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Microstructural development and electrical properties of lead zirconate titanate composite films

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Dihydroxyalcohols (DIOL route) and 2-methoxyethanol (MOE route) are two of the most commonly used solvents in preparing sol-gel lead zirconate titanate (PZT) films. The employment of the PT(MOE) film as a buffer layer for PZT(DIOL) films not only offers advantages of more precise film thickness and better adhesion to substrate, but also reduces the crystallization temperature, improves the surface smoothness, and increases the grain size of the PZT(DIOL)/PT(MOE) composite films. The PT (MOE) buffer layer also improves electrical properties, such as polarization-electric field behavior, fatigue endurance, and leakage behavior, of PZT films. © *2006 Springer Science + Business Media, Inc.*

1. Introduction

Lead zirconate titanate (PZT) films exhibit excellent ferroelectric, piezoelectric, pyroelectric and dielectric properties. They are therefore useful in applications such as nonvolatile memory, electromechanical and imaging devices [1]. Controlling the thickness and roughness of the films is important in frequency-tuning applications, including film bulk acoustic wave resonators. The thickness of the films determines the resonating frequency, while the roughness of the films greatly influences the loss of bulk acoustic waves. The thickness of PZT films required in this kind of application is approximately 1 μm in the frequency band of about 1.5 GHz [2]. It takes a long time to fabricate PZT films with a thickness in the order of 1 μm by methods such as sputtering. Sol-gel processing is well known to provide the advantages of low cost, precise control of composition, the ability to fabricate a large area and high reproducibility. The thickness of the films can be controlled in several ways like the viscosity of the precursor or the speed of spin coating. The viscosity of the precursors depends strongly on the type of the solvent, the concentration of the solutes and the type and amount of additives. Sol-gel processes that adapt 2-methoxyethanol (MOE route) [3–5] and dihydroxyalcohols (DIOL route) [6–9] as solvents are two of the most frequently used systems. The MOE and DIOL routes yielded films with a thickness of approximately 0.03–0.1 and 0.5–1 μm, respectively in their mostly used ranges of concentration. Using the MOE route to create a film with a thickness in the order of 1 μm is very tedious and time-consuming. The PZT films with a thickness of over 1 μm are easy to prepare by the DIOL route, but the thickness cannot be precisely controlled and the film adhesion to the substrate is poor. In contrast, the adhesion of MOE films to the substrate is better than that of DIOL films. If PZT films fabricated by the MOE route are used as buffer layers for PZT films deposited by the DIOL route, the precision of the thickness can be controlled to within 0.01–0.03 μm and the adhesion of the spin-coated PZT films can be greatly improved.

Furthermore, the crystallization of the perovskite phase in these two types of PZT films occurs at different temperatures. It is interesting to study the effect of this MOE buffer layer on crystallization, microstructure, and electrical properties of the resultant PZT composite films. Since PZT films with higher Ti/Zr ratio crystallize at lower temperatures, the composition of the MOE film was chosen as $PbTiO_3$ (PT) to enhance the effect of the MOE buffer layer on the microstructural development of the resultant films.

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This study reports and discusses the effect of the MOE PT buffer layer on the resultant microstructure and electrical properties of the PZT composite films.

2. Experimental procedures

The preparation of PZT films by DIOL and MOE routes has been described elsewhere [9–11]. The starting materials of the DIOL route are lead acetate trihydrate, zirconium *n*-propoxide, titanium diisopropoxide bispentanedionate, acetylacetone and 1, 3 propanediol [9]. The starting materials of the MOE route are lead acetate trihydrate, titanium isopropoxide and 2-methoxyethanol [11]. The substrate used in this investigation is $LaNiO_3$(LNO)/Pt/Ti/SiO_2/Si. For the sputtering of LNO [12], the LNO targets were made by sintering of calcined powder at 1000°C for 3 h using conventional mixing-oxides method. Sputtering was carried out at a power of 2.5 W/cm^2 with a high purity gas composed of 25% O_2 + 75% Ar under a working pressure of 10 mTorr at 350°C. The thickness of LNO was 100 nm. The thick PZT ferroelectric films were fabricated by the DIOL route to have a composition of $Pb(Zr_{0.53}/Ti_{0.47})O_3$ (PZT) plus 15% excess PbO. The composition of the other MOE film used for controlling the thickness and improving film adhesion, was chosen as $PbTiO_{3,}$ which is well known to crystallize at a lower annealing temperature than PZT films [13]. The film formed by the MOE route had a composition of $PbTiO_3$ (PT) with 15% excess PbO to compensate for lead loss. Two films were prepared: one comprised a single layer of PZT(DIOL), and the other comprised a layer of PZT(DIOL) and a layer of PT(MOE). After the remnant organics decomposed, the films were annealed at 550–700°C for 20 min in an atmosphere of oxygen. The thickness of the PZT (DIOL) film and the composite PZT(DIOL)/PT(MOE) film was 0.50 and 0.53 μm, respectively. The thickness of each layer of PT(MOE) film was 0.03 μm, therefore, the total thickness of the composite film was simply the sum of the two component films. Top electrodes were Pt dots of 100 μm diameter, which were dc-sputtered on the PZT films. The polarization-electric field (P-E) hysteresis loops were performed with a RT66A ferroelectric tester from Radiant Technologies. An HP8116A pulse generator, which generates ± 10 V, 1 MHz square waves, was externally connected to a Radiant Technology RT-66A test system to measure fatigue characteristics. The leakage behavior was measured with a HP 4140B pA meter/DC voltage source.

3. Results and discussion

3.1. Microstructural development

The crystal structures of ferroelectric films were determined by X-ray diffraction (XRD) with Cu K_α radiation. Fig. 1a and b present the XRD patterns of PZT(DIOL) and PZT(DIOL)/PT(MOE) films grown on LNO/Pt electrodes at 550–700°C for 20 min. The PZT(DIOL) film grown at 550°C comprised a pyrochlore phase; the perovskite phase was initiated at 600°C. In contrast, the perovskite phase became the dominant phase in the PZT(DIOL)/PT(MOE) film at 550°C. The crystallization temperature of the perovskite phase was thus reduced by approximately 50°C with the presence of the PT(MOE) buffer layer. The PT(MOE) layer transformed into perovskite phase at approximately 450°C. The perovskite in the PT(MOE) layer was able to enhance the crystallization of perovskite in the PZT(DIOL) layer, which resulted in the lower crystallization temperature of the PZT/PT composite films than that of PZT(DIOL). The intensity of (100) peak of the perovskite phase in the PZT(DIOL)/PT(MOE)/LNO composite film annealed at 650°C was distinctly higher than those of the films annealed at other temperatures. It was most likely because the (100) orientation of the perovskite phase grew much faster than other directions at this temperature that the film was much highly (100) oriented. The intensity of the (110) peak of the 650°C film was lowered as compared with those observed for 600 and 700°C-annealed film.

Fig. 2 presents the surface microstructures of these two films annealed at 650°C and observed by scanning electron microscopy, indicating that the PZT/PT composite film has an average grain size which is much larger (about 0.45 μm) than those in the single PZT film (about 0.15 μm). Earlier studies reveal that PZT films with higher Ti content have smaller grains [14]. The larger average grain size of the PZT/PT composite film than that of the single PZT film cannot be explained as a simple, additive phenomenon. To clarify the growth mechanism of the composite films, further observation of the cross-section image of the films by TEM or SEM will be helpful. It was tentatively speculated that the crystallization of perovskite phase was originated from the PT (MOE) buffer layer. The perovskite phase in the PZT layer crystallized heterogeneously on areas where the perovskite in the PT layer touched the PZT layer. Since the heterogeneous crystallization of the perovskite in PZT layer only occurred on areas touched by perovskite of the PT layer, the perovskite not only propagated vertically but also horizontally in the PZT layer, yielding large grains in the PZT.

The roughness of the PZT(DIOL)/PT(MOE) and PZT(DIOL) films is approximately 2.0 nm and 6.5 nm, respectively as determined by atomic force microscopy. The PT(MOE) buffer layer improves the roughness of the ferroelectric PZT(DIOL) films. The improvement of roughness was not observed in the pure DIOL route with PT(DIOL) [12] introducing as a seeding buffer layer, i.e. PZT(DIOL)/PT(DIOL) films. The perovskite phase crystallizes at lower temperature in the PT(MOE) film than in the PT(DIOL) film, approximately 450 and 500°C, respectively. The higher the difference of the crystallization temperature between the PZT and PT layers is, the more the perovskite crystallization depends on the PT layer, and the more effective the PT buffer layer on the microstructural development of the PZT films is. When crystallization temperatures of these two layers are close, perovskite phase tends to form at the same time in both layers

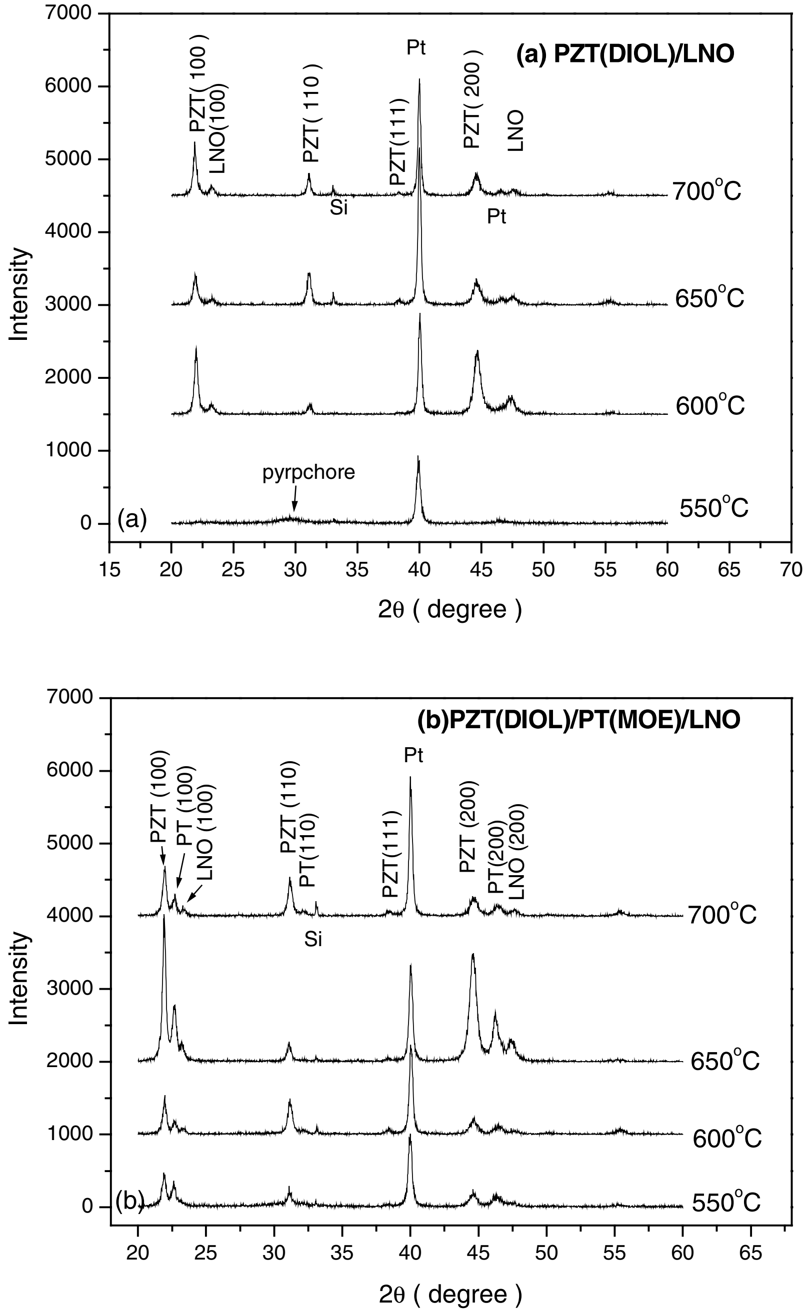

Figure 1 XRD patterns of (a) PZT(DIOL) and (b) PZT(DIOL)/PT(MOE) films annealed at 550–700°C for 20 min.

separately. Consequently, the crystallization of perovskite in the PZT layer becomes independent of the PT buffer layer. Thus no improvement of surface roughness in the pure DIOL PZT/PT film has been found. The improvement of surface roughness in the PZT(DIOL)/PT(MOE) composite film is advantageous for high- frequency microelectronic applications, which generally requires a smooth surface to eliminate high-frequency energy loss.

3.2. Electrical properties

Fig. 3 shows that the PZT/PT composite film has almost the same coercive field ($E_C = 52.0$ kV/cm) as, and a higher remanent polarization ($P_r = 21.1$ μC/cm^2) than the single PZT film (49.0 kV/cm, 16.4 μC/cm^2). PT films typically have much higher coercive fields and lower remnant polarizations than PZT films. The combined PZT/PT film should theoretically have a much higher apparent coercive field and lower apparent remnant polarization than the single PZT film. While inter-diffusion of Zr and Ti between layers is possible, the mean composition generally corresponds to a lower Pr and a higher *Ec* than the $Pb(Zr_{0.53}Ti_{0.47})O_3$ film. The improvement of ferroelectric behavior of the composite PZT/PT film is attributed to its increasing grain size enhanced by the PT(MOE) layer. Large grains provide the advantage of lowering the

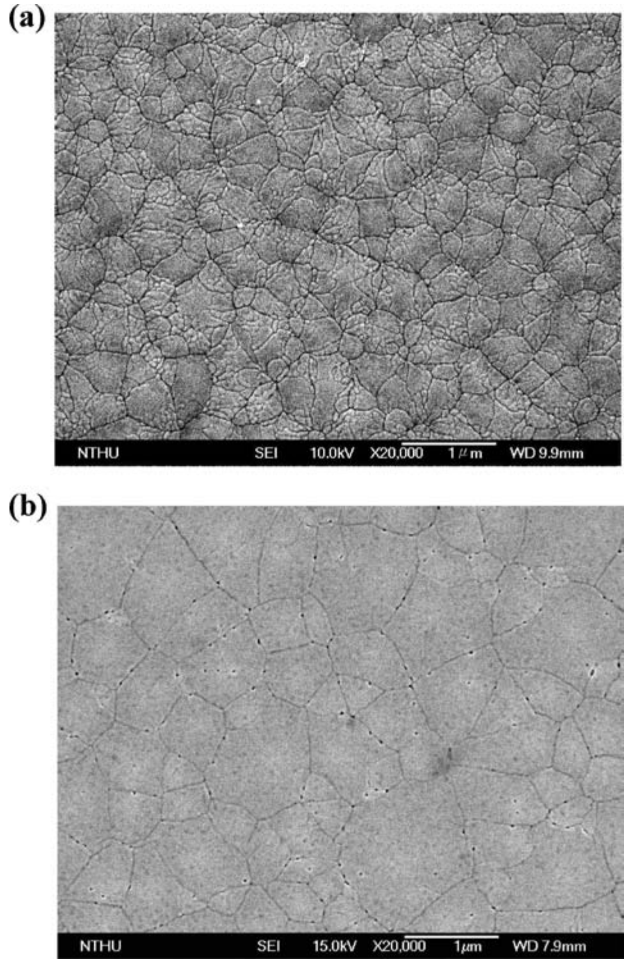

Figure 2 Scanning electron micrographs of (a) PZT(DIOL) and (b) PZT(DIOL)/PT(MOE) films annealed at 650°C for 20 min.

coercive field (E_C) and raising the remnant polarization (P_r) of PZT films.

Fig. 4 illustrates the degradation of the normalized switchable polarization $\pm(P^* - P^\wedge)$ as a function of the number of electric switching cycles. P^* represents the switching polarization between the two pulses with opposite polarity and $P^\wedge$ represents the nonswitching polarization between two pulses with the same polarity. The data of a single PZT(DIOL) film on Pt/Ti/SiO_2/Si substrate were plotted in Fig. 4 for comparison. The switchable polarization clearly declines after 10^6cycles for the PZT film on the bottom Pt electrode; the fall is around 23% after 10^6,cycles and over 60% after 10^9cycles. In contrast, the switchable polarization of both PZT and PZT/PT films on the LNO electrode only slightly changes even after10^9cycles. The improvement is mainly due to the LNO electrode [15] which greatly improves the fatigue endurance of the PZT ferroelectric films. Notably, the PT(MOE) buffer layer does not negatively influence the polarization endurance of the ferroelectric films.

Fig. 5 shows the current density against the electric field of the PZT and PZT/PT films. The figure demonstrates a pronounced improvement of the leakage behavior with the PT buffer layer. Both the single PZT and the PZT/PT composite films exhibit low leakage current density (around 5×10^{-8} A/cm^2) at electric fields below 100 kV/cm but the PZT(DIOL)/PT(MOE) composite film has a much higher breakdown strength (of around 300 kV/cm), which is about one and half times that of the single PZT film. A higher Ti content in the PZT film is generally believed to be associated with a larger leakage current density, because the variable valence of Ti ions (Ti^{+3}, Ti^{+4}) causes electron hopping. However, the incorporation of a PT(MOE) layer improves the leakage behavior of the PZT(DIOL) film. The increase of the

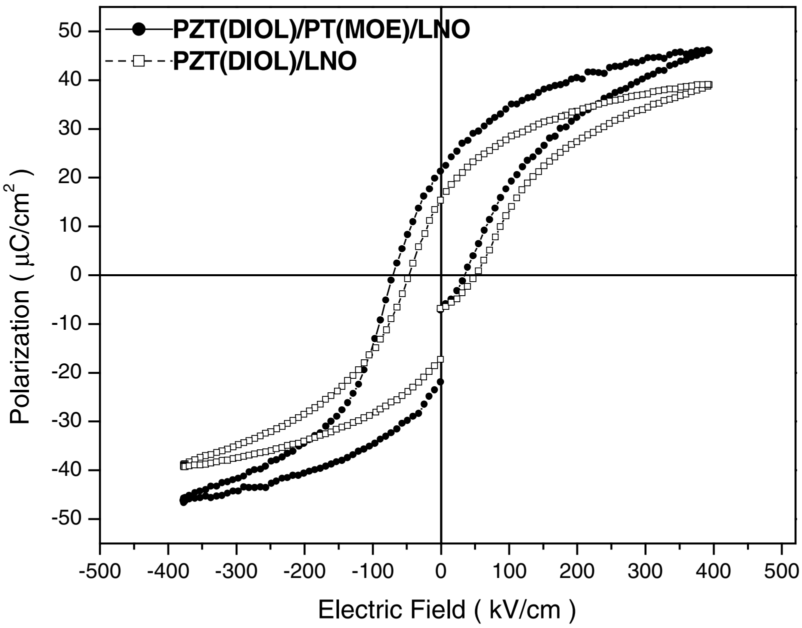

Figure 3 P-E hysteresis curves of PZT(DIOL) and PZT(DIOL)/PT(MOE) films annealed at 650°C for 20 min.

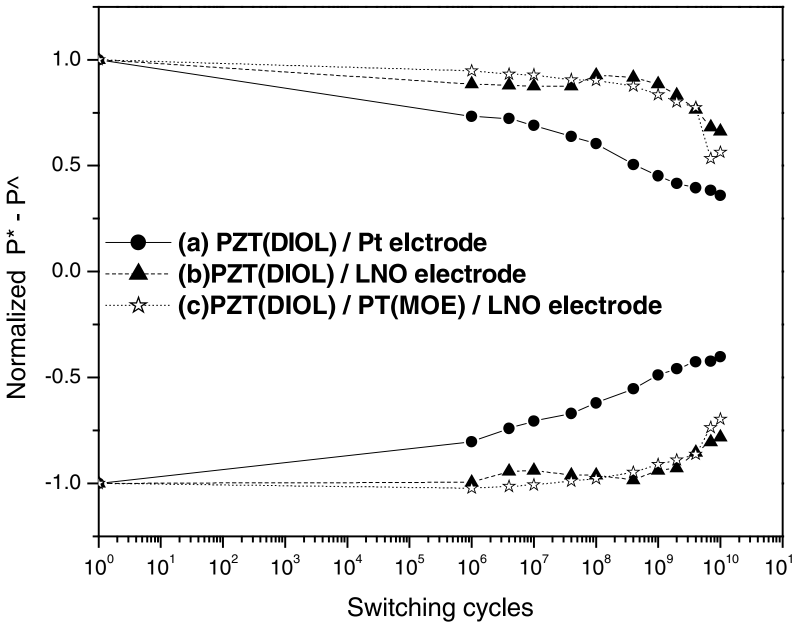

Figure 4 Fatigue endurance of PZT(DIOL) and PZT(DIOL)/PT(MOE) films annealed at 650°C for 20 min.

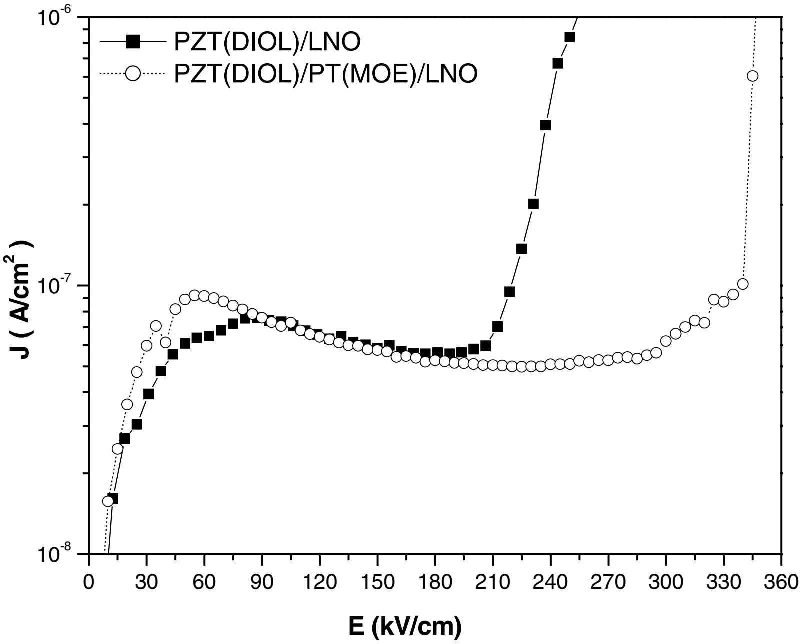

Figure 5 J-E curves of PZT(DIOL) and PZT(DIOL)/PT(MOE) films annealed at 650°C for 20 min.

breakdown strength is believed to be caused by the microstructural characteristics of the PZT(DIOL)/PT(MOE) film. The smoother surface of the PZT(DIOL)/PT(MOE) film results in higher breakdown strength and the larger grains of the film provide less leaking grain boundary paths. Both characteristics tend to improve the leakage behavior.

4. Conclusions

We demonstrated that the PT (MOE) buffer layer not only offers advantages of more precise thickness and better adhesion, but also reduces the crystallization temperature, improves the surface smoothness, and increases the grain size of the PZT(DIOL)/PT(MOE) composite films, in comparison with a single PZT (DIOL) film alone. These characteristics are important in ensuring compatibility with semiconductor technology and high-frequency tuning microelectronic applications. The PT (MOE) buffer layer also improves electrical properties, such as polarization-electric field behavior, fatigue endurance, and leakage behavior, of PZT films.

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