A study on the microstructure of preferred orientation of lead zirconate titanate (PZT) thin films

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The lead zirconate titanate (PZT) thin films were fabricated using sol-gel spin coating onto Pt/Ti/glass substrates. Effects of the holding time for pyrolysis and the coating cycle on the preferred orientation of the PZT thin films were studied. The films were fabricated with different coating cycles (3, 5, 7, 9, 11), dried at 330 °C for different holding times (5, 30, 60 min), and then annealed at the same temperature of 650 °C using rapid thermal annealing (RTA). The preferred orientations of the films were investigated using x-ray diffraction and glancing angle x-ray diffraction. The microstructure and the selected area diffraction pattern of the PZT thin films were also investigated using scanning electron microscopy (SEM) and transmission electron microscopy (TEM), respectively.

I. INTRODUCTION

Sol-gel and metal-organic decomposition (MOD) processes currently attract much attention because of high purity, large deposition area, and easy composition control for the preparation of lead zirconate titanate (PZT) thin films. Earlier studies on the fabrication of PZT thin film using the sol-gel method mainly concentrated on the transformation of the amorphous gel film to the perovskite phase during annealing. The perovskite transformation of the sol-gel processed PZT thin film has been reported to be controlled by the nucleation in the other studies.\(^1,2\) Since the nucleation is the rate-limiting step in the perovskite transformation, the creation of numerous heterogeneous nucleation sites is important to achieve the perovskite phase formation. The Pt/Ti layer has been known to serve as the nucleation site and to affect the perovskite transformation of the PZT thin films deposited on the Pt/Ti/SiO\(_2\)/Si substrate.\(^3,4\) Therefore, the most frequently reported substrate material is Pt/Ti/SiO\(_2\)/Si. Other factors, such as composition (Zr/Ti ratio), heating rate, annealing temperature, drying condition, and water content, which affect the transformation of perovskite phase, have been reported.\(^2,5-9\)

Recently, many studies on the control of the preferred orientation of the PZT films on various substrates have been reported because the preferentially oriented or epitaxial films show better electrical properties: the P-E hysteresis and the pyroelectric coefficient.\(^10-12\) We have fabricated (100) and (111) oriented PZT thin films on Pt/Ti/glass substrates using the sol-gel method.\(^11\) Brooks and co-workers also reported the fabrication (100) and (111) oriented PZT thin films on Pt/Ti/SiO\(_2\)/Si using the sol-gel method.\(^13\) However, the mechanism of the preferred orientation formation of sol-gel derived PZT thin films is not fully understood.

In this study, we prepared (100) and (111) oriented PZT thin films on Pt/Ti/glass substrates using sol-gel spin coating. Effects of the holding time for pyrolysis and the coating cycle on the orientation of the PZT thin films were studied. The films were fabricated with different coating cycles (3, 5, 7, 9, 11), dried at 330 °C for different holding times (5, 30, 60 min), and then annealed at the same temperature of 650 °C using rapid thermal annealing (RTA). The preferred orientation of the films was observed using x-ray diffraction. The depth profiling of the preferred orientation of the thin film was measured using glancing angle x-ray diffraction. In order to confirm the depth profiling results, the microstructure and the selected area diffraction of the PZT thin films were investigated using scanning electron microscopy (SEM) and transmission electron microscopy (TEM), respectively. The overall observations were speculated with the microstructure of the preferred oriented PZT thin films.

II. EXPERIMENTAL PROCEDURE

PZT thin films were fabricated using a modification of the sol-gel deposition procedure developed by Budd and co-workers.\(^14\) The precursor solution was prepared from lead acetate trihydrate [Pb(CH\(_3\)COO)\(_2\) \cdot 3H\(_2\)O], zirconium n-propoxide [Zr(C\(_3\)H\(_7\)O)\(_4\)], and titanium iso-propoxide (Ti(CH\(_3\))\(_2\)CHO\(_4\)). The concentration used in this study was Pb\(_{1.05}(Zr_{0.52}, Ti_{0.48})O_{3.05}\). Lead acetate was dissolved in 2-methoxyethanol (CH\(_3\)CH\(_2\)CH\(_2\)OH) on heating for 1 h to remove residual water. Excess Pb (5 mole %) was added to enhance the formation of the perovskite phase and to improve electrical properties. The dehydrated solution was cooled to 100 °C, and the 2-methoxyethanol solutions of Zr-n-propoxide and Ti-isoproxide were added. The solution was again heated...
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FIG. 1. The XRD patterns obtained for the PZT films fabricated with (a) 3, (b) 5, (c) 7, (d) 9, and (e) 11 coating cycles. Refer to the heating schedule in the text.

FIG. 2. The XRD patterns of the PZT films heat-treated at 330 °C for the pyrolysis for (a) 5 min, (b) 30 min, and (c) 60 min. The films were fabricated with 9 coating cycles and finally annealed at 650 °C for 1 min using RTA.

at 110 °C for 2 h to be redistilled, and then refluxed for 10 h to form a complex alkoxide. The final concentration of the solution was adjusted to 0.8 M by addition of 2-methoxyethanol. The stock solution was cooled down to room temperature. A precursor solution for the thin films was prepared by mixing an equal volume of the stock solution and the 2-methoxyethanol solution consisting of water (water/alkoxide ratio, \( r_w = 0.5 \)) and nitric acid (0.04 M). The thin films were deposited by spin-coating at 3000 rpm for 30 s onto Pt/Ti/Corning 7059 glass. After the deposition process, the coated film was dried at 330 °C for different holding times (5, 30, 60 min) for pyrolysis using a small oven. This coating and drying procedure was repeated from 3 to 11 cycles, and the effect of the thickness depending on the coating cycle was investigated on the orientation of the film. The coated films were finally annealed at 650 °C for 1 min in air using rapid thermal annealing (RTA) with a heating rate of about 60 °C/s. The crystalline structures of the obtained PZT thin films were analyzed by x-ray diffraction (XRD) with Cu Kα radiation. The depth profiling of the orientation of the thin film was investigated using glancing angle x-ray diffraction. For the confirmation of the depth profiling of the thin film using glancing x-ray diffraction, the microstructure and the selected area diffraction pattern of the film were observed using SEM and TEM, respectively.

III. RESULTS AND DISCUSSION

Figure 1 shows the XRD patterns obtained for the PZT films fabricated with different coating cycles. All films were dried at 330 °C for 5 min for pyrolysis after the coating at each cycle. These films were finally heat-treated at 650 °C using RTA for 1 min. The patterns show that the grain orientation of the film strongly depends on the coating cycles. All films consist of mainly the perovskite phase without the pyrochlore phase within the detection limit of the XRD. The Pt–Ti intermetallic compound peak was weakly observed. Previous work reported that the Pt–Ti intermetallic compounds on the boundary between Pt and PZT films served as the...
perovskite nucleation site during the heat treatment for the crystallization. The films coated up to seven cycles [Figs. 1(a), 1(b), and 1(c)] show typical XRD patterns of polycrystalline PZT. However, the intensity of the (111) peak significantly increases and those of the other peaks decrease with increasing the coating cycle from nine cycles [Figs. 1(d) and 1(e)]. Compared with the relative peak intensity of the (111) peak of the nine-cycle coated film that of the 11-cycle coated film is higher.

Figure 2 shows the XRD patterns of the PZT films all heat-treated at 330 °C for the pyrolysis, but for different holding times. The films were finally annealed at 650 °C for 1 min using RTA. The film heat-treated for 5 min [Fig. 2(a)] shows a strong (111) preferred orientation. However, the films heat-treated at 330 °C for 30 min and 60 min show (100) preferred orientation [Figs. 2(b) and 2(c)]. The reason for observed orientation change is not known but may be speculated with the amount of the residual acetate content along the skeletal backbone in the dried films. The residue may affect the nucleation and the growth of the perovskite phase. We have studied further to elucidate this change and the details will be published in the near future.

Generally, the standard θ-2θ XRD measurement is employed for the crystallographic analysis of thin films. The x-ray beam usually penetrated the entire portion of the film and a part of the substrate, and the XRD patterns represent both the film and the substrate. Glancing angle XRD uses a thin film attachment to set a very low angle of incidence. This method suppresses the diffraction intensity from the substrate. Therefore, the peaks from the substrate are absent or relatively small in the spectra, and the peak overlap may be eliminated. The depth profiling of the film may also be performed by changing the glancing angle. As the angle decreases, we may get the XRD pattern generated near the surface of the thin films. As the angle increased, the x-ray penetrates deeper inside the film and the substrate, and the resulting XRD pattern represents both the film and the substrate. Figure 3 shows glancing angle x-ray diffraction patterns of a PZT thin film fabricated with nine coating cycles, dried at 330 °C for 5 min, and annealed at 650 °C for 1 min using RTA. From Fig. 1(d) and Fig. 3(f), we knew that the film consisted of mainly the perovskite phase without pyrochlore phase within the detection limit of the XRD and has a strong (111) preferred orientation. But the glancing angle x-ray diffraction patterns show clearly that the film consists of a minor amount of pyrochlore phase. As the glancing angle decreased (as the XRD pattern became to represent the phase information near the surface of the film), the relative intensity of the (111) plane decreased, which indicates that the (111) preferred orientation near the surface is relatively poor.
FIG. 5. TEM micrograph and selected area diffraction (SAD) patterns of (a) upper and (b) lower layers of PZT thin film and (c) Pt layer.

to that of the interface between the film and the substrate. By further reduction of the glancing angle to \( \theta = 1^\circ \) [Fig. 3(a)], Pt peak was not observed, which may indicate that the x-ray did not penetrate the film and that the XRD pattern represents the phase information near the surface of the film. The near surface of the thin film consists of the pyrochlore phase and randomly oriented perovskite grains.

Figure 4 shows the SEM images of the microstructures of the PZT thin films. The surface of the film is smooth and void free [Fig. 4(a)]. Figure 4(b) shows the SEM images of the fracture surfaces of the thin film fabricated with nine coating cycles. The films have a smooth surface. The thickness of the film is approximately 500 nm and consists of two layers. The upper layer consists of small grains. The glancing angle x-ray diffraction pattern of the film [Fig. 3(a)] showed that the upper layer consisted of randomly oriented perovskite grains and minor pyrochlore phase. In contrast, the lower layer shows a typical fracture surface of they crystalline
Figure 3 also showed that the diffraction pattern was changed to (111) preferred orientation as the glancing angle increased (as the penetration depth of the x-ray increased). The observations made in the SEM micrographs of the fracture surface are consistent with those made in the glancing angle x-ray diffraction.

Figure 5 shows the cross-sectional microstructures and the selected area diffraction (SAD) patterns of the PZT thin film of which the glancing x-ray diffraction pattern is shown in Fig. 3. Because the aperture size of SAD is 10 nm, we selected a grain boundary region consisting of several grains for characterizing the phase and the orientation of the grains. Figures 5(a) and 5(b) represent the microstructure and the SAD pattern of the randomly oriented region at the upper layer [Fig. 4(b)] and the (111) oriented region at the lower layer [Fig. 4(b)], respectively. The average grain size of the upper layer is smaller than that of the lower layer, which was also observed in the SEM images (Fig. 4). The SAD patterns are not similar to each other, which may indicate that the orientations of the upper layer and lower layer are not the same. The orientation discrepancy between the upper and the lower layers corresponds to the observations made in the depth profiling using the glancing angle x-ray (Fig. 3) and the SEM images (Fig. 4). Figure 5(c) shows the microstructure and the SAD pattern of the Pt layer. Pt layer shows (111) preferred orientation, and the layer thickness was approximately 180 nm. A Ti barrier layer was not observed between the Pt layer and the glass substrate. Most Ti may diffuse into the Pt layer and form Pt–Ti intermetallic compounds.

IV. CONCLUSION

We have investigated the effects of the holding time of the drying process and the coating cycle on the orientation of the PZT thin film. The PZT thin films were fabricated using sol-gel spin coating onto a Pt/Ti/glass substrate and dried at 330 °C for different coating cycles and holding times of between 5 and 60 min for pyrolysis. Finally, the PZT thin films were annealed at the same temperature of 650 °C using RTA for 1 min. The (111) oriented thin film was obtained using the nine-coating cycle and dried at 330 °C for 5 min. However, the (100) oriented films were obtained using different holding times (30 and 60 min) at the same coating cycle or seven-coating cycle at the same holding time. From the results of depth profiling of thin film using glancing angle x-ray diffraction, we may conclude that the film consists of two layers. The upper layer of the film has randomly oriented grains and pyrochlore phase, but the lower layer has a (111) oriented perovskite crystalline phase.

REFERENCES