THE EFFECT OF ANNEALING TEMPERATURE ON PROPERTIES OF PZT CERAMIC FILMS PREPARED VIA SPIN-COATING PROCESS

Marut Khieokae[1], Kanut Jinpak[2], Suphattra Kritwattanakorn[3], Suwimol Jairtalawanich[4], Tinno Kwandee[5] and Pichitchai Butnoi[6]

[1,2,3,4,5,6]Lecturer, Department of Industrial Technology, Faculty of Technical Education, Rajamangala University of Technology Krungthep, 2 Nang linchi Road, Tungmahamek, Sathon, Bangkok 10120 Thailand,

[1]marut.k@mail.rmutk.ac.th, [2]lershbhundtu.s@mail.rmutk.ac.th, [3]suphatra.k@mail.rmutk.ac.th, [4]suwimol.j@mail.rmutk.ac.th, [5]Tinno.k@mail.rmutk.ac.th, [6]pichitchai.b@mail.rmutk.ac.th

ABSTRACT

In this work, lead zirconate titanate $Pb(Zr_{0.52}Ti_{0.48})O_3$ or PZT films under 20% mol of Pb-excess were fabricated on $Ti/SiO_2/Si$ wafer by spin-coating method. The PZT films were annealed at different temperatures of 550, 600 and 650 $^{\circ}C$ 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 film thickness slightly increased with increasing annealing temperatures.

KEYWORDS: PZT ceramic films, Spin-coating, annealing temperature, AFM

1. Introduction

Lead zirconate titanate [$Pb(Zr_{0.52}Ti_{0.48})O_3$ or PZT] film are widely used in electronic devices such as memory, micro electro mechanical system (MEMS) sensors actuators and high power transducers due to their high piezoelectric performance [1-3]. Nowadays, the increasing demand of thin materials or portable devices, it has been researched and developed piezoelectric materials with lightweight and high performance. Moreover, PZT 52/48 composition has attracted great attention and its composition is close to the morphotropic phase boundary (MPB) which exhibited excellent ferroelectric and piezoelectric properties [4-6].

A variety of methods were used to prepare PZT ceramic films such as Rf-magnetron sputtering [7], chemical vapor deposition (CVD) [8], screen printing [9] and sol-gel dip coating [10, 11]. 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 verry attractive method. It is inexpensive and simple for film preparation. Spin coating is a technique for using centrifugal force to prepare films from solution. The solution is dispensed onto the center of a substrate, which is then rotated at high speed. The thickness of films can control by the spin speed and the viscosity of the solution [12-14]. However, it is difficult to obtain uniform phase structure and flat surface morphology by spin coating [14]. Additionally, the annealing process under heat treatment results in film cracking. As a result, dense, crack-free coatings with good surface roughness are required to form PZT ceramic films with good electrical properties.

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. Experimental

Lead acetate trihydrate [$Pb(CH_3CO_2)_2{\cdot}3H_2O$, 99% of purity (Sigma-Aldrich)], zirconium (IV) propoxide solution [$Zr(OCH_2CH_2CH_3)_4$, 70wt.% in 1-propanol (Sigma-Aldrich)], Titanium (IV) isopropoxide, $Ti[OCH(CH_3)_2]_4$, 97% of purity, (Sigma-Aldrich), 2-methoxyetanol and acetylacetone were used as raw materials of sol-gel method to prepare the PZT precursor solution. Firstly, $Pb(CH_3CO_2)_2{\cdot}3H_2O$ was dissolved in 2-methoxy- ethanol and continuous stirred at room temperature (RT) until cleaned solution. Then, the prepared solution was vacuum distilled at 120 ^{o}C. At the same time, [$Zr(OCH_2CH_2CH_3)_4$ and $Ti[OCH(CH_3)_2]_4$ were weighed and dissolved in 2-methoxyetanol in a separate container under Ar atmosphere. After that, all solutions were mixed in a flask and mixed solution was refluxed at 120 ^{o}C for

2 h. After distillation, the clear and light-yellow solution is kept stirring to cooled to RT. The PZT solution was controlled to be 0.5 M.

The PZT films were fabricated by spin-coated on Ti/SiO_2/Si substrates at 500 rpm for 10 sec. and 3000 rpm for 30 sec. subsequently given a pyrolysis treatment at 400 ^{o}C for 10 min. Then, annealed at different temperature of 550, 600 and 650 ^{o}C for 30 min. in air, with heating rate of 5 ^{o}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 temperatures of 550, 600 and 650 ^{o}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 [15, 16]. However, the number of unknowns 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. 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 ^{o}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.

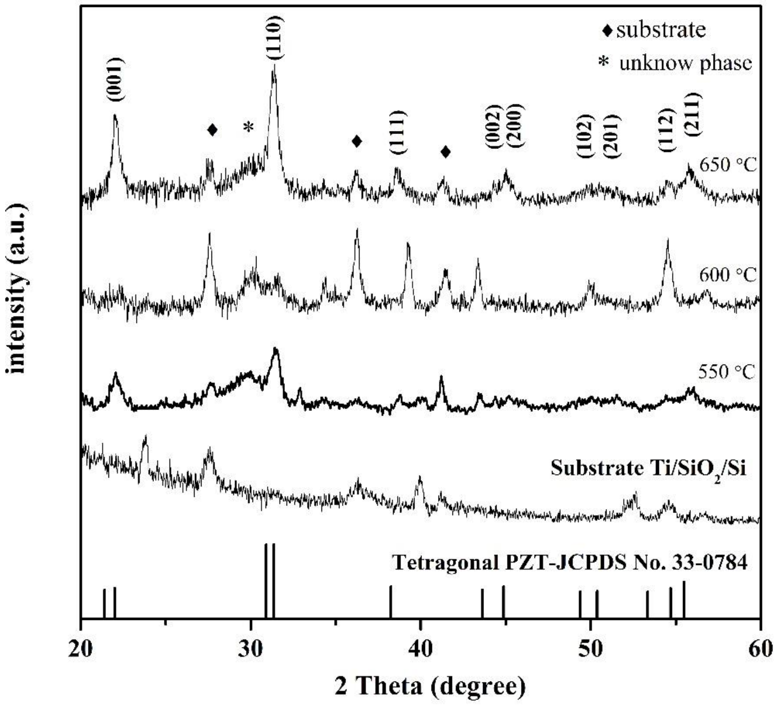

Figure 1 **XRD patterns of PZT ceramic films annealed at different temperature of 550, 600 and 650 °C for 30 minutes.**

Table 1 **The PZT ceramic films properties at various annealing temperature**

Ceramic films properties	Annealing Temperature (°C)		
	550	600	650
Thickness (μm)	0.7 ± 0.2	0.8 ± 0.1	0.9 ± 0.1
Grain size (nm)	244 ± 32	273 ± 28	270 ± 20
RMS (nm)	10.5 ± 0.3	8.6 ± 0.4	8.4 ± 0.2

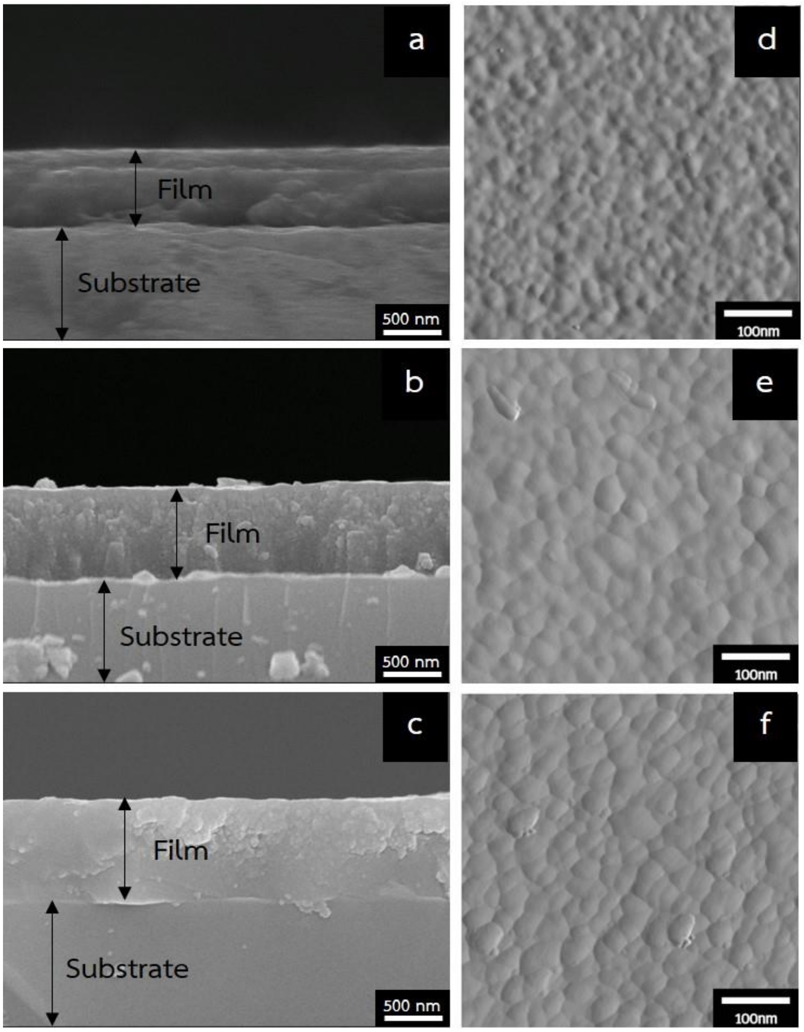

Figure 2 Cross-sectional SEM, (a) – (c) and surface SEM, (d) – (f) of PZT ceramic films annealed at different temperature of 550, 600 and 650 °C.

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 [3, 17]. 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 ^{o}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 ^{o}C., respectively. The surface roughness of PZT ceramic films can be significantly smoothed up by increase the annealing temperature.

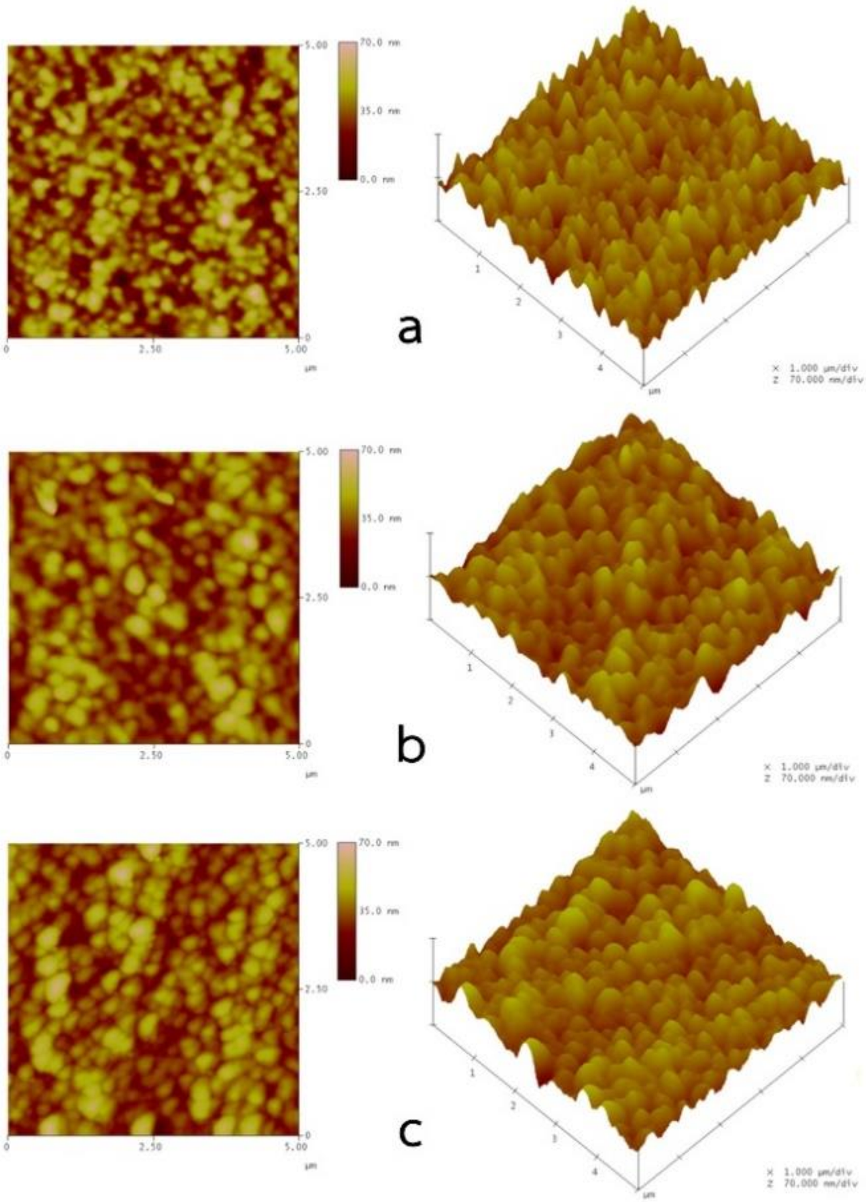

Figure 3 AFM images of PZT ceramic films annealed at different temperature of 550, 600 and 650 °C.

4. Discussions

After spin-coating, on Si-wafer substrates were coated with a gel - solution, good bonded to the substrate by capillary force [18]. Then, gel solution became a ceramic film by annealing process. Liquid volatilizing to be formed crystallinity as ceramic films [19, 20].

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 [5, 17]. The grain growth occurring at high temperature processes, the ionic mobility increases with increasing temperature, which explain by grain-boundary diffusion [17, 18]. Meanwhile, grain growth significantly increases the grain size and surface roughness. Resulting in narrowing the gap between grain boundaries or merging of other grains in the meantime [21]. 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 [22]. SEM and AFM images indicate that a fine grain size, around 270 nm, a densely and smooth surface without porosity could be found after annealing 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 surface roughness was improved with increasing annealing temperature. The PZT ceramic film annealed at 650 °C shows high perovskite phase, high smooth surface. The higher degree of perovskite phase in the ceramic film annealed at 650 °C for possible as good electrical properties of PZT ceramic film device.

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Author's Profile

Marut Khieokae received the M.Eng. degree in Metallurgical Engineering from Faculty of Engineering, Chulalongkorn University, Thailand. Currently, he is a lecturer in the department of Industrial Technology, Faculty of Technical Education, Rajamangala University of Technology Krungthep, Thailand. His research interests focus on the metallic material, structure, and mechanical properties of metal.

Kanut Jinpak received the B.S.Ind.Ed. degree in Industrial Engineering from King Mongkut's University of Technology Thonburi, Thailand. Currently, he is currently a lecturer in the department of Industrial Technology, Faculty of Technical Education, Rajamangala University of Technology Krungthep, Thailand. His research interests focus on metallic materials, metal casting, and metal welding processes.

Suphattra Kritwattanakorn received the M.Eng. degree in Manufacturing Engineering from Institute of Engineering, Suranaree University of Technology, Thailand. Currently, she is currently a lecturer in the department of Industrial Technology, Faculty of Faculty of Technical Education, Rajamangala University of Technology Krungthep, Thailand. Her research interests focus on simulation models, production planning, and control.

Suwimol Jairtalawanich received the M.Eng. degree in Industrial Engineering from Faculty of Engineering Chulalongkorn University, Thailand., Thailand. Currently, she is currently a lecturer in the department of Industrial Technology, Faculty of Technical Education, Rajamangala University of Technology Krungthep, Thailand. Her research interests focus on process improvement, quality control and management, waste reduction, and time study.

Tinno Kwandee received the M.T. degree in Master of Technology from the Technological University of the Philippines, Philippines. Currently, he is a lecturer in the department of industrial technology at the Faculty of Technical Education, Rajamangala University of Technology Krungthep, Thailand. His research interests focus on metallic materials, metal casting, and metal welding processes.

Pichitchai Butnoi received the Ph.D. degree in Materials Science from the Faculty of Science, Chiang Mai University, Thailand. Currently, he is a lecturer in the department of industrial technology at the Faculty of Technical Education, Rajamangala University of Technology Krungthep, Thailand. His research interests focus on the fabrication and characterization of energy storage systems based on piezoelectric materials.

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