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Synthesis of Crack-Free PZT Thin Films by Sol-gel Processing on Glass Substrate

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Abstract

PZT thin films deposited on glass substrates have been proposed for many applications such as adjustable optics in future X-ray telescopes. Sol-gel method is widely utilized to prepare PZT thin films due to its low reaction temperature, uniform mixing of reactants, and precise control of component. Crack-free transparent PZT thin films were prepared by dip-coating the solutions of complex alkoxides. PZT thin films were calcined at various temperatures and characterized by X-ray diffraction, field emission scanning electron microscopy to examine the surface morphology, and FT-IR spectroscopy. The XRD analysis confirmed the formation of perovskite phase at 600 °C. FE-SEM results showed nucleation of PZT perovskite phase. Furthermore, the average grain size was measured in the range of 55 to 190 nm.

Keywords: PZT; sol-gel; thin film; perovskite phase; characterization.

1. Introduction

Lead zirconate titanate (PZT), Pb(Zrx,Ti1-x)O3, is one the most well-known perovskite solid solutions with superior piezoelectric constants and ferroelectric properties in the morphotropic phase boundary (MBP) composition x~0.53, Shakeri et al. (2014). Owing to the great properties, PZT has been widely used in electronic devices and micro/nano-electromechanical systems such as high frequency transducers, sensors, and actuators as different forms of 1D, 2D or bulk ceramics, Wang et al. (2015), Seregin et al. (2015). Recently, new investigations into ferroelectric photovoltaic

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effect of specific materials such as PZT thin films have opened new horizons for photonic devices, Yuan et al. (2014). Among the synthesis techniques of perovskite ceramics, sol-gel method is extensively applied due to its exclusive advantages including exactly controllable stoichiometry, capability to mix the reactants uniformly and obtaining high product purity, and cost effectiveness, Shakeri et al. (2012), Yasseri et al. (2014). In order to exploit the potential benefits of PZT thin films in photonic industries, the films should be deposited on glass substrate. However, synthesis of crack-free PZT thin films by sol-gel processing on glass substrate is considered a challenging issue. Due to the great shrinkage occurring in sol-gel technique and different thermal expansion coefficients of the PZT layer and the glass substrate, the films are highly prone to crack during the heat treatment step, Cheng et al. (2006). Moreover, the typical PZT calcination temperature (~750 °C) is above the glass transition temperature and results in distortion of the substrate. In this paper, a modified sol-gel route as well as an appropriate heat treatment procedure have been used to synthesize crack-free PZT films on glass substrate with a proper perovskite crystallinity in low calcination temperature.

2. Experimental

Zirconium n-propoxide (Zr(OCH2CH2CH3)4, 70% in 1-propanol, Sigma–Aldrich), titanium isopropoxide (Ti(OCH(CH3)2)4, Merck), lead acetate trihydrate (Pb(CH3COO)2·3H2O, Merck), glacial acetic acid (CH3COOH, Merck), n-butanol (C4H9OH, Merck), methanol (CH3OH, Merck), diethanol amine (DEA, HN(CH2CH2OH)2, Merck), and deionized water (18.2 MΩ), all in reagent grade, are used in order to prepare PZT (53:47). Commercial glass slides with the thickness of 2 mm was used as a substrate. The sol preparation procedure has been defined elsewhere, Shakeri et al. (2014). In the sol preparation step, DEA and water were used with the molar ratio (DEA/(Ti+Zr)) of 0.5 and the molarity was reached 0.33 M by adding n-butanol. Before the film preparation, the substrates were cleaned in alcohol. PZT sol was dip-coated onto the substrates in 10-16 steps, using a withdrawal speed of 30 mm/min. After each dip coating step, the films were dried on a hot plate at ~220 °C for 5 min and then calcined in a preheated furnace for 5 min. The calcination temperature varied from 550 to 650 °C so as to investigate the optimum condition. X-ray diffractometer (XRD), Philips DW 1730, was utilized to examine the phase structure of PZT thin films using Cu Kα radiation. The surface morphology of the films were examined by field emission scanning electron microscopy (FE-SEM), Hitachi S4160. A Fourier transform infrared (FTIR) spectrometer, NEXU670, was utilized to study the sol reactions.

3. Results and discussion

Figure 1 illustrates the XRD patterns of PZT thin films calcined at 550 °C. In Fig. 1a the thin film was dried and calcined for 5 min after each coating step. A high intensity peak at ~29.6 ° implies the sample contains a considerable volume of pyrochlore phase and the perovskite phase peak can be seen only at ~31.1 ° according the JCPS file no. 50-0346. Figure 1b shows the XRD pattern of the film calcined for another 30 min at 600 °C in the final step of film preparation procedure. Although this heat treatment method is typical in other studies, Yang et al. (2005), it could be seen that this method improves the structure and persuades the formation of perovskite phase. However, pyrochlore phase can be seen in the structure. The reason may be due to the fact that the temperature of 550 °C is not high enough to cause the perovskite crystals fully nucleate and growth on metastable pyrochlore phase. Applying the 30 min final calcination results in the formation of perovskite phase and more evaporation of lead from the PZT films, which could stimulate the pyrochlore phase formation, Shakeri et al. (2014). It should be noted that there was an observation of growing the pyrochlore phase even by increasing the drying time from 5 min to 10 min. Moreover, increasing the time of calcination brings about high diffusion of glass substrate impurities to the PZT layers and stabilizes the pyrochlore formation. Fig. 2 indicates the XRD patterns of PZT thin films calcined at different temperature of 550, 600, and 650 °C for 5 min after each coating step. In order to trace the pyrochlore peaks more accurately, 2 theta of 25 ° - 40 ° is shown in Fig. 2. Considering the XRD results, it is obvious that raising the calcination temperature to 600 °C leads to substantial increase in the crystallinity of perovskite phase. The amount of pyrochlore phase is negligible. However, more increase in calcination temperature causes a mere growth in the intensity of pyrochlore peaks.
Fig. 1. XRD patterns of PZT thin films calcined at 550 °C for (a) 5 min in each coating step; (b) for 5 min in each coating step and for another 30 min in final coating step.

Fig. 2. XRD patterns of PZT thin films calcined at different temperatures.

The results prove that 600 °C is a proper temperature for nucleation and growth of the perovskite phase. At 650 °C, there is more tendency for pyrochlore phase to form again due to the great evaporation of lead ions in every coating step. Furthermore, the diffusion of substrate impurities can cause the pyrochlore stabilization. It should be noted that 30 min calcination at the final coating step at 600 °C and 650 °C did not indicate any significant change in crystal structure. The surface morphology of the thin films calcined at 600 and 650 °C are shown in Fig. 3. The FE-SEM investigation illustrated fine and dense PZT thin films without any sign of crack and porosity. At 600 °C, the perovskite crystal structures and grain boundaries are detectable in Fig. 3a. The perovskite average grain size is varied from small grains of 55 nm to large grains of 190 nm. By increasing the temperature to 650 °C, another type of perovskite morphology is formed in the PZT thin films surface which is called rosette type structure, Brunckova et al. (2011). The rosette includes perovskite grains with average grain size of 45 nm and is separated by a fine-grained matrix of pyrochlore phase. The reason for creation of this crystal structure type is due to high evaporation of PbO from the surface of PZT thin films at 650 °C. Decreasing in the lead concentration results in fine-grained pyrochlore formation in the surface. These results are in accordance with the XRD results, which showed growth in the intensity of
pyrochlore phase peak at 650 °C. In order to investigate the quality of sol’s chemical bonds, FT-IR diagram of the sol, dried powder, and calcined powders at 600 °C for 1h are plotted in Fig. 4. Symmetric and asymmetric stretching modes of the COO⁻ ligand lead to formation of two peaks at 1410 and 1550 cm⁻¹, which represent the joint between acetate arms and alkoxide precursors. Moreover, stretching vibration of C = O bands in acetate group causes a peak at 1710 cm⁻¹. A peak broadening in the wavenumber of 1010 to 1060 cm⁻¹ results from C-OH band of isopropanol secondary alcohol caused by esterification reaction of titanium isopropoxide, Birnie (1999). Stretching mode of O–H linked to Ti and Zr causes a broad peak at 3360 cm⁻¹ which has relatively low intensity. DEA can decrease the hydrolysis of metal alkoxides and lead to the formation of isopropanol as a secondary alcohol and decrease in OH ligand. It can be seen that the intensity of organic-phase peaks reduces after drying procedure. Nevertheless, the peaks belonging to acetate groups are not completely eliminated and represent incomplete removal of acetate during the drying, which prevents the rapid contraction of the film at this step and consequently avoids the formation of cracks. The gradual slope of the diagram in the range of 1750 to 3000 cm⁻¹ may be due to existence of -NH₃⁺ and indicates the formation of another type of DEA complex in the form of Ti(R-NH₃). This kind of complex is not removed until the calcination process and is not detectable in the sol because of high volume of organic phase. After the calcination step, the great growth of the peak at 570 cm⁻¹ indicates metal-O-metal bonds of the PZT and consequently proper crystallization of the PZT ceramic at 600 °C.

Fig. 3. FE-SEM micrographs of PZT thin films calcined at (a) 600 °C; (b) 650 °C.

Fig. 4. FT-IR spectra of PZT (a) sol; (b) dried powder at 220 °C; and (c) calcined powder at 600 °C.
4. Conclusion

Thin films of PZT ceramic are successfully synthesized on glass substrate without any sign of cracks and porosity. Thin films poses pure perovskite crystal structure by calcination of each layer at 600 °C for 5 min. The average grain size of films was in the range of 55 to 190 nm. Increasing the calcination temperature to 650 °C led to formation of pyrochlore phase and rosette type morphology. FT-IR analysis indicates proper elimination of organic phases at drying temperature of 220 °C and great crystallization of metal-O-metal bonds at the calcination temperature of 600 °C.

References


