

The effect of annealing temperature on properties of PZT ceramic films prepared via spin-coating process

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Abstract

In this work, lead zirconate titanate $\text{Pb}(\text{Zr}_{0.52}\text{Ti}_{0.48})\text{O}_3$ or PZT films under 20% mol of Pb-excess were fabricated on $\text{Ti}/\text{SiO}_2/\text{Si}$ wafer by spin-coating method. The PZT films were annealed at different temperature of 550, 600 and 650 °C for 30 min under atmosphere. The effects of annealing temperature on microstructure, surface morphology and phase formation of PZT ceramic films were investigated by Field-emission scanning electron microscope (FE-SEM), Atomic force microscopy (AFM) and X-ray diffraction (XRD), respectively. The PZT ceramic films exhibited perovskite phase that crystallographic orientations increased with increasing annealing temperatures. Moreover, the average grain sizes and films thickness slightly increased with increasing annealing temperatures.

Keywords : PZT films; Spin-coating; annealing temperature; AFM

1. Introduction

Lead zirconate titanate $[\text{Pb}(\text{Zr}_{0.52}\text{Ti}_{0.48})\text{O}_3$ or PZT] film are widely used in electronic devices such as memory, micro electro mechanical system (MEMS) sensors actuators and high power transducer due to their high piezoelectric performance. Nowadays, the increasing demand of thin materials or portable

devices, it has been researched and development piezoelectric materials with light weight and high performance. Moreover, PZT 52/48 composition has attracted great attention, its composition is close to the morphotropic phase boundary (MPB) which exhibited excellent ferroelectric and piezoelectric properties (Butnoi et al., 2013).

A variety of methods were used to prepare PZT ceramic films such as Rf-magnetron sputtering (Ma et al., 2021), chemical vapor deposition (CVD) (Li et al., 2001), screen printing (Simon et al., 2001), sol-gel drip coating (Shakeri et al., 2014) etc. Among those methods, sputtering and spin-coating methods have received higher than other methods. The ceramic films fabricated by sputtering process exhibit high dense morphology and good electrical properties. However, the sputtering process is expensive process due to it operate under high vacuum for long time deposition. Therefore, spin-coating is very attractive method. It is inexpensive and simple for film preparation.

In this work, we present a method of precursor solution and PZT ceramic film fabrication by a sol-gel method deposited on substrate via spin-coating technique, and then characterize the prepared films to obtain their properties such as phase formation, morphologies, and microstructure.

2. Methodology

Lead acetate trihydrate [$\text{Pb}(\text{CH}_3\text{CO}_2)_2 \cdot 3\text{H}_2\text{O}$, 99% of purity (sigma-Aldrich)], zirconium (IV) propoxide solution [$\text{Zr}(\text{OCH}_2\text{CH}_2\text{OH})_4$, 70wt.% in 1-propanol (sigma-Aldrich)], Titanium (IV) isopropoxide, $\text{Ti}[\text{O}(\text{CH}_2\text{CH}_3)_2]_4$, 97% of purity, (Sigma-Aldrich), 2-methoxyethanol and acetylacetone were used as raw materials of sol-gel method to prepare the PZT precursor solution. Firstly, $\text{Pb}(\text{CH}_3\text{CO}_2)_2 \cdot 3\text{H}_2\text{O}$ was dissolved in 2-methoxy-ethanol and continuously stirred at room temperature (RT) until cleaned solution. Then, the prepared solution was vacuum distilled at 120°C. At the same time, $\text{Zr}(\text{OCH}_2\text{CH}_2\text{OH})_4$ and $\text{Ti}[\text{O}(\text{CH}_2\text{CH}_3)_2]_4$ were weighed and dissolved in 2-methoxyethanol in a separate container under Ar_2 atmosphere. After that, all solution were mixed in a

flask and mixed solution was refluxed at 120°C for 2 h. After distillation, the clear and light-yellow solution is kept stirring in order to cooled to RT. The PZT solution was controlled to be 0.5 M.

The PZT films were fabricated by spin-coated on $\text{Ti}/\text{SiO}_2/\text{Si}$ substrates at 500 rpm for 10 sec. and 3000 rpm for 30 sec. subsequently given a pyrolysis treatment at 400 °C for 10 min. Then, annealed at different temperature of 550, 600 and 650 °C for 30 min. in air, with heating rate of 5 °C/min.

The phase formation was identified using XRD technique (X'Pert Pro MPD, PANalytical). The films thickness was characterized by FE-SEM (JSM-6335F, JEOL). The surface morphologies were observed by an atomic force microscope (AFM, Nanoscope III, Digital Instruments). While the surface roughness and grain size were obtained from these AFM images.

3. Results

After the PZT ceramic films are annealed at different temperature of 550, 600 and 650 °C for 30 min. The phase formation is analyzed using XRD and the XRD patterns of PZT ceramic films with different annealing temperatures and standard peak of tetragonal PZT ceramic are presented in **Figure 1**. We can see that the diffraction intensity of 001 and 110 peaks is increased with increasing anneal temperature and it shows the highest value at an annealed 650°C. In addition, the perovskite and unknown phase coexist in these films. However, the number of unknown decreased with increasing temperature, while the crystallinity was found to increase.

The cross-section and surface morphologies of PZT ceramic films are characterized by using FE-SEM and displayed in **Figure 2**.

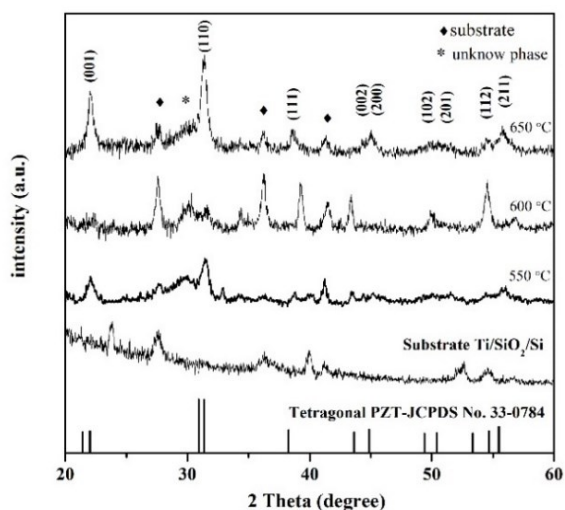


Figure 1 XRD patterns of PZT ceramic films annealed at different temperature of 550, 600 and 650 °C for 30 minutes.

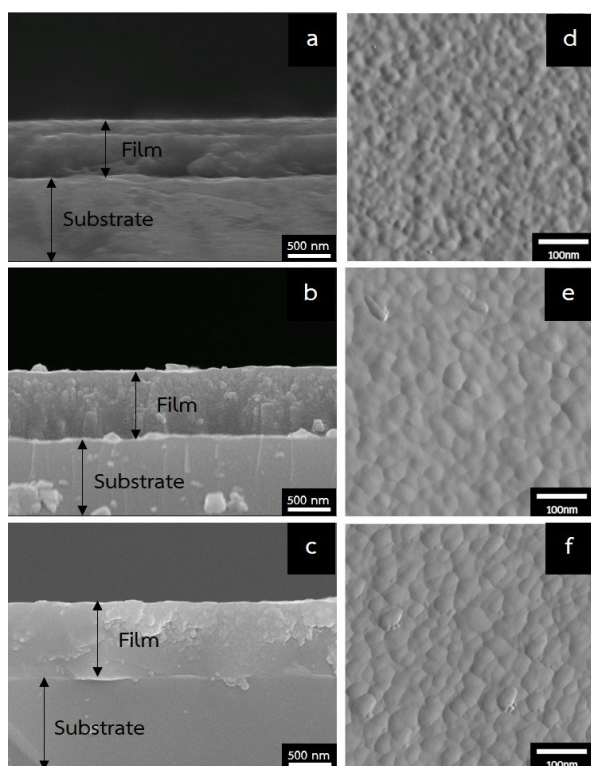


Figure 2 Cross-sectional SEM, (a) – (c) and surface SEM, (d) – (f) of PZT ceramic films annealed at different temperature of 550, 600 and 650 °C.

From cross-section image (**Figure 2(a)-(c)**) can observe that the PZT ceramic films coated on the substrate have a well bonded with Si-wafer. All

samples exhibited uniform thickness and high density. The ceramic films showed average thickness of 707, 827 and 900 nm, respectively. Moreover, the thickness slightly increased with increasing annealing temperature from 550 to 650° C. However, a slight increase can be observed in the average grain size with increasing annealing temperature. As seen in **Figure 2(c-e)** and **Table 1**.

Table 1 The PZT ceramic films properties at various annealing temperature

Ceramic films properties	Annealing Temperature (°C)		
	550	600	650
Thickness (µm)	0.7	0.8	0.9
Grain size (nm)	244	273	270
RMS (nm)	10.5	8.6	8.4

To analyze the dependence of surface roughness and surface morphologies of the PZT ceramic films on Si-wafer substrates are also characterized by atomic force microscopy (AFM) as shown in **Figure 3**. The grains and Root Mean Square (RMS) surface roughness were determined from AFM images. According to the results of AFM surface morphology, the initial surface shows a high RMS roughness of 11 nm of the sample annealed at 550 °C. Although, the roughness of the PZT ceramic films was decreased to about 8.6 nm and 8.4 nm for samples annealed at 600 and 650 °C, respectively. The surface roughness of PZT ceramic films can be significantly smoothed up by increase annealing temperature.

4. Discussion

After spin-coating, on Si-wafer substrates were coated with a gel - solution, good bonded to the substrate by capillary force. Then, gel solution was

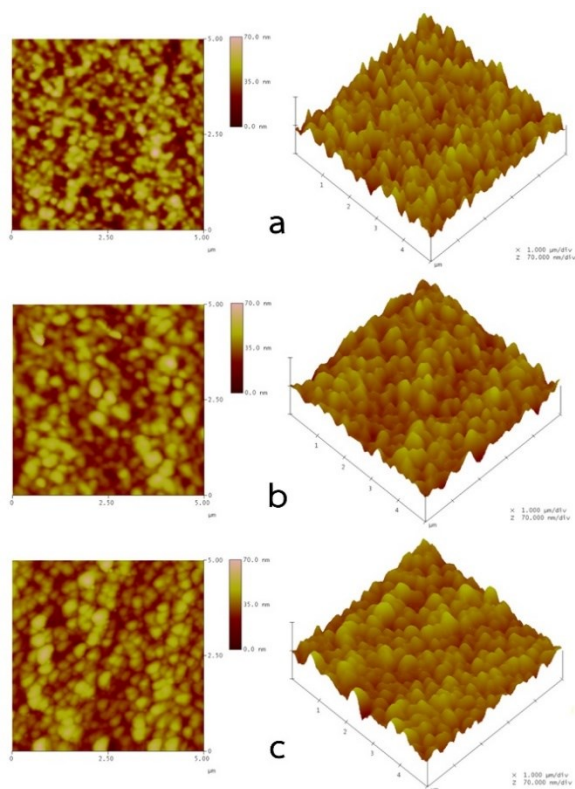


Figure 3 AFM images of PZT ceramic films annealed at different temperature of 550, 600 and 650 °C.

becoming a ceramic film by annealing process. Liquid volatilizing to be formed crystallinity as ceramic films. However, crystal structure depends on annealing temperature. From this result, the gel solution was transformed into perovskite phase of the PZT tetragonal structure of annealing at 650 °C for 30 min., In addition, an amorphous structure has been observed, the amorphous phase is not formed into completed crystals at the annealing condition. The perovskite phase increase with increasing annealing temperature. The PZT ceramic film, annealed at high temperature can improve surface roughness because of grain growth effects (Garbacz et al., 2018). The grain growth occurring at high temperature processes, the ionic mobility increases with increasing temperature, which explains by grain-boundary diffusion. Meanwhile, grain growth significantly increases the grain size and surface

roughness. Resulting in narrowing the gap between grain boundary or merge of others grain in the meantime (Kim et al., 2005). It is well known that the electrical properties of ceramic films such as dielectric, ferroelectric, and piezoelectric properties are strongly influenced by grain size and porosity. Generally, remnant polarization of hysteresis loops and dielectric constant are increased while the grain size decreases. In contrast, the ferroelectric and piezoelectric properties increased with large grain size (Zhu et al., 2007). SEM and AFM images indicate that a fine grain size, around 270 nm, a densely and smooth surface without porosity could be found after annealed at 650 °C. It is for possibility as piezoelectric film application.

5. Conclusion

In this work, lead zirconate titanate $Pb(Zr_{0.52}Ti_{0.48})O_3$ ceramic films under 20% mol of Pb-excess were successfully fabricated by spin-coating technique. The PZT ceramic film annealed at 650 °C show high perovskite phase, high smooth surface. The surface roughness was improved with increasing annealing temperature.

6. Acknowledgements

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7. References

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