Study of Hydrolysis on Pb(Zr\textsubscript{x}Ti\textsubscript{1-x})O\textsubscript{3} Synthesis Using Zirconium(IV) Nitrate as Precursor and Their Densification Process

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ABSTRACT

Pb(Zr\textsubscript{x}Ti\textsubscript{1-x})O\textsubscript{3} (PZT) has extensive application in electronic components as a thin layer. The densification layer is controlled by some factor such as precursor composition and heating techniques. Moreover, hydrolysis reaction and heating rate are also effecting the PZT synthesis. Zirconium(IV) nitrate stabilized by PEG-acetate was proposed as the precursor in this work. The PZT synthesis (55:45) was varied in \( R_w \) ratio by comparing water mole and the total mole of metal. The PZT obtained from \( R_w = 0, 6, 9, \) and 12 are coated on silicon substrates and annealed with at 650°C using various heating rates of 1, 5, 10, and 30 °C/min. The characterization and analysis of synthesized PZT were performed with FTIR and a microscope. Thermal dynamic behaviour and crystal orientation are also observed. The results show that PZT synthesis using zirconium(IV) nitrate as precursor and PEG-acetate was stable and reproducible. The effect of increasing the heating rate causes the dissipating PZT agglomeration, while the addition of water causes the cracking of crystals becomes more massive.

Key word: PZT synthesis, water hydrolysis, heating rates, thin film

INTRODUCTION

Pb(Zr\textsubscript{x}Ti\textsubscript{1-x})O\textsubscript{3} or PZT is a ferroelectric material that has been widely used in advanced sensor micro-electric mechanical systems (MEMS) applications [1], transducers, actuators [2], dielectric in organic thin film transistor (OTFT) fabrication [3], and non-volatile memory (NVRAM) [4]. In many applications, PZT with a thin film on the substrate is preferred because it has the advantage of flexibility, space saving [5] and high energy efficiency [6]. Many factors, such as precursor composition control, coating, and sintering techniques, influences the yield of the PZT thin film on the substrate.

Previously, PZT synthesis had been performed using zirconium-organic source such as Zr(OCH\textsubscript{2}CH\textsubscript{2}CH\textsubscript{3})\textsubscript{4} with some stabilizers substitute diethanolamine (DEA) [7], 2-methoxyethanol (MOE) [8], and ethylene glycol [9]. However, the stabilizers alternate such as polyol-acetate with zirconium(IV) nitrate, were rarely done than that of Pechini process. On the other hand, the addition of a mole of water, as a precursor control factor, can affect metallo-organic condensation reaction in sol structure to being PZT gel densification [10].
The hydrolysis reaction is initialized by water to the metallo-organic molecule and further reaction releases alcohol or water molecule. The general reaction described as follows [11]:

\[
\begin{align*}
M(OR)_x + mH_2O &\rightarrow M(OR)_{x-m}(OH)_m + mROH \text{ (hydrolysis)} \quad (1) \\
2M(OR)_{x-m}(OH)_m &\rightarrow (RO)_{x-m}(OH)_{m-1} \\
2M(OR)_{x-m}(OH)_m &\rightarrow (RO)_{x-m}(OH)_{m-1} \\
M-O-M(OR)_{x-m}(OH)_{m-1} + H_2O &\rightarrow \text{ water condensation} \quad (2) \\
M-O-M(OR)_{x-m-1}(OH)_m + ROH &\rightarrow \text{ alcohol condensation} \quad (3)
\end{align*}
\]

Hydrolysis of precursors with an amount mole of water, transforms the region phase of PZT crystals to the broad range a perovskite structure around ~800°C [9]. In addition to that, the heating techniques are required to prevent evaporation of Pb on the precursor that can reduce compactness of ceramic, stoichiometry [12] and crystalline phase [13]. Ryu et al. [14] reported that the solid-state PZT synthesis is denser with increasing heating rate but is not alteration in doped Nb₂O₅ ceramic. Chen and co-workers [15] had been observed the effect of heating rate to crystalline morphology as a thin film using PZT from zirconium(IV) octanoate precursor. Their work resulting in a dense fine-grained morphology at high heating rates. In contrast, Hall and co-workers [16] who observed the effect of heating rate of doped PZT reported that the best crystal growth was obtained using the lowest rate used in their work. For this reason, it is important to investigate the sol-gel synthesis of film tailored-PZT from Zr(IV) nitrate precursor using the same variable.

This paper informs a new simple method for synthesizing PZT from zirconium(IV) nitrate as precursor and their affecting factors. The paper focus is only to two factors namely water hydrolysis that affect the stability on polycondensation reaction and heating rates that affect the crystal grain. The other effects like solvent ratio, speed, coating volume and heating temperature may be recommended to the further research. The characterization and analysis of synthesized PZT were conducted by XRD, thermal analysis, FTIR, and optical microscope.

**EXPERIMENT**

**Chemicals and Instrumentation**

Chemical reagents were used for precursor synthesis such as titanium(IV) propoxide 98% zirconium(IV) nitrate pentahydrate, acetic acid glacial, and polyethylene glycol 600, all supplied by Sigma-Aldrich. Lead(II) acetate trihydrate 99% was also used and supplied by Merck. The coating substrates, silicon wafer (1 0 0) is cleaned by RCA-1 and RCA-2 which was made from ammonium hydroxide 25%, hydrochloride acid 37% (from Merck) and hydrogen peroxide 50% (from PIP).

The instruments for synthesis and sols tailoring are analytical balance (Ohaus Pioneer PA214), a set of reflux apparatus (Iwaki), micropipette 10-100 μL (Soconex), muffle furnace (Carbolite 1000), and spin coater (VTZ-100). The sol-gel was analysed by thermogravimetric (TGA/DSC Mettler Toledo Star eSystem). The powder and film were characterized by XRD (Philips X’pert Cu Ka₁ = 1.54060 Å), infrared spectrophotometer (Shimadzu FTIR-8400S) and optical microscope (Olympus BX51).

**Synthesis and Manufacture of PZT Film**

**PZT sol synthesis**

The sol-gel synthesis procedure was adapted from the works of Qing et al. [17] and Zak et al. [18]. Mole fraction of Zr:Ti which on Pb(ZrₓTi₁₋ₓ)O₃ used is 55:45, near the
morphotropic phase boundary (MPB). The molarity of PZT sol was 0.15M in 1:1 (acetic acid:PEG-600) and considered as a total solvent. The sol-gel reaction firstly reacted from zirconium(IV) nitrate pentahydrate by half of the total acetic acid in a reflux apparatus at 120 °C for one hour. Then, the temperature was lowered down, titanium(IV) propoxide was then added and the mixture was continued for 15 minutes of stirring. Next, PEG-600 was added and the mixture was refluxed for 30 minutes at 70 °C. Separately, an excess of lead(II) acetate trihydrate (2% weight), to avoid volatilization during sintering, was refluxed at 80 °C using half of total acetic acid for one hour. The final step is dripping lead(II) acetate solution into Zr/Ti sols while stirred for 30 minutes and followed by refluxing it at 60 °C for one hour. The clear yellowish sol-gel solution was obtained after aging the mixture for three days without further distillation to eliminate water.

**PZT Solution Hydrolysis**

Solutions of PZT which produced from sol-gel synthesis were hydrolysed by mixing an equal water volume based on the degree of hydrolysis, as shown in the following equation [9]:

\[
R_w = \frac{[\text{H}_2\text{O}]}{[\text{Pb(Zr,Ti)O}_3]}
\]

\(R_w\) is a degree of hydrolysis PZT solution, compared by adding some molar of water to the total mole of metal. The hydrolysis was completed in \(R_w = 3.0\) and elsewhere \(R_w = 1.5\) [19], but for observation of hydrolyzing effects, it was developed to higher number of \(R_w\). PZT solution 0.5mL was placed on Eppendorf tube and added a water volume that calculated from hydrolysis with a variation of 0, 6, 9 and 12; followed by centrifuging the solution for three minutes. Water contains solution was aged to 3 days before applying the coating. The compaction process dependent on water effect is performed by observing some functional group in FTIR spectra of the three-phases (solution, gelation, and ceramic powder).

**Substrate Coating and Annealing**

The silicon wafer must be cleaned with RCA-1 and RCA-2 to remove the organic and inorganic impurities that may hold on the surface, such as oil or metal salt. The presence of impurities can disturb the coating as detailed by Kern [20]. Silicon oxidation is formed with nitric acid to make hydrophilic surface [21]. Every clean wafer was coated twice at 1500 rpm for 60 seconds using 50 µL PZT sol volume. The same procedure was repeated for each variation \(R_w\) and heating rate.

The wafer coated PZT is annealed on muffle furnace for each \(R_w\) variation at 10°C/min and 30 °C/min heating rate. The plateau sintering was conducted at 650°C for two hours. The grain growth morphology was observed with a microscope by comparing \(R_w\) and heating rate effects. Furthermore, XRD and thermogravimetric analysis were used to investigate the material properties.

**RESULT AND DISCUSSION**

**Sol-gel Synthesis of Precursor**

PZT synthesis was completed in 1:1 ratio of acetic acid to PEG-600 in 6 mL total volume (Figure 1). They are two synthesis examples that were done at different times for testing the reproducibility of the synthesis method. The results were slightly diverse in colour after three days of aging. The product from the second attempt (figure 1b) has a more reddish colour compared to the first attempt (figure 1a) due to difficulty to maintain constant
temperature during the reflux process of zirconium(IV) nitrate. However, two sols did not show any observable turbidity or cloudyness. Therefore, the precursor stoichiometric control can be performed, and synthesis method can be repeated. Furthermore, this synthesis method is considered easy to perform and using only two solvents e.g. acetic acid and PEG-600, as the replacement of ethylene glycol [17].

Figure 1. Sol-gel PZT synthesis (a) First synthesis, (b) The second synthesis shows more reddish

Studies of Precursor Thermal Analysis

The thermal analysis was performed with an amount PZT sols in scanning temperature of 25°C to 800°C for 30°C/min rate. The TGA curve (Figure 2) shows very slow weight loss process occurring to 350°C, then the weight losses drastically at close to 450 °C. Below 350°C, evaporation of water and organic volatile molecules is likely occurred which shows weight loss of about 5%, whereas close to 450°C, about 85% weight loss of sample was related to crystalline PZT formation and firing area of non-volatile organic as ligand complex.

Two significant DSC peaks was detected at 200 °C and 430°C and correspond to exothermic reaction in process. The DSC peak at 200°C is presumably the decomposition temperature of the oxyacetacrylate complex group on gels related to 8% weight loss sample

Figure 2. Thermogram of PZT gels.
The second peak (430°C) is related to the burning reaction of organic ligand residues and the early forming PZT perovskite crystallization phases. A similar observation of the exothermic peaks is also reported and discussed by Bruncková et. al. [10], which was 250 °C and 440 °C and correspond to 31.8% and 40.5% of weight loss.

**Infrared Spectrum Analysis**

The PZT sols at ambient temperature, 100 and 300°C, were observed using FTIR spectrometers to inspect the change of organic functional groups. In addition, the 200° and 430°C temperature peaks which has detected from thermogravimetric analysis were also selected to observe. The decomposition of the organic compound in all temperatures as vibration band is shown in Figure 3.

![Figure 3. IR spectra of PZT sol, gels and powder; spectra a, b, and d, are PZT at 25, 100, 300 °C heating, spectra e and e at DSC exothermic peaks, and spectra f at 650 °C annealing temperature.](image)

A broad peak around 3450 cm\(^{-1}\) (*mark 1*) is the vibration of -OH functional group from polyethylene glycol 600, acetic acid and water. The broad peak is getting invisible as the temperature increases from ambient temperature to 650°C, which is observed as crystallization region based on DSC-TGA. Similarly, peaks around 2876 cm\(^{-1}\) (*mark 2*) for \(sp^3\)-CH stretching vibration and 1295 cm\(^{-1}\) (*mark 5*) for -CO twist vibration from acetic acid, were also decreased in intensity as the temperature reach 650°C.

The vibration of ester group was observed around 1736 cm\(^{-1}\) peak (*mark 3*), which obtained from PEG and acetic acid, and the intensity is decreased at 300°C temperature. This presumably indicates a difficult ester removal due to the high molecular weight derived from PEG-600. In contrast, the ester group that synthesized from ethylene glycol as precursor was easily removed by distillation [9]. The weak peaks (*mark 4*) around 1550 and 1470 cm\(^{-1}\),
indicate an asymmetry vibration of -COO with coordinate mode bidentate chelating to metal. Upon heating to 200°C, the peak decrease as the weak acetic group is disappeared. A small peak detected around 543 cm\(^{-1}\) is expected to be the M-O-M vibrational bond (mark 6). Overall, the infrared functional peaks remain unchanged up to 300°C, indicating a strong ligand attachment to metal. In addition, the unchanged infrared functional peaks between 25 and 100°C resembling the stability of sols at certain temperature.

**Growth Crystal Analysis**

The XRD data was collected from dried sols annealed at 650°C for 2 hours to powder form. The powder pattern (figure 3) shows no significant change in crystals orientation found either at heating rates of 10°C/minutes or 30°C/minutes. However, slightly visible in peak intensity which indicates to larger crystallizations was formed at low heating rate. This peak intensity was associated to perovskite structure that increase high density of ceramic PZT. In addition, an undesirable structure of Pb pyrochlore arises from ZrO\(_2\) formation associated to PbO formed during sintering process [9].

The concentration of perovskite in the bulk sample was calculated from the total perovskite intensity compared to the total peak intensity. The peaks of perovskite structure at \(d = 2.35\) Å and two minor peaks at \(d = 2.88\) Å and 1.66 Å were corresponded to \(2\theta = 38.3, 31.1\) and \(55.3°\). The pyrochlore peaks was observed for the \(d\) values of 2.62, 3.02, 3.12 Å that represent of \(2\theta = 34.2°\) (3 1 1), 29.6° (2 2 2), and 28.6° (4 0 0). The degree of perovskite \(f_{hk}\) orientation used was the (1 0 1) orientation intensity and compared to the total perovskite intensity. This calculation methods had been used and further explained by Bose *et. al* [22].

![XRD data of PZT gels is annealed for two hours at 650°C.](image)

**Figure 3.** XRD data of PZT gels is annealed for two hours at 650°C. ● Perovskite peak, ▲ Pyrochlore peak.

The heating rate effect toward the PZT structure is presented in Table 1 that describes the perovskite structure content and perovskite orientation dependence on the heating rates. The perovskite structure formation increases in a lower heating rate of 10°C/min by percentage perovskite of 64.87% compared to 30°C/min which is 61.21%. This phenomenon related to more time of reduction oxygen which occurs in the pyrochloric structure.
Pb(Zr,Ti)$_3$O$_7$ that also undergo change at lower heating rates. Its orientation can be seen in Figure 3 at $2\theta = 30.9^\circ$ for $h k l$ (1 0 1) over 10° and 30°C/min peak. The (1 0 1) orientation in low heating rate is slightly high (67.54%) than in higher heating rate which indicates grain growth, presumably change of pyrochlore to perovskite structure. The pyrochlore structure was formed by metastable nanocrystalline which not completely decomposes to form perovskite structure because an inadequate activation energy during nucleation [23]. For these reasons, the heating rate is recommended to be carried out in a lower heating rate to increase the perovskite structure formation rather than that of pyrochlore structure.

Table 1. XRD structure content identification

| Heating Rate (°C/min) | Σ Perovskite Intensity | Σ Pyrochlore Intensity | Perovskite Content (%) | $f_{h k l}$ (1 0 1) in perovskite (%) |
|-----------------------|------------------------|------------------------|------------------------|-------------------------------------|
| 10                    | 2144                   | 1161                   | 64.87                  | 67.54                               |
| 30                    | 1070                   | 678                    | 61.21                  | 62.15                               |

**PZT Thin Film**

**Effect of Heating Rate**

Figure 4 shows the results of variations in heating rate without water addition ($R_w = 0$) to study the PZT film formation (200x magnification). The cracked film was formed in 10°C/min (figure 4c) and 30°C/min rate (figure 4d) that shows a massive crack in both film. This cracking film left some area without any PZT grain that show black color in top area of substrate (figure 4c and 4d).

Moreover, at the low heating rate, the cracking was not found in the film and white agglomeration was forms (figure 4a, 4b). This phenomenon has corresponded to the change

![Figure 4](image-url)
of pyrochlore structure into perovskite that started to grow at low heating rate as indicated on XRD data (figure 3). Furthermore, the perovskite structure PZT thin film tend to have spherical morphology (in high magnification) [24] and have white colour [25] which was not observed upon high heating rates. Meanwhile, the pyrochlore structure has a rosette-shaped morphology that likely dominates in the high rate.

Effect of Hydrolysis

The observation of water effects on the PZT sols that play a role as a catalyst to form the ester ligand (reaction 1 and 2) was observed in the film boundary crack at 10°C/min heating rate. Figure 5 shows the surface and cracking crystal of PZT films at $R_w = 0$ upon the addition of water. As also shown at $R_w = 0$, the agglomeration of PZT still present in the bottom boundary while ruptured crystalline like glass-crack observed above the boundary at $R_w = 6$. This condition is all observed in high water ratio in which all undergo tremendous crystal crack.

![Figure 5](image)

**Figure 5.** Images of PZT film (200x magnification) coated in silicon substrate at heating rate $10^\circ$C/min dependence ($R_w = 0$ (a), 6 (b), 9 (c), 12 (d)).

CONCLUSION

The PZT synthesis from zirconium (IV) nitrate precursor with PEG600-acetic acid (1:1) solvent were performed and reproduced. The resulting sols did not show any precipitation or turbidity due to the stability of PEG-600. The effect of a low heating rate increases the chance of perovskite structure formation and leads to the agglomeration of the film, whereas high heating rates yields a cracked film. The addition of water to PZT sol causes the cracking become wider and eliminate the film agglomeration.

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