Deposition and Characterization of Perovskite $Pb_{1-x}La_x(Zr,Ti)O_3$ (PLZT) Thin Films by Combustion Chemical Vapor Deposition (CCVD)

Y.D. Jiang, T.J. Metzger, X. Xu, T.A. Polley, and A.T. Hunt,
MicroCoating Technologies, Inc., Atlanta, GA

Key Words: Combustion CVD, Electro-optic coating, Electrooptic, Ferroelectric

ABSTRACT

Ferroelectric thin films have attracted attention for applications including nonvolatile ferroelectric random access memory (FRAM), integrated waveguides, optical switches, pyroelectric infrared (IR) detectors and piezoelectric devices. Lead lanthanum zirconate titanate (PLZT) is a leading candidate material for surface optical waveguide devices due to its excellent electro-optic properties including its transparency in the visible and near IR regions of the electromagnetic spectrum. This paper presents the synthesis and characterization of PLZT (10 mol% La, Zr/Ti = 60/40, 10/60/40) thin films on single crystal (100) LAO, (100) MgO and *c*-sapphire (α-Al_2O_3) substrates deposited by the low-cost, open-atmosphere combustion chemical vapor deposition (CCVD) technique. Experimental results show that both deposition temperature and substrate materials play critical roles in determining the PLZT film quality. Pole figure measurements reveal that PLZT films were epitaxially grown on both LAO and MgO substrates. However, only textured PLZT films with multi-orientations were obtained on *c*-sapphire. The surface roughness (RMS) of PLZT film deposited at 975°C on *c*-sapphire is about 2.25 nm at a thickness of about 400 nm. Electro-optic and optical properties of PLZT films are still being investigated.

INTRODUCTION

Lead-based ferroelectric materials such as lead zirconate titanate ($Pb(Zr,Ti)O_3$, PZT), a member of the perovskite structure family with a general formula ABO_3, is a solid solution of lead titanate ($PbTiO_3$, PT) and lead zirconate ($PbZrO_3$, PZ) with different Zr/Ti ratios. It is well known that their physical properties can be modified by changing the Zr/Ti ratio and substituting a part of Pb ion by trivalent ions. Among the trivalent dopants, lanthanum (La) has been found the most suitable element for increasing the density and other physical properties of the materials [1,2] . PZT and La doped PZT (PLZT) have been extensively investigated for applications, such as dynamic random access memories (DRAM) [3,4], nonvolatile ferroelectric random access memories (FRAM) [5,6], sensors and actuators for micro-electromechanical systems (MEMS) [7,8], infrared detectors [9,10], electro-optic modulators [11,12], and optical displays [13,14], due to their excellent ferroelectric, piezoelectric, pyroelectric, and electro-optical properties. For these applications, it is essential to grow a highly oriented or epitaxial microstructure in order to reduce leakage current, dielectric loss, and light scattering, and improve dielectric strength. Thus the synthesis and processing of epitaxial PZT and PLZT thin films have been investigated intensively.

PZT or PLZT thin films have been deposited by several traditional techniques, such as sol-gel [2,7,11], metal organic chemical vapor deposition (MOCVD) [10], sputtering [4], and pulsed laser deposition (PLD) [15], on different substrates. There have also been many reports on the effects of deposition conditions of these techniques and post-deposition heat treatments on the material and physical properties of PZT or PLZT films. However, there have been just few reports on the effects of substrates published.

In this study, PLZT thin films were grown on single crystal magnesium oxide (MgO), lanthanum aluminate ($LaAlO_3$, LAO), and *c*-sapphire (α-Al_2O_3) substrates by a novel, open-atmosphere technique, combustion chemical vapor deposition (CCVD). The influence of deposition temperature and substrate on the microstructure and crystallinity of films were then investigated.

Combustion Chemical Vapor Deposition (CCVD)

The innovative, patented CCVD process [16–19], which is proprietary to MicroCoating Technologies, Inc. (MCT), has demonstrated its advantages while yielding equal or better quality coatings than other techniques at a lower cost. The key advantage of the CCVD technology is its ability to deposit thin films in the open atmosphere from inexpensive precursors. Furthermore, there is no need for costly furnaces, vacuum equipment, reaction chambers, etc. A schematic diagram of the CCVD set-up is shown in Figure 1. Typically, precursors are dissolved in a combustible solvent that also acts as the fuel for the flame. This solution is atomized to form submicron droplets by means of the Nanomiser™ technology, proprietary to MCT (patent pending). These droplets are then convected by a supplemental oxygen stream to the flame where they are combusted. A substrate is coated by simply drawing it over the flame plasma containing the activated deposition species. The heat from the flame provides the energy required to evaporate the droplets and for the precursors to react and deposit on the

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substrates. By adjusting solution concentrations and constituents, a wide range of coating stoichiometries and compositions can be achieved. This is especially valuable for achieving the desired composition and thin film characteristics. Furthermore, the CCVD technique uses inexpensive, soluble precursors that do not need to have a high vapor pressure. Hence, precursors for the CCVD process tend to be between 10 and 100 times less expensive than those used in traditional CVD processes. Physical structure and chemical composition of the deposited films can be tailored to the specific application requirements; this greatly facilitates the rational design of thin films.

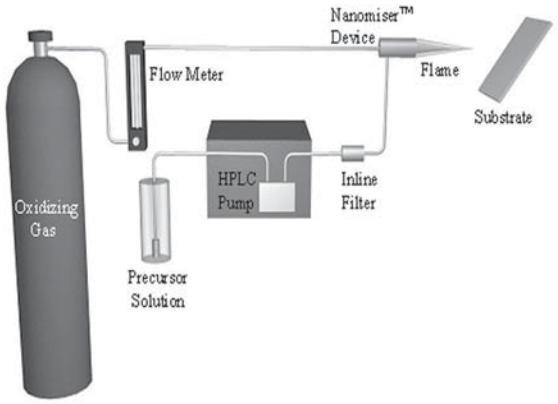


Figure 1: Schematic representation of the open-atmosphere CCVD system showing its major components

In summary, the CCVD technology offers the following capabilities and benefits: no need for a specialized chamber, use of inexpensive precursors, excellent composition control, suitable for continuous production, wide choice of substrates, no line-of-sight limit, straightforward integration into existing production processes, accelerated development cycle for new applications, and environmentally friendly.

EXPERIMENTAL PROCEDURES

PLZT thin films were deposited on cleaved single crystal (100)-MgO, one side polished single crystal (100)-LAO, and two side polished single crystal *c*-sapphire ((0001)) using the CCVD process as represented in Figure 1. Appropriate amounts of lead 2-ethylhexanoate (Strem Chemicals, 41.9% Pb), lanthanum 2-ethylhexanoate (Alfa Aesar, 3.71% La), zirconium 2-ethylhexanoate (Strem Chemicals, 6.0% Zr), and titanium-(di-i-propoxide)-bis(acetyl-acetonate) (Strem Chemicals, 9.9% Ti) were dissolved in organic solvents, such as iso-propanol or toluene to form deposition solutions. The ratio of Zr to Ti was 60:40 and La dopant was 10 mol% in solution, and 5% of extra Pb was added to the solution to compensate the loss of Pb during the depositions due to its high vapor pressure at high temperature. The total cation concentration in solutions was 0.0025 M. The deposition time was typically 30 min at a deposition temperature of 925 – 1025°C. The key process parameters are summarized in Table 1 below.

The substrate temperature was about 200°C lower than the deposition temperature. The distance between flame and substrate was 1-2 cm depending on the deposition temperature. There was no independent heating of the substrates for these depositions. Substrates were ultrasonically cleaned in toluene and rinsed in isopropanol and deionized water prior to depositions.

The constituent phases were identified and pole figure measurements were conducted by X-ray diffractometry (XRD) using a Siemens Hi-STAR area detector XRD system with a Cu K_{α} radiation operated at 50 kV and 40 mA. The cross sectional view and surface morphology were observed by a scanning electron microscope (SEM) with a field emission gun (Hitachi, S-800). Film surface roughness was measured by a optical profilometer (Burleigh Instruments, Inc.).

Table 1: Deposition conditions of PLZT thin films

Deposition Parameters	Value
Deposition temperature (°C)	925-1025
Deposition time (min)	30
Solution concentration (M)	0.0025
Zr to Ti ratio in solution	60:40
La dopant level (mol%)	10
Extra Pb in solution (mol%)	5
Solution flow rate (ml/min)	3

RESULTS AND DISCUSSION

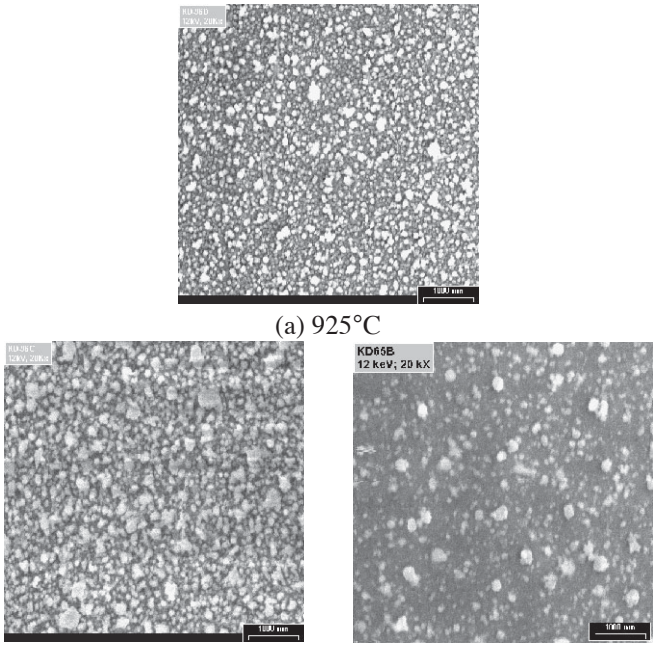
The key CCVD process parameters affecting the film quality include deposition temperature, supplemental oxygen, solution concentration, and atomization of solution. In order to optimize these parameters, the Design-of-Experiments (DOE) statistical protocol was used to study the dependence of film quality on these key process parameters. It was found that the deposition temperature played a critical role in determining the film quality. Therefore, in this study PLZT films were deposited at different temperatures on the three different substrates, respectively, to try to obtain optimized temperature and film quality for each substrate.

PLZT on LAO substrate

LAO has a pseudo-cubic structure with a = 0.379 nm. It is a widely used substrate for depositing ferroelectric and high temperature superconductor materials due to their similar structures and low lattice mismatch. The lattice constant of 10 mol% La doped PZT with Zr/Ti=65/35, which is labeled as PLZT (10/65/35), is 0.4078 nm. Therefore, the lattice mis-

match between LAO and PLZT (10/65/35) is as small as 7%, which is small enough to grow epitaxial films.

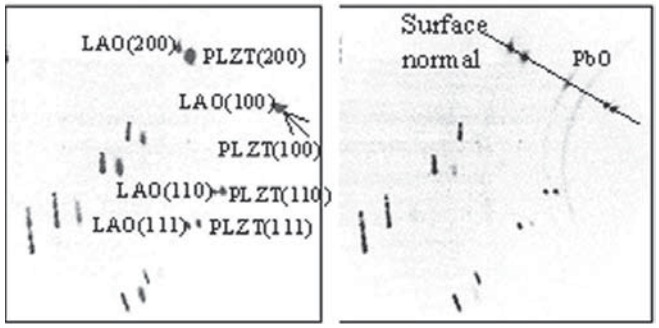
Figure 2 shows the surface morphologies of the as-grown PLZT thin films deposited at different flame temperatures on LAO substrate. It is clear that the PLZT film deposited at 1025°C is dense, although there are some hillocks on the surface. The area detector XRD patterns (Figure 3) show concentrated diffraction spots from the deposited PLZT films that align well with the corresponding diffraction spots of LAO substrate, indicating that the PLZT film was epitaxially grown on (100)-LAO substrate with (100) plane parallel to the substrate surface. There are no other mis-oriented planes such as (110) or (111) aligned to the surface, and no metastable phases such as pyrochlore and other minor phases were found from the PLZT film deposited at 1025°C (Figure 3(a)).



(a) 925°C

(b) 975°C (c) 1025°C

Figure 2: SEM morphologies of PLZT films deposited at different temperatures on LAO substrate



(a) 1025°C (b) 925°C

Figure 3: Area detector XRD patterns of PLZT thin films deposited on LAO at different temperatures

Pole figure measurement is a powerful method to determine the in-plane alignment between the epitaxial film and its substrate. In this study, PLZT (111) reflections were used to perform the pole figure collection and to detect the presence of the in-plane alignment because of its 2θ separation from the LAO (111) plane. As shown in Figure 4, four sharp spots of the PLZT (111) reflections were observed every 90° along the ϕ direction. These results indicate that the PLZT thin film has a perfect epitaxial relationship with the LAO substrate, and the orientation relationship between the PLZT film and LAO substrate is PLZT (100)//LAO(100) and PLZT (110)// LAO(110).

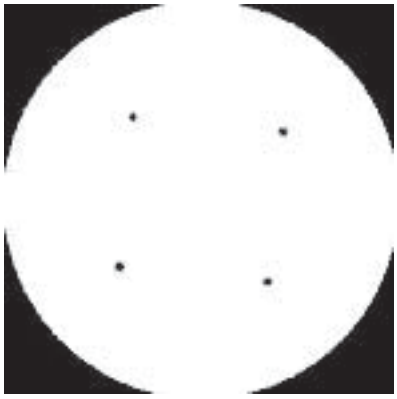


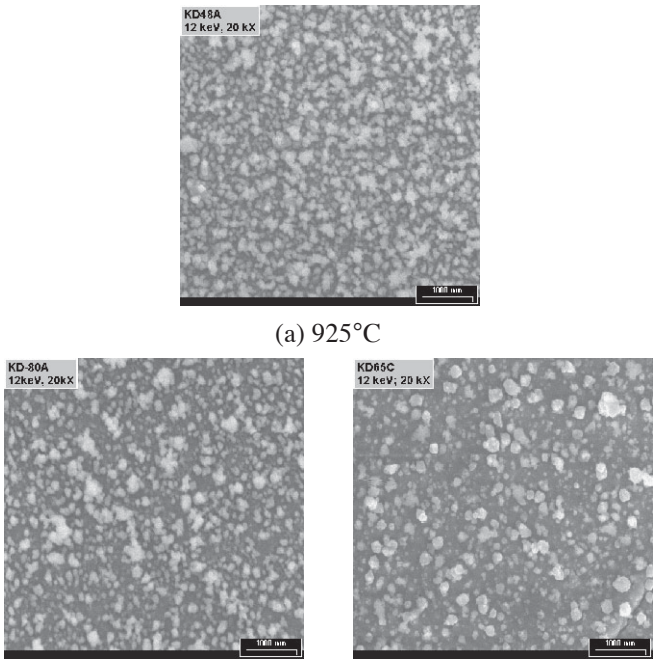
Figure 4: (111) pole figure of a PLZT thin film deposited at 1025°C for 30 min on LAO, showing epitaxial growth of PLZT thin film

The films deposited at lower temperatures (925°C and 975°C) show rough surfaces and microstructures with low density. It was also found from XRD that PbO were present in the PLZT film deposited at 925°C (Figure 3(b)), suggesting that the concentration of Pb precursor in solution was too high for the actual deposition temperature. When the deposition temperature was higher than 1025°C, XRD measurements revealed that a Pb deficient phase was formed in the film because of the increased volatility of Pb at higher temperatures.

PLZT on MgO substrate

MgO has a cubic crystal structure. Its lattice parameter is 0.4213 nm. Like LAO, it is common substrate to deposit epitaxial ferroelectric thin films. The difference between MgO and LAO is that the lattice parameter of MgO is larger than that of PLZT, hence the PLZT film is in a tensile stress state in the PLZT/MgO system. However, the lattice parameter of LAO is smaller than that of PLZT, so the PLZT is in a compressive stress state in the PLZT/LAO system. Also the lattice mismatch between MgO and ferroelectric thin films is even smaller than that between LAO and ferroelectric films. For example, for PLZT (10/65/35), the lattice mismatch is about 4%. Therefore, the growth behavior of PLZT films on MgO substrate could be different from PLZT on LAO.

Figure 5 shows the SEM morphologies of PLZT thin films on cleaved MgO substrates deposited at different temperatures. They have morphologies similar to the PLZT films on LAO. At lower temperatures (925 and 975°C), the PLZT films have very rough and low density surfaces. When the deposition temperature was increased to 1025°C, the film was much denser, but still had some hillocks on the surface. Since the PLZT films were deposited on cleaved MgO substrates, it is difficult to measure the real surface roughness of the films versus deposition temperatures.

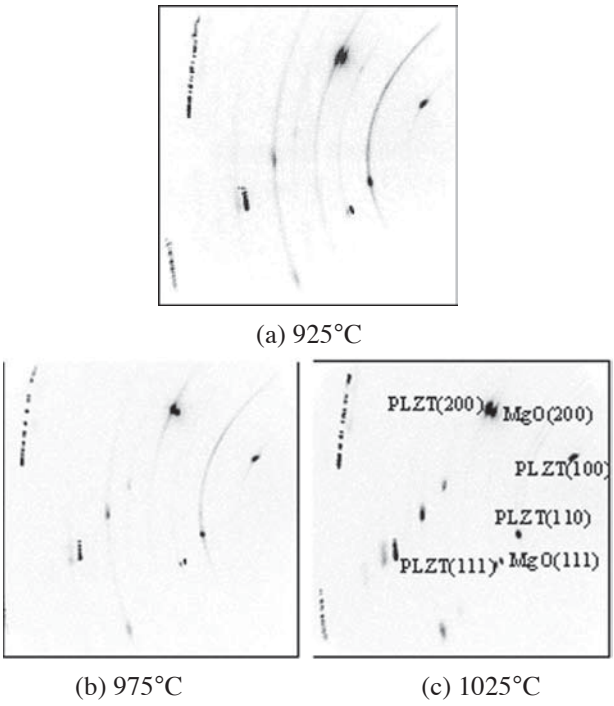


(a) 925°C

(b) 975°C (c) 1025°C

Figure 5: SEM morphologies of PLZT films deposited at different temperatures on MgO substrate

Although PLZT films on MgO show similar morphologies as PLZT films on LAO, their orientations and phases present are different. The area detector XRD patterns of PLZT thin films on MgO are shown in Figure 6. It can be found that [*l*00] orientations of PLZT films are aligned well with the normal surface orientation of the MgO substrate. There are also both in-plane and out-of-plane randomly oriented grains formed at lower temperatures (925 and 975°C). With increasing deposition temperature, the random orientations were decreased, and the diffracted spots from PLZT films became more concentrated, suggesting crystallinity and epitaxy became better. At 1025°C, there was little out-of-plane random orientation, and only minor (110) in-plane random orientation (Figure 6 (c)). For all deposition temperatures on MgO, there were no additional phases detected. The orientation relationship between PLZT and MgO is PLZT(100)//MgO(100). Since the Chi angle between PLZT(100) and PLZT (110) is about 45°, the in-plane orientation relationship between PLZT and MgO is PLZT(110)//MgO(110), although there is no MgO (110) peak because of its extinction.



(a) 925°C

(b) 975°C (c) 1025°C

Figure 6: Area detector XRD patterns of PLZT thin films deposited on MgO at different temperatures

In order to confirm the change of crystallinity and epitaxy of PLZT films on MgO with deposition temperatures, the 2ϕ integration of (110) peaks of PLZT films along the Chi direction was plotted in Figure 7. It is clear that with increasing temperature, the background was reduced, the peak intensity increased, and the peak became narrower, indicating a increased crystallinity and epitaxy. The in-plane epitaxial ratio was calculated by dividing the integration of (110) peak in the Chi range of –81° to –74° by the integration within the whole Chi range. The results are presented in Figure 8. When the deposition temperature increased from 925°C to 1025°C, the in-plane epitaxial ratio of PLZT films increased from 28% to 82%, and the FWHM of the PLZT epitaxial peak decreased from 3.2° to 1.0°, suggesting better epitaxy and crystallinity at higher temperatures.

The epitaxial growth was confirmed by the pole figure measurement performed on the PLZT film deposited at 1025°C using the (111) reflections (Figure 9). Four concentrated spots, which correspond to the (111) poles, were observed at ϕ = 0, 90, 180, and 270°C.

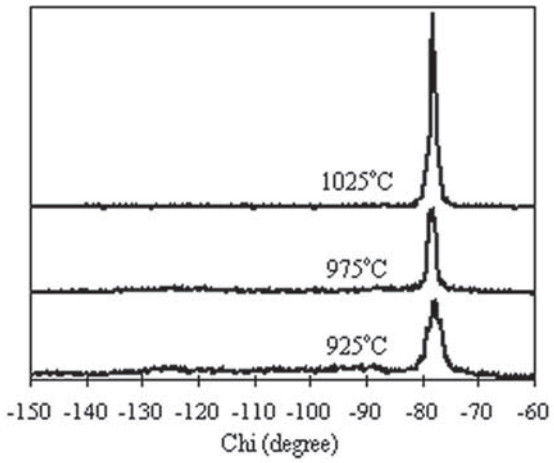


Figure 7: 2 θ integration along Chi direction of PLZT films at different temperatures

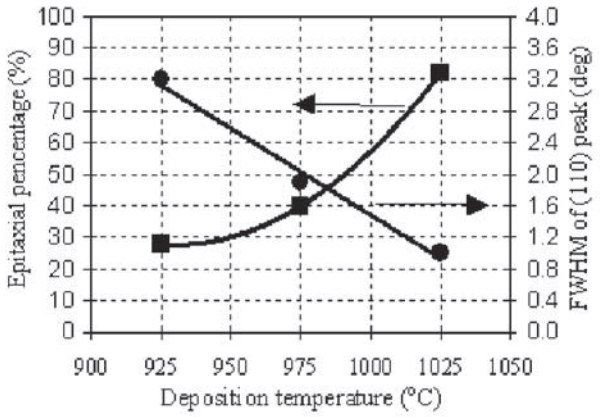


Figure 8: FWHM and epitaxial ratio of (110) peaks of PLZT films at different temperatures

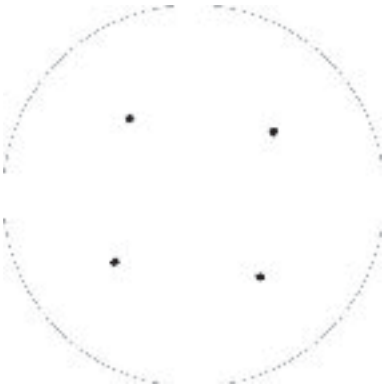
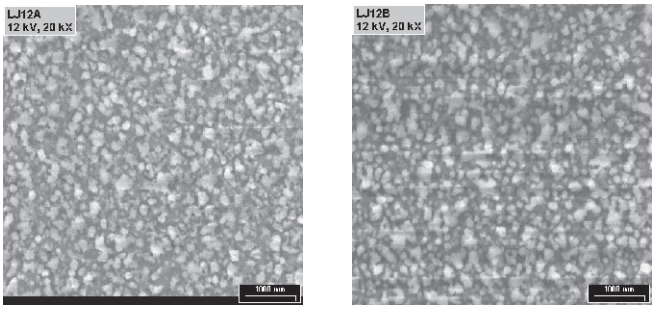


Figure 9: (111) pole figure of a PLZT thin film deposited at 1025°C for 30 min on MgO, showing epitaxial growth of PLZT thin film

PLZT on *c*-sapphire substrate

Sapphire (α-Al_2O_3) has a hexagonal crystal structure with a = 0.4759 nm and c = 1.299 nm. It is widely used to deposit ferroelectric materials for electro-optic applications, since it has smaller refractive indices than those of PLZT, which is necessary for the optical confinement in waveguide devices. Sapphire has a different crystal structure than LAO or MgO. Also, the lattice mismatch between PLZT and sapphire is much larger than those between PLZT and LAO or MgO. Therefore, the growth of PLZT on sapphire is different from that of PLZT on LAO or MgO.

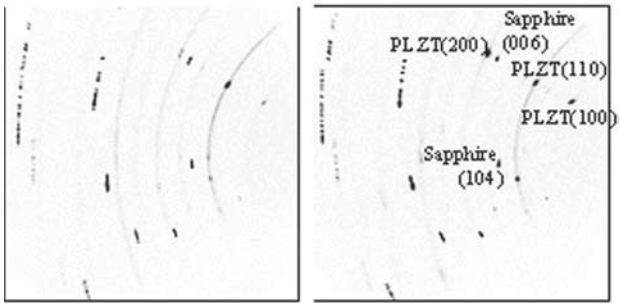
Figure 10 shows the SEM morphologies of PLZT films deposited at different temperatures on sapphire. They are similar to the morphologies of PLZT films on MgO and LAO at lower temperatures, which indicates a different growth behavior of PLZT on sapphire. Optical profilometry measurements showed a surface roughness (root mean square) of ~2.25 nm for 975°C deposited PLZT and 2.90 nm for 1025°C deposited PLZT at a thickness of about 250 nm.



(a) 975°C (b) 1025°C

Figure 10: SEM morphologies of PLZT films deposited at different temperatures on *c*-sapphire

The area detector XRD patterns (Figure 11) show that PLZT film has multi-orientations with a significant amount of random orientation. At 975°C, the textured PLZT film has (100), (110), as well as (111) planes aligned parallel to the substrate surface, while the 1025°C deposited one has just (100) and (110) parallel to the surface. In both cases, (110) is the predominant preferred orientation.



(a) 975°C (b) 1025°C

Figure 11: Area detector XRD pattern of PLZT films deposited at different temperatures on *c*-sapphire

The results reported here are preliminary results of ferroelectric PLZT thin films on LAO, MgO, and sapphire substrates. Deposition conditions, such as solution concentration, composition, and deposition temperature, need to be further optimized to improve the surface roughness and morphologies of PLZT films on LAO and MgO while keeping their epitaxial growth. For PLZT on sapphire, in addition to surface roughness and morphology, crystallinity needs to be further improved to obtain the predicated (111) epitaxial growth [14].

SUMMARY

Ferroelectric PLZT thin films have been successfully deposited on LAO, MgO, and *c*-sapphire using the combustion chemical vapor deposition technique and inexpensive precursors. Both the deposition temperature and substrate material have significant effects on the film quality, such as morphology and epitaxy. For LAO and MgO substrates, depositions at 1025°C led to epitaxial growth of PLZT thin films, however, for sapphire substrates, only textured PLZT films were obtained at both 975 and 1025°C. The surface roughness of PLZT deposited at 975°C on sapphire is about 2.25 nm at a thickness of about 250 nm. Deposition conditions need to be further optimized to improve the surface morphology of PLZT on LAO and MgO substrates, and both the surface and epitaxy of PLZT on sapphire substrate. The electro-optic properties of the CCVD PLZT films have not been tested thus far.

ACKNOWLEDGMENTS

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