Annealing-induced changes in chemical bonding and surface characteristics of chemical solution deposited $\text{Pb}_{0.95}\text{La}_{0.05}\text{Zr}_{0.54}\text{Ti}_{0.46}\text{O}_3$ thin films

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ABSTRACT

We report the effect of post deposition annealing temperature ($T_a = 550$ and 750 °C) on the surface morphology, chemical bonding and structural development of Lanthanum doped lead zirconate titanate ($\text{Pb}_{0.95}\text{La}_{0.05}\text{Zr}_{0.54}\text{Ti}_{0.46}\text{O}_3$; referred to PLZT) thin films prepared using chemical solution deposition method. Atomic force microscopy demonstrates formation of nanocrystallites in the film annealed at $T_a = 750$ °C. X-ray photoelectron spectroscopy (XPS) analyses indicate that the binding energies (BE) of the Pb 4f, Zr 3d, and Ti 2p doublet experience a positive energy shift at $T_a = 750$ °C, whereas the BE of O 1s and La 3d doublet show negative shift with respect to the BE of the films annealed at $T_a = 550$ °C. Thermal induced crystallization and chemical modification is evident from XPS results. The Ar⁺ sputtering of the films reveal change in oxidation state and chemical bonding between the constituent atoms, with respect to T_a . Raman spectroscopy used to study phonon-light interactions show the shift in longitudinal and transverse optical modes with the change in T_a , confirming the change in phase and crystallinity of these films. The results suggest annealing at $T_a = 750$ °C yield crystalline perovskite PLZT films, which is essential to obtain photovoltaic response from devices based on such films.

Keywords: PLZT, chemical solution deposition, XPS, chemical bonding, Raman spectroscopy

1. Introduction

Lead zirconate titanate ($\text{Pb}(\text{Zr,Ti})\text{O}_3$, PZT) of perovskite structure is the most extensively studied ferroelectric material near the morphotropic phase boundary (MPB). The interest in PZT is derived from the unique ferroelectric, dielectric, pyroelectric, piezoelectric, and electro-optic properties of the material. By virtue of these electronic and optical properties, PZT meets the requirements for numerous technological applications. This material is used in nonvolatile random access memory (NVRAM), high power dielectric energy storage, high-performance ferroelectric capacitors, infrared sensors, and micro-electromechanical systems (MEMS) [1-3]. Recently, doping of PZT has been actively considered by the scientific and research community to further improve the properties of this material. For instance, PZT doped with Nb (PNZT) shows the improvement in ferroelectric response and effective transverse piezoelectric coefficient making it attractive for infrared devices and piezo MEMS [4, 5]. Likewise, La doped PZT (PLZT) is observed to enhance the optical properties of the system making it appropriate for optical MEMS, modulators/transducers, and smart sensors [6-8]. Nowadays, efforts are directed towards using this material for photovoltaic (PV) devices which utilizes the combination of optical transparency and ferroelectric properties [9, 10]. The ability of ferroelectric thin films to produce photo-voltage without the need of p-n junction as required in traditional semiconductor solar cells and the existence of bulk PV effects make them promising for solar cell applications [11] which could be exploited to meet enhanced efficiency requirements.

PLZT films can be prepared by a wide variety of physical and chemical deposition methods. However, the chemical solution deposition method (CSD) is an attractive choice to prepare these films due to the ease of crystalline film fabrication at low temperatures and scaling up the growth process to a large scale at low cost. In general, ferroelectric thin films exhibit

mixture of perovskite and pyrochlore phases. Existence of the pyrochlore phase deteriorates the material and device performance [12, 13, 14]. Since PV effect in these materials originates from the perovskite phase, thus it is essential to obtain crystalline perovskite films to maintain both ferroelectric and photovoltaic properties [15, 16]. The structure and properties of thin films depend on multiple factors such as substrate, bottom electrode, processing conditions: pyrolysis time, and temperature, annealing ambient, time, temperature, and ramp rate. Thus, the key to design efficient photovoltaic devices using PLZT is the fabrication of pyrochlore free thin films which is usually performed by: heat treatment under PbO, annealing in oxygen atmosphere, and **crystallization** at higher temperature.

In our previous work, we reported variation in optical properties of these films as a function of annealing/crystallization temperature (T_a) in the range of 550-750 °C. It was observed that the higher $T_a = 750$ °C resulted in pyrochlore free perovskite phase while lower $T_a = 550$ °C exhibited pyrochlore phase whose effect was clearly evident in the optical properties [17]. However, understanding the morphology, chemical bonding at the interface or within the film, and phonon-light interaction with respect to T_a , is equally important to utilize these films for practical applications. Thus, in the present work, Atomic force microscopy (AFM), X-ray photoelectron spectroscopy (XPS), and Raman spectroscopy were utilized to examine the $\text{Pb}_{0.95}\text{La}_{0.05}\text{Zr}_{0.54}\text{Ti}_{0.46}\text{O}_3$ (PLZT) thin films annealed at two extreme crystallization temperatures T_a (550 and 750 °C). The results obtained are presented and discussed.

2. Experimental Details

2.1. Film fabrication

PLZT thin films, with composition ($\text{Pb}_{0.95}\text{La}_{0.05}\text{Zr}_{0.54}\text{Ti}_{0.46}\text{O}_3$) near the morphotropic phase boundary (MPB) were fabricated on platinized silicon substrates by chemical solution deposition process. PLZT solution with a concentration 0.4 M was prepared using lead acetate trihydrate ($\text{Pb}[\text{CH}_3\text{COO}_2]_2 \cdot 3\text{H}_2\text{O}$), lanthanum acetate ($\text{La}[\text{CH}_3\text{COO}]_3$), zirconium propoxide ($\text{Zr}[\text{OCH}_2\text{CH}_2\text{CH}_3]_4$), and titanium butoxide ($\text{Ti}[\text{OCH}_2\text{CH}_2\text{CH}_2\text{CH}_3]_4$) as precursors and 2-methoxyethanol ($\text{CH}_3\text{OCH}_2\text{CH}_2\text{OH}$) as solvent. Spin coating method was used to prepare the films where the substrate is held in position using vacuum chuck and then rotated at a high speed to spread the solution by centrifugal force. In this work a rotation speed of 3000 rpm for 30 sec was used to spread the solution on Pt/TiO₂/SiO₂/Si wafers. The coated film was subsequently hydrolyzed at 120 °C for 2 min, and pyrolyzed at 350 °C for 2 min, using a hot plate. The coating process was repeated three times to achieve film thickness of 210 nm. All the films were then crystallized at 550 and 750 °C in a continuous flow of oxygen for 2 minutes using rapid thermal annealing (RTA) furnace. Further details about the preparation process are discussed in our previous work [17, 18].

2.2. Film Characterization

AFM images (512 scan lines & 512 pixels per scan line) were acquired with an integral gain of approximately 2, a proportional gain of approximately 50, and an amplitude setpoint of 300 mV. The drive amplitude varied between 30 and 180 mV. The images were then subjected to a 3rd order flattening procedure using the Veeco Nanoscope software to remove the non-linear background artifact introduced by the piezo scanner. Following the flattening procedure, the

surface roughness was quantified over five areas of $1\ \mu\text{m} \times 1\ \mu\text{m}$ on the $5\ \mu\text{m} \times 5\ \mu\text{m}$ scan size images [19].

The chemical states and the bonding of the PLZT films were investigated using X-ray photoelectron spectroscopy (XPS). A Kratos Axis 165 XPS system with a monochromated $\text{AlK}\alpha$ (1486.6 eV) X-ray source was used to perform the measurements. The base pressure in the measurement chamber was maintained $\sim 10^{-9}$ Torr. The XPS survey spectra were obtained over the binding energy (BE) range of 0–900 eV using an analyzer pass energy of 160 eV with an energy step of 1 eV. The high resolution (HR) spectra were collected with an energy step of 0.1 eV and analyzer pass energy of 80 eV. Survey and high resolution scans were taken before and after sputtering using Argon ion gun operating at 5 keV for 70 sec. The binding energies were calibrated with reference to the C1s peak at 284.5 eV. The Pb 4f , La 3d , Zr 3d , Ti 2p and O 1s core level XPS data were recorded for the purpose of detailed chemical analysis of the samples. Lorentzian fitting was used to deconvolute the La 3d and Ti 2p peaks from the experimental high-resolution XPS core level spectra.

The Raman scattering measurements were performed on a Jobin-Yvon HR800 UV spectrophotometer equipped with Peltier cooled charge-coupled device detector. A He-Ne laser line with a wavelength of 632.81 nm was used as an exciting source. The incident laser beam with a power of ~ 12 mW was focused on the films. The Raman scans were taken in spectra range of $70\text{--}600\ \text{cm}^{-1}$ at a resolution of $1.3\ \text{cm}^{-1}$. The measurements were conducted at room temperature in a backscattering configuration.

3. Results and discussion

3.1. Atomic Force Microscopy

The AFM images of the PLZT films crystallized at 750 °C are shown in Figure 1. The topographic image and the corresponding 3D image are presented. The uniform, granular morphology across the film surface is evident. The root mean squared (RMS) roughness of the film is measured as 4.06 nm. The as-deposited films (not shown) are mostly amorphous in nature. Although low RMS roughness of 0.77 nm is obtained, no crystallite grains are observed on the film surface. The topographic image of the film crystallized at 550 °C could not be measured but is expected to have the RMS roughness between as-deposited and film crystallized at 750 °C. Thus, the crystallization temperature decides the granular morphology of the films.

The effect of post-deposition annealing temperature on the crystal structure of the PLZT films annealed at $T_a=550-750$ °C has been reported elsewhere [17]. The X-ray diffraction patterns revealed that the film crystallized at 550 °C exhibited pyrochlore phase whereas the higher T_a (750 °C) resulted in only perovskite peaks. The importance of T_a was clearly evident in the disappearance of pyrochlore phase at higher T_a , which accounts for promoting the structural order in the film. The film crystallized at 750 °C exhibited (110) preferential orientation whereas the film crystallized at 550 °C showed only (100) peak [17].

3.2. X-ray Photoelectron Spectroscopy

The XPS survey spectra of PLZT films are shown in Figure 2. The typical spectra obtained for as-prepared and Ar^+ ion sputtered PLZT films are displayed. The XPS peaks due to various elements are indicated in Figure 2. For the as-prepared films, all the spectral peaks obtained from both the films ($T_a= 550$ and 750 °C) are identified as the core levels of the

components, except the C 1s peak, which is commonly noted for PLZT films prepared by other methods as reported widely in the literature [20-22]. The carbon peak in the XPS spectra is due to adventitious carbon from exposure to air following PLZT film fabrication, before being placed in the XPS system. However, sputtering with Ar^+ ions fully eliminated the C 1s peak in the survey scans which is a clear indication that the carbon is a result of adsorbed species on the film surface due to air exposure. It is also noted that the spectral peaks of the associated elements of the PLZT became more intense after sputtering the film surface with Ar^+ ion, as is evident in the XPS spectra.

The high resolution spectra of Pb 4f, La 3d, Zr 3d, Ti 2p and O 1s before and after Ar^+ sputtering allowed us to probe the chemical information of the PLZT films. The core level XPS data of Pb 4f is presented in Figure 3. The core level photoelectron spectra of Pb exhibits the doublet corresponding to spin-orbit splitting. The binding energy (BE) values of Pb $4f_{5/2}$ and Pb $4f_{7/2}$ of the films annealed at 550 and 750 °C are presented in Table 1. The BE values of Pb $4f_{5/2}$ and Pb $4f_{7/2}$ for both as-prepared and Ar^+ sputtered films indicate the chemical states of Pb bonds in PLZT. However, the BE position and shape evolution of the Pb peak as a function of T_a indicates the changes in chemical bonding of Pb in PLZT films. The BE values of Pb $4f_{5/2}$ and Pb $4f_{7/2}$ are 141.9 eV and 137.9 eV, respectively, for PLZT films annealed at 550 °C. Similarly, for films annealed at 750 °C, the BE values of Pb $4f_{5/2}$ and Pb $4f_{7/2}$ are noted at 143.6 eV and 138.7 eV, respectively. Compared to the BEs of Pb 4f levels for films at lower T_a (550 °C) the BEs are located at higher values for as-prepared PLZT film annealed at higher T_a (750 °C). A positive shift of 0.8 eV is, thus, evident for the Pb doublet with increasing T_a . It should be noted that, as reported and widely accepted in the literature, the BE shift in oxide compound arises due to the rearrangement of electronic charge around the constituent atoms [23-25]. Therefore, the variation

observed in the BE values of Pb 4f doublet noted in this work must be due to change in the chemical state of Pb in PLZT films as a function of T_a . The BE of Pb 4f_{7/2} at 138.7 eV and the spin orbit splitting $\Delta E(\text{Pb } 4f_{5/2}, 4f_{7/2}) \sim 4.9 \text{ eV}$ for PLZT films at $T_a=750^\circ\text{C}$ characterizes the chemical state of Pb fully oxidized and existence of its single, highest oxidation state in PLZT. The reported BE and $\Delta E(\text{Pb})$ values for Pb in single, highest oxidation state are in close agreement with the values reported in the literature for PZT [26, 27] and PLZT [28-30]. However, the evolution of Pb peak shape and BE values are quite interesting for the Ar⁺ ion sputtered PLZT films. The sputtered film ($T_a=750^\circ\text{C}$) shows multiple peak structure as displayed in the Figure 4(b). The multiple peak nature of Pb core level upon Ar⁺ ion sputtering is an indicative of the existence of more than one chemical state of Pb ions. The Pb 4f_{5/2} exhibit twin peaks at 142.4 and 144 eV and Pb 4f_{7/2} show pair of peaks at 137.5 and 139.1 eV. The additional peaks are located at 139.1 and 144 eV. Among the constituent elements, Pb is highly volatile and susceptible to the chemical state reduction upon Ar⁺ ion sputtering [28, 30]. It is also reported that the growth process of thin films at higher temperature results in the surface loss of Pb leading to departure from the ideal perovskite stoichiometry [30, 31]. Note that such Pb loss can degrade the dielectric and ferroelectric properties [31]. Furthermore, it was demonstrated that Pb loss or reduction can occur by the surface bombardment by a wide variety of ions such as He⁺, Ar⁺, Ne⁺, Xe⁺ and Kr⁺ ions even with low energies, as low as down to 400 eV [32]. Thus, we believe that the multiple peak structure is due to the Ar⁺ ion induced reduction of the Pb ions and, hence, the existence of mixed valence state of Pb. Based on the obtained spectral features, it can be concluded that the lower T_a results in PbO or PbO₂ whereas the higher T_a results in Pb₃O₄ [27]. Further Ar⁺ sputtering causes the change in oxidation state of Pb²⁺ to Pb⁴⁺ [27]. However, while the mixed valence state is clearly evident, it can be noted in the spectra that the

existence of Pb in metallic state can be completely ruled out in any of these PLZT films in this work. Usually Pb 4f peak is located at ~136 eV [31]. No peak or peak shift characterizing elemental Pb was evident in any of these as-deposited or heat treated or Ar⁺ ion sputtered PLZT films.

Figure 4 presents the core level photoelectron spectra of La 3d. The data shown are for PLZT films at variable T_a and also before and after Ar⁺ sputtering of the film surfaces. It is evident that the spectra of the samples without any Ar⁺ sputtering exhibits a simple La 3d_{3/2} and La 3d_{5/2} spin-orbit doublet, while the spectra of the films after sputtering with Ar⁺ ions exhibit a multiplet with two discrete peaks for each of the spin-orbit doublet. The respective BE values of La 3d levels are also presented in Table 1. For both as-prepared and sputtered scans, the lower T_a (550 °C) results in positive shift of the BE peaks with respect to the higher T_a (750 °C). The BE values for La 3d core level are noted as expected for La in its highest single oxidation state in PLZT films. However, for some reason and unlike the case of Pb, the La peaks experience slightly higher BE shift for films at 550 °C when compared to those at 750 °C. . Clearly, the spin-orbit splitting for La i.e., $\Delta E(\text{La } 3d_{3/2} - \text{La } 3d_{5/2})$, lies in the range of 16.6-17.0 eV, which closely matches the reported value [33]. As observed in the case of Pb, the Ar⁺ ion sputtering results in additional splitting towards higher energy side. The peaks La 3d_{3/2} and 3d_{5/2} located at BE values of 856.5 and 839.5 eV for T_a= 550 °C and 855.9 and 839.3 eV for T_a= 750 °C can be attributed to the **La bonded** in PLZT with its highest single oxidation state (La³⁺) [30]. The additional splitting caused by the Ar⁺ ion sputtering can be due to the charge transference from nearly degenerate ligand of O 2p to the empty orbital of La 4f resulting in 3d⁹4f¹ final state, as reported widely in the literature [30, 33-35].

The Zr 3d core-level spectra of both the as-prepared and sputtered films are shown in Figure 5. The spectra exhibit a spin-orbit doublet of Zr 3d_{3/2} and 3d_{5/2}. The corresponding BE values of Zr 3d doublet are listed in Table 1. The BE values obtained for the film crystallized at higher T_a (750 °C) indicate a positive BE shift (0.3 eV) compared to the films crystallized at lower temperature (550 °C). The shift in BE with the change in T_a is attributed to the effect of heat treatment because Zr⁴⁺ is the thermodynamically stable state [27]. The Ar⁺ ion sputtering induced effects are minimal on the Zr 3d levels compared to either Pb or La. The BE values of Zr 3d doublet along with the spin orbit splitting $\Delta E(\text{Zr } 3d_{3/2} - \text{Zr } 3d_{5/2}) \sim 2.4 \text{ eV}$ for **all** the PLZT films match very well with those reported in the literature and characterizes the single, highest chemical state of Zr [20, 27, 34].

The Ti 2p core-level spectra of as-prepared and Ar⁺ ion sputtered films at variable T_a are presented in Figure 6. The spectra indicate spin-orbit doublet of Ti 2p_{1/2} and 2p_{3/2}. The BE values of respective peaks are presented in Table 1 along with those of Pb, La and Zr. The BE values of Ti 2p level exhibit a clear change as a function of crystallization temperature for both as-prepared and Ar⁺ ion sputtered scans. Compared to PLZT films at T_a = 550 °C, films at 750 °C exhibit a positive BE shift (0.3 eV). Similarly, Ar⁺ sputtered film shows a positive BE shift of 0.8 eV for the PLZT films crystallized at higher T_a. The difference in chemical bonding of Ti results in the BE shift which is useful to know the change in the chemical valence state of the films crystallized at different temperatures. Based on the BE values, it appears that the lower T_a results in the mixed chemical valence state of titanium i.e., Ti⁴⁺ and Ti³⁺, where majority may be in lower chemical valence state due to observed low BE [26, 27]. On the other hand, with higher BE values and positive shift, the chemical state of Ti is single and fully oxidized i.e., Ti⁴⁺ state. Thus, the Ti 2p_{1/2} and 2p_{3/2} peaks of the doublet correspond to Ti⁴⁺ (TiO₂) for 750 °C and Ti³⁺

(Ti₂O₃) for 550 °C crystallized PLZT films. Generally, insufficient oxygen has the tendency to translate the valence state of Ti from Ti⁴⁺ (TiO₂) to Ti³⁺ (Ti₂O₃) [37]. Additionally, it is known that the perovskite phase transformation in PLZT occurs within a particular range of crystallization temperature, thus the crystallization temperature decides the phase, chemical valence state and the crystalline quality of the films. Therefore, at 550 °C, thermal energy provided is insufficient to allow the film to fully crystallize into perovskite phase which causes the Pb loss, as observed in Figure 3. This inhibits the PLZT crystallization in proper perovskite phase which has already been observed in the XRD patterns as reported elsewhere [17]. The spin orbit splitting $\Delta E(\text{Ti } 2p_{1/2} - \text{Ti } 2p_{3/2}) \sim 5.8 \text{ eV}$ along with the BE values noted for PLZT films at 750 °C agree with the literature and characterizes Ti in single, 4⁺ chemical state [20, 27, 34].

The core-level photoelectron spectra of O 1s for as-prepared and Ar⁺ ion sputtered films under variable T_a are shown in Figure 7. The XPS high resolution spectra of both the films crystallized at 550 and 750 °C exhibit a shoulder peak in addition to the main peak of O 1s. However, Ar⁺ ion sputtering of the surface changes the doublet feature into single O 1s peak, which is characteristic of oxygen bonded in PLZT films. It should be noted the additional contribution is due to the fact that these samples are exposed to the air before introducing into the XPS chamber. Therefore, surface adsorbed and/or chemisorbed oxygen is expected on the surface. A careful analysis is made by deconvoluting the spectral components and considering the BEs of respective components. The lower BE components in as-prepared scans located at ~529.5 eV (T_a= 550 °C) and ~529.9 eV (T_a= 750 °C) correspond to oxygen bonded in PLZT. The higher BE component located at ~531.7 eV can be attributed to hydroxyl (oxygen bonded to hydrogen) or carbonyl (oxygen bonded to carbon) groups adsorbed on the surface [27, 38]. Such features for O 1s were also reported by Wakiya et al for epitaxial PZT films [30]. It is to be noted

that after Ar^+ ion sputtering, the other component at higher BE disappears and O 1s spectra becomes single peak single component. These observations clearly indicate that the higher BE component noted in O 1s core level spectra is due to the surface carbonyl or hydroxyl bonds, which can be easily removed after sputtering the surface layer of the film [27, 37]. The BE value obtained for the film crystallized at higher T_a (750 °C) is in agreement with the reported value for PZT/PLZT thin films [20, 27].

3.4. Raman Spectroscopy

Raman spectra of PLZT films are shown in Figure 8. The optical phonon modes in tetragonal phase of ferroelectric PLZT consist of $3A_1+4E+B_1$ modes. The A_1 and E are both Raman and infrared active, and B_1 is only Raman active mode. Of all the modes, the three A_1+E modes originate from the three T_{1u} modes of the cubic phase, one E and B_1 mode arise from the T_{2u} silent mode. Each of the $3A_1+4E$ modes split into longitudinal optical (LO) mode with polarization parallel to wave vector and transverse optical (TO) mode with polarization is perpendicular to wave vector [38-40]. The scheme used to present the Raman active A_1 and E phonons is shown in the Table 2 where the numbers 1-4 used to denote the modes, increase with the increase in the frequency of the particular mode. Thus, all the modes including one B_1 mode together form 15 optical phonons in the Raman spectra [40-43]. The $E(4LO)$ and $A_1(3LO)$ modes could not be detected as both of them exhibit frequencies above 600 cm^{-1} , which are beyond the detection range chosen in this work and the remaining 13 modes are shown in the spectra. The modes at wavenumber around 80, 110, 141, 186, 207, 285, 345, 410, 445, 515 and 554 cm^{-1} are identified as $E(1TO)$, $E(1LO)$, $A_1(1TO)$, $A_1(1LO)$, $E(2TO)$, $E(3TO+2LO)+B_1$, $A_1(2TO)$, $E(3LO)$, $A_1(2LO)$, $E(4TO)$ and $A_1(3TO)$ respectively for the film crystallized at higher temperature, $T_a = 750\text{ °C}$. However, the modes in the film crystallized at lower temperature, $T_a =$

550 °C show shift towards higher wavenumbers by 2-5 cm^{-1} . The modes obtained for higher T_a are similar to the results reported in the literature [39, 41-44]. The crystallization temperature dependence of the peak positions of the modes is clearly evident in Raman spectra. The vibration modes are used to study the phase change in the ferroelectrics. No appreciable change is observed in the soft phonon modes, i.e., $E(1\text{TO})$ and $A_1(1\text{TO})$, with the change in T_a . However, the shift observed in high frequency Raman modes at lower T_a indicates the change in crystallinity of the film. As observed in the XRD data [17], the higher T_a results in PLZT perovskite phase developed with tetragonal structure and lower T_a results in combination of perovskite and pyrochlore phase, thus the change reflected in Raman spectra can be attributed to phase change and the decrease in tetragonality in the films.

4. Conclusions

The chemical solution deposited PLZT thin films were crystallized at 550 and 750 °C. AFM demonstrated the nanocrystalline morphology of the PLZT films annealed at $T_a = 750$ °C. The XPS studies revealed that T_a affects the chemical state of the films. The core level XPS spectra showed that the film crystallized at 750 °C is the characteristic existence of the cations in their respective single, highest chemical valence state in PLZT. XPS data of films at $T_a = 550$ °C indicate that some of the cations, especially Pb and Ti, experience lower chemical states, which could be the reason for not inducing the ideal perovskite structure as noted in our earlier work using XRD data [17]. The shift in phonon vibration modes towards higher frequency observed in Raman spectra of the films also support the chemical quality of PLZT films crystallized at 750 °C. The results obtained using AFM, XPS and Raman spectroscopy coupled with XRD data clearly indicate that crystallization temperature of 750 °C is essential to obtain pyrochlore free films which are nanocrystalline and chemically homogeneous.

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Figure Captions

Figure 1. AFM image of chemical solution deposited PLZT thin films crystallized at 750 °C.

Figure 2. XPS survey scan of PLZT films crystallized at 550 and 750 °C. The scans shown here are obtained from as-prepared and Ar⁺ ion sputtered samples. The disappearance of C 1s peak after sputtering is illustrious.

Figure 3. Core level spectra of Pb 4f. (a) PLZT films before Ar⁺ ion sputtering, (b) PLZT films after Ar⁺ ion sputtering. The spin-orbit splitting and changes in the spectra before and after Ar⁺ sputtering are evident.

Figure 4. Core level spectra of La 3d. (a) PLZT films before Ar⁺ ion sputtering, (b) PLZT films after Ar⁺ ion sputtering. The spin-orbit splitting and changes in the spectra before and after Ar⁺ sputtering are evident.

Figure 5. Core level spectra of Zr 3d. (a) PLZT films before Ar⁺ ion sputtering, (b) PLZT films after Ar⁺ ion sputtering. The spin-orbit splitting and changes in the spectra before and after Ar⁺ sputtering are evident.

Figure 6. Core level spectra of Ti 2p. (a) PLZT films before Ar⁺ ion sputtering, (b) PLZT films after Ar⁺ ion sputtering. The spin-orbit splitting and changes in the spectra before and after Ar⁺ sputtering are evident.

Figure 7. Core level spectra of O 1s. (a) PLZT films before Ar⁺ ion sputtering, (b) PLZT films after Ar⁺ ion sputtering. The high BE component is due to carbonyl and/or hydroxyl bonds on the surfaces of the films. The higher BE component disappears after Ar⁺ ion sputtering.

Figure 8. Raman spectra of PLZT films as a function of T_a.

Table 1. Binding energy peak positions of the core levels of Pb, La, Zr, Ti and O.

T_a	Scan	Pb				Zr		Ti		O	La			
		4f_{5/2}		4f_{7/2}		3d_{3/2}	3d_{5/2}	2p_{1/2}	2p_{3/2}	1s	3d_{3/2}		3d_{5/2}	
550 °C	As prepared	142.8		137.9		184.3	181.9	463.7	457.9	531.7 & 529.5	853.9		835.7	
	Sputtered	141.9		137		185.2	182.8	463.9	458.1	531.1	856.5	852.3	839.5	835.5
750 °C	As prepared	143.6		138.7		184.6	182.2	464	458.2	531.5 & 529.9	852.7		835.1	
	Sputtered	144	142.4	139.1	137.5	185.8	183.4	464.7	458.9	530.5	855.9	851.5	839.3	834.7

Table 2. Raman active A_1 and E modes.

--	--	E(4TO)	E(4LO)
$A_1(3TO)$	$A_1(3LO)$	E(3TO)	E(3LO)
$A_1(2TO)$	$A_1(2LO)$	E(2TO)	E(3LO)
$A_1(1TO)$	$A_1(1LO)$	E(1TO)	E(3LO)

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6

Figure 7

Figure 8

Table 1. Binding energy peak positions of the core levels of Pb, La, Zr, Ti and O.

T _a	Scan	Pb				Zr		Ti		O	La			
		4f _{5/2}		4f _{7/2}		3d _{3/2}	3d _{5/2}	2p _{1/2}	2p _{3/2}	1s	3d _{3/2}		3d _{5/2}	
550 °C	As prepared	142.8		137.9		184.3	181.9	463.7	457.9	531.7 & 529.5	853.9		835.7	
	Sputtered	141.9		137		185.2	182.8	463.9	458.1	531.1	856.5	852.3	839.5	835.5
750 °C	As prepared	143.6		138.7		184.6	182.2	464	458.2	531.5 & 529.9	852.7		835.1	
	Sputtered	144	142.4	139.1	137.5	185.8	183.4	464.7	458.9	530.5	855.9	851.5	839.3	834.7

Table 2. Raman active A₁ and E modes.

--	--	E(4TO)	E(4LO)
A ₁ (3TO)	A ₁ (3LO)	E(3TO)	E(3LO)
A ₁ (2TO)	A ₁ (2LO)	E(2TO)	E(3LO)
A ₁ (1TO)	A ₁ (1LO)	E(1TO)	E(3LO)