annealed at 650°C for 60 minutes: (a) 0 mole%, (b) 5 mole%, (c) and (d) 10 mole% excess Pb



(a)

(b)

(c)

Figure 8 Micrographs of PZT thin films annealed at 700°C for 30 minutes : (a) 0 mol% (b) 5 mol% and (c) 10 mol% excess Pb

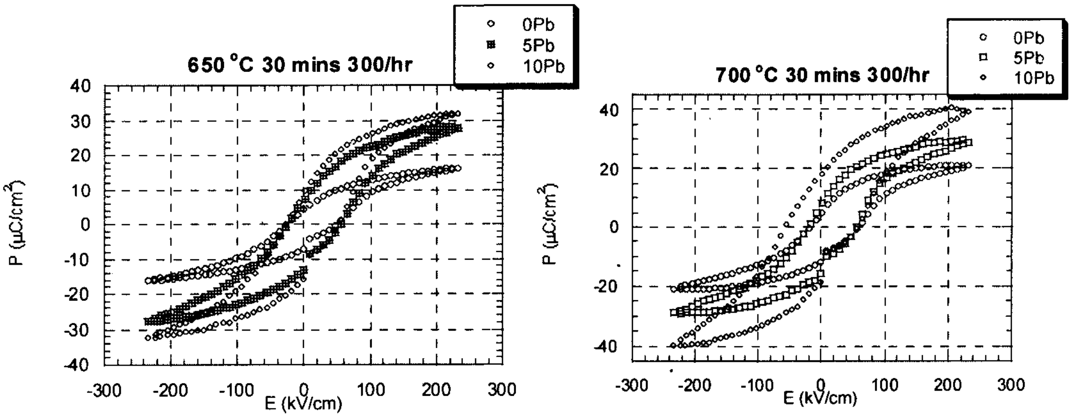


Figure 9 The hysteresis loops of sol-gel PZT thin films containing excess Pb ranging from 0 to 10 mole%: (a) films annealed at 650°C and (b) films annealed at 700°C for 30 minutes.

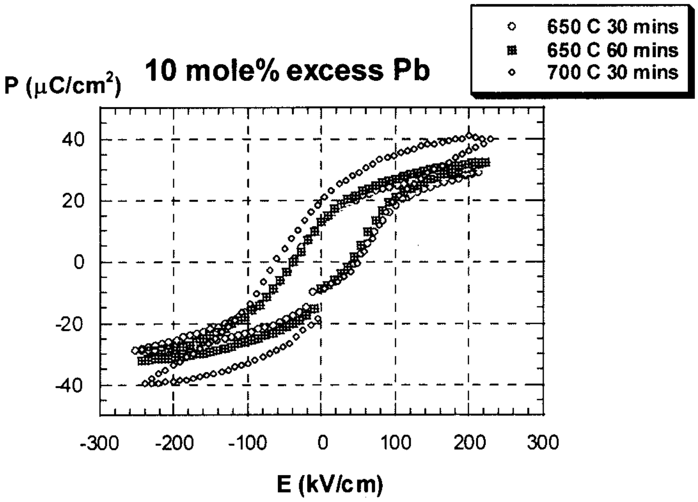


Figure 10 The hysteresis loops of sol-gel PZT thin films with 10 mole% excess Pb at different annealing conditions.

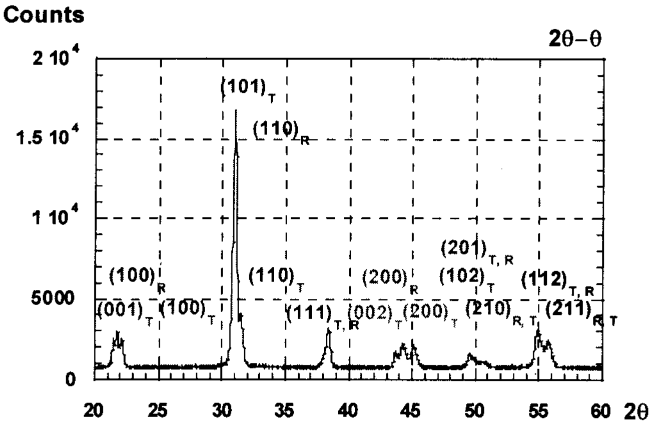


Figure 11 XRD pattern of PZT powders sintered at 800°C for 4 hours.

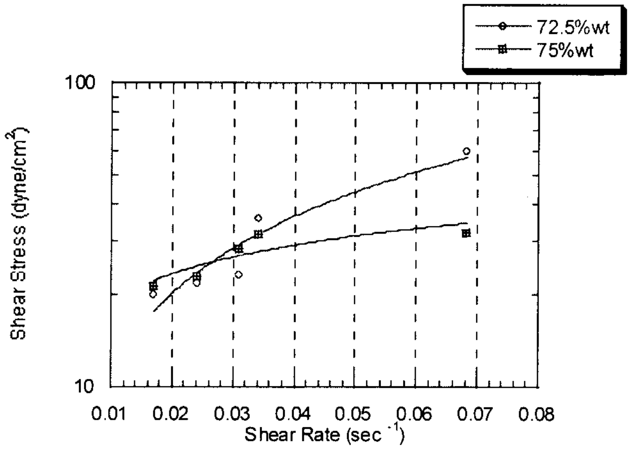


Figure 12 The relationship between the shear stress and shear rate of different pastes.

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