Effect of Addition Pb Content on Lead Titanate Thin Films for MIM Capacitor

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Abstract. Lead titanate (PbTiO$_3$) has been precisely studied on the films preparation due to its unique perovskite structure having ferroelectric behaviour with high permittivity factor for complex storage applications such as capacitor, transistor, and ferroelectric random access memory. In the need to have high quality (PbTiO$_3$) thin films, the lead (Pb) volatilization during crystallization process by means of applying heat treatment as part of crystal growth purpose must be realized. Therefore addition of Pb excess is the highest consideration in lead based composite to ensure perfect crystal growth ever form as well as yield to great particles polarization. There are some issues like fatigue, imprinting, and leakage current that need to be considered to assess the thin films performance. However, the present study focuses only on the crucial issue of leakage current behaviour of the nanoscaled thickness that might be in relation to the microstructural properties of the thin films. Thus, the influence of having extra Pb content might ascertain the benefits of PbTiO$_3$ thin films towards high performance metal-insulator-metal capacitor.

Keywords: Lead titanate thin films; extra lead content; surface morphology; leakage current density behaviour; nanoscaled thickness films; resistivity behaviour

1. Introduction

Lead based ceramic materials have been discovered since more than 30 years ago. Lead titanate PbTiO$_3$ with the unique perovskite structure promotes broad range of device application due to the outstanding properties; one of them is high dielectric permittivity. Variety techniques of PbTiO$_3$ thin films have been prepared by using radio frequency magnetron sputtering [1]–[3], metal organic chemical vapor deposition, MOCVD [4]–[6], pulsed laser deposition, PLD [7]–[9], and sol-gel derived spin coating method which involves solution to gelatinous films transformation by using spin coating technique [10]–[13]. Sol-gel process offers ability to control the stoichiometry composite, obtain extremely thin films homogeneity, deposition of large area, and can be done at room temperature. These being the reasons to in line with the cost effective and time efficient in producing high quality thin films performance. Therefore, the solutions need to be carefully prepared in order to gain high purity elements prior to films deposition. It is compulsory in sol-gel process to be familiar with the type of starting materials, the range of molar concentration, and also the addition of extra Pb excess (5~25mol%) purposely for preparing PbTiO$_3$ films [2], [14], [15]. The purpose of adding Pb excess is

to compensate the Pb deficiency in the thin films during high heat treatment that causing to the defect of A-site, ABO3-perovkite structure which leads to the permanent failure as ferroelectric material.

In this study, the PbTiO$_3$ thin films were prepared by sol-gel derived spin coating technique with extra Pb excess (5~20mol%), to reveal the effect towards nanostructural changed and electrical properties.

2. Experimental Method

This study presents the actual experimental investigation towards characterization of PbTiO$_3$ thin films based on simple configuration of metal-insulator-metal, MIM for capacitor application. Basically, solution deposition method through spin coating techniques is the most preferable technique to produce large deposition area of highly resistive materials as well as keep in pace with industrial needs. Thus, low cost production with zero defect performance could yield to major achievement in the most discrete device fabrication challenges. Here, we followed the simple process of solution-to-gelatinous transformation according to Bao *et al* procedure with alternate starting materials which can be referred in [10].

2.1. PbTiO3 solutions

The PbTiO$_3$ precursor solutions were prepared by simple sol-gel method in air mixed-oxide, at room temperature. The starting materials involved alkoxide material, Titanium tetraisopropoxide, TTiP (Sigma Aldrich, 97%) and lead acetate trihydrate (Sigma Aldrich, 99.9%) with the solvent, 2-methoxyethanol (Sigma Aldrich, 99.9%). First, the lead acetate trihydrate powders were dissolved in 2-methoxyethanol stirred at 100°C for about 1hour. Then, titanium isopropoxide was added to the solutions and stirred continuously for the next 1hour. The solutions were first prepared at different concentration (0.1~ 0.5mol) in previous study as reported elsewhere. It was found that 0.4mol solution is the most preferable concentration that brings to extended investigation that precisely makes for the present study. After that, the prepared solution was added with extra Pb excess (10 and 20mol%) referred to the actual concentration, named the samples as PbEq, Pb10, and Pb20. Then, a little drop of methanol was added before the solutions undergone for a day ageing process at room temperature.

2.2. Thin films depositions and characterization

The deposition process of PbTiO$_3$ was setup under 3000rpm spin speed for about 30s onto cleaned 200nm indium tin oxide (ITO) coated nglass substrate. Prior to the deposition process, the solutions were putted in ultrasonic bath at 50°C about 20mins to form even smaller particulates ensured nice dispersion of multicoated thin films. Then, the prepared films were dried to remove residual organic matters at 150°C for 10mins and continued for five times repeated coating at same conditions. Lastly, in crystallization process, the films were annealed at 500°C for 30mins and let them cooled off at room temperature. These two steps of heat treatment process are to ensure the films were under crack free conditions.

The characterization of PbTiO$_3$ thin films was carried out for electrical and structural investigation with gold (Au) as metal contact based on configuration Au/PbTiO$_3$/ITO/glass substrate illustrated in Fig. 1. The thin films characterizations were specifically investigated by two point probes solar simulator (BUKOH KEIKI CEP-2000) to determine thin films resistivity, surface profiler (Veeco) for film thickness measurements, and atomic force microscopy, AFM (Park System XE-100) and field emission scanning electron microscopy respectively (FESEM-JEOL) for structural of thin films.

3. Result and Discussions

3.1. Structural Properties

Preparation of the thin films at 0.1~0.5 mol is to ensure that the initial concentration can be maintained throughout developing the PbTiO$_3$ thin films for storage application mainly as capacitor discrete device. Such that, the surface morphology of 0.1 to 0.5mol concentration were observed by AFM with 10μm of scan size and 2.50 of scan rate as shown in Figure 1. It is revealed that the average surface

roughness can be as low as 0.388nm found at 0.4mol concentration films. At 0.5mol concentration, the films tend to have such high roughness about 5.255nm due to the large gap of hills and valley at surface films. Entire results of average surface roughness at various molar concentrations were tabulated in Table 1.
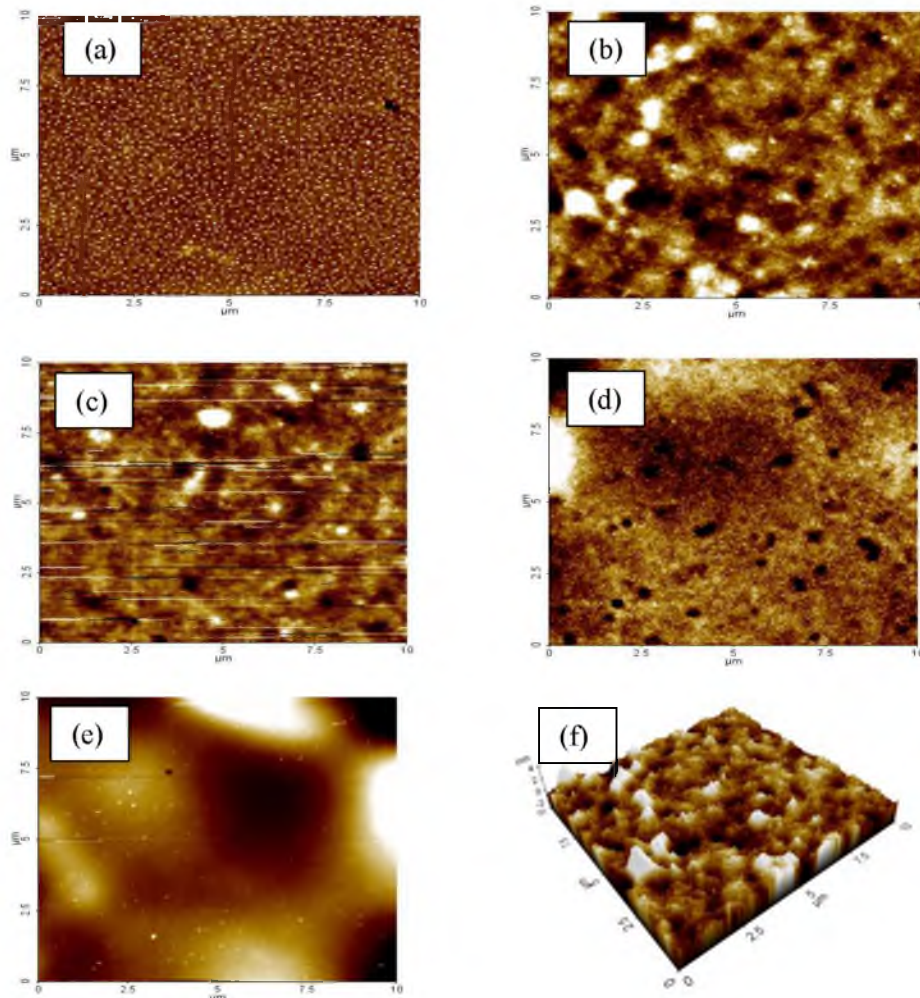

Figure 1. AFM result of PbTiO$_3$ thin films varied at different molar concentration, (a) 0.1mol, (b) 0.2mol, (c) 0.3mol, (d) 0.4mol, (e) 0.5mol, and (f) 3-D view of 0.4mol.

Table 1. Average surface roughness of PbTiO$_3$ thin films at various molar concentrations.

Molar concentration (mol)	Average surface roughness
0.1	1.057 nm
0.2	0.593 nm
0.3	0.482 nm
0.4	0.388 nm
0.5	5.255 nm

Thus, 0.4mol prepared PbTiO$_3$ solutions were then ready for three samples that simply according to the addition of Pb content prior to one day ageing process, known as PbEq, Pb10, and Pb20. Instead of identifying the RMS values of surface roughness, the prepared films were through FESEM observation in order to assess preferred grains size, less grain boundaries existence, also densification of the grains. Thus, Figure 2 shows the surface morphology and cross-sectional view of the films surface.

From the figure, it is clearly seen that the grains growth have much influenced by the used of ITO electrode. The nanostructured PbTiO$_3$ thin films were obtained very high dense films for PbEq without having actual grain structure. On the other hand, seems that both Pb10 and Pb20 samples were having amorphous structure shows the presence of combined flakes and grains distribution on films surface. However, Pb10 sample managed to performs such a uniform structure compared to Pb20 samples where flakes , whereas the Pb10 sample was having uniform gain distribution, though multi structures formation like combination of flakes and grain structure was obtained due to the influenced of ITO surface that has probability of high surface roughness. Therefore, Pb10 sample was carried out for grain size measurement that achieved around 55.65nm that in well agreement with the study worked by Cheng et al; 50nm grain size of polycrystalline films [16]. Moreover, from the cross sectional view of the films in Figure 2(d), Pb10 sample formed a highly densification films along with thickness measurement of 418nm. Entire films thickness measurements are tabulated in Table 2 along with the resistivity and conductivity results.
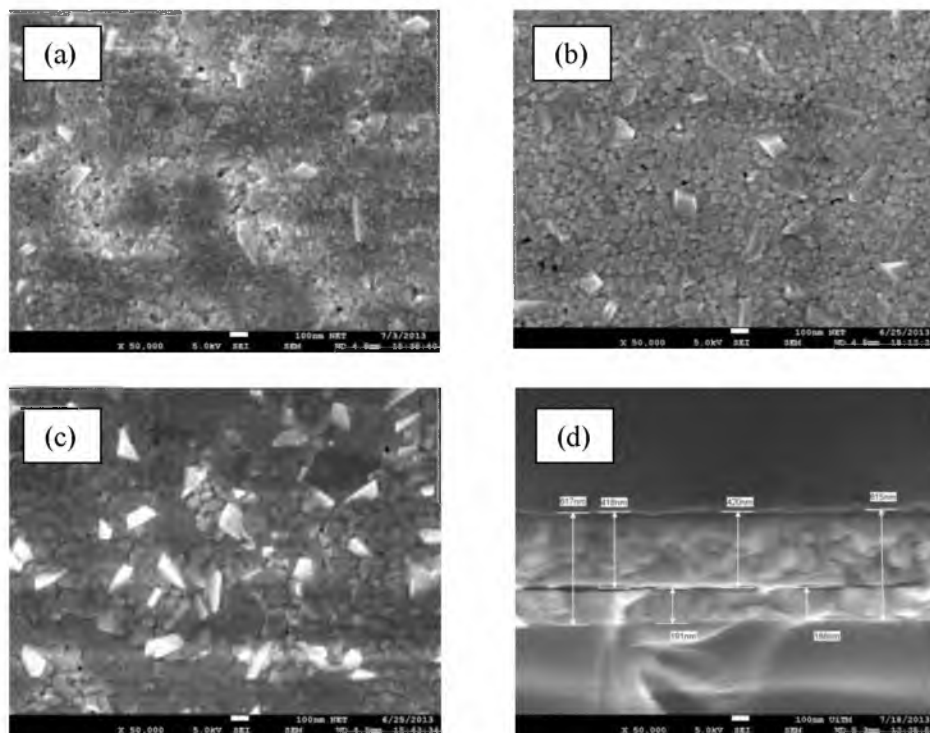
Figure 1. FESEM result of PbTiO$_3$ surface morphology at influence of addition Pb content (a) PbEq, (b) Pb10, (c) Pb20, and (d) cross-sectional view of Pb10. (x50,000 magnification)

3.2. Electrical Properties
3.2.1. Resistivity behaviour. In this investigation, the resistivity and conductivity were calculated and tabulated in Table 2. The reason to have resistivity behaviour of the thin films is to show the interesting factor that employing lead titanate for MIM capacitor in general. Theoretically, this

material typically behaves insulate to the passage of heat and electricity at films thickness dependency [17].

Table 2. Summary of Films Thickness, Resistivity, and Conductivity Behaviour of PbTiO$_3$ thin films at Influence of Extra Pb Content.

Sample	Thickness	Resistivity	Conductivity
PbEq	239 nm	2.200x10^5 Ω.cm	4.544x10^{-6} S.cm^{-1}
Pb10	418 nm	3.035x10^5 Ω.cm	3.295x10^{-6} S.cm^{-1}
Pb20	359 nm	2.731x10^5 Ω.cm	3.660x10^{-6} S.cm^{-1}

The result shows that highest films resistivity was obtained at Pb10 samples (3.035x10^{5}Ω.cm) which consisted to the thickness measurement (418nm). In other words, addition of 10mol% extra Pb content offers high densification addition to less grain boundaries resulted to high resistivity films.

3.2.2. Current density behaviour. In actual I-V characteristic in ferroelectric thin films are known as total switching current (J$_S$) that performed by polarization current (J$_P$) and electronic current (J$_E$) as previously stated in [18]. Besides that, there are other things need to take into account at such as, the true leakage current (J$_L$) and also the current that may be affected by ageing factor (J$_A$) as proposed in [19]. Park *et al* in his excellent study on the effect of oxygen vacancy in ferroelectric perovskite materials will permanently leads to fatigue, imprinting, and leakage current one of them [20]. Herein, the issue of leakage current in thin films processing is the most critical concern in memory device application.
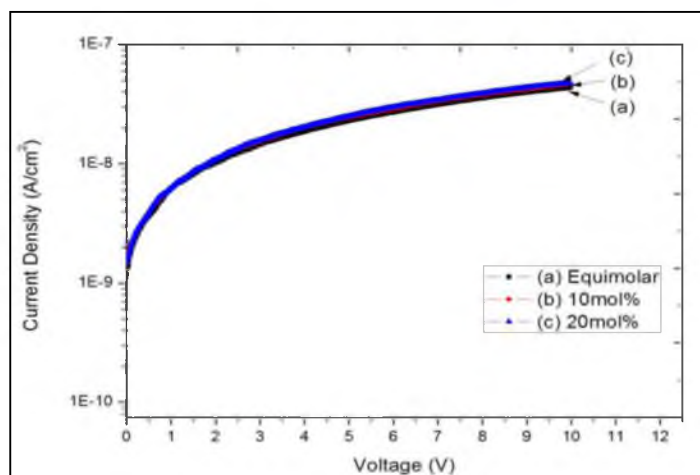

Figure 3. Plot of current density of PbTiO$_3$ thin films measured under 10V

Therefore, this study managed to obtain current-voltage characteristic (log *J* versus *V*) result as depicted in Figure 3 at such low leakage current density found under 1.00x10^{-7}A/cm^2. The voltage is applied with a step of 0.1V for each measurement at room temperature. It is noted from the figure that the current is exponentially increase under low applied voltage (5V), followed by a saturation region at higher voltages. Herein, the J-V characteristic in this study were found typically a form of mixed Schottky and Poole-Frenkel emission that reported as MIM capacitor in [13], [18].

However, such low leakage current existed might be due to the presence of interfacial layer between the films and bottom electrode as proven in Figure 2(d). This layer kind of known as a 'dead layer' creates even small conductivity whenever 0.0V being applied to the device. It also consisted to the study reported by Tang *et al* that worked on the electrical behavior of calcium doped leat titanate

films [22]. Apart of that, Chiu *et al* discovered that the leakage current level is high in most polycrystalline structure (~10^{-4}A/cm^2) for Ta$_2$O$_5$ thin films [21] in relation with the improvement made by Jia *et al* in [23] that used Ru$_2$O as bottom electrode for polycrystalline bilayer films which had captured much interest on this study to keep going on having bilayer configuration in future.

4. Conclusion

Briefly, PbTiO$_3$ thin films were successfully prepared through economical and low temperature crystal growth of sol-gel derived spin coating method. This work highlights the significant effect of adding extra Pb content towards resistivity and leakage current density behaviour of the nanoscaled thickness thin films MIM capacitor. This is one of the criteria need to be acknowledged as part of research work related to ferroelectric ceramic material.

Here, Pb10 samples have demonstrated polycrystalline structure as well as denser films observed by FESEM images at x50,000 magnification and found 55.65nm of grain size. This promotes to the electrical properties measured by I-V measurement that the Pb10 films having very high resistivity value; 3.035×10^5 Ω.cm at 418nm thickness as well as low leakage current density; 1.00×10^{-7}A/cm^2 under ohmic region. Therefore, addition of 10mol% Pb content is the most preferable amount that promotes as great dielectric layer in high MIM capacitor performance.

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