The potential role of amorphous lead titanate thin films as nanodielectric layer for capacitor applications

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Abstract. A Study of thin films preparation faces many challenges due to the environmentally sensitivity that could initiate effect towards device performance. Requirement to fabricate the passive device like capacitor at such nanoscaled thickness is quite challenges that would initiate the effect on the device performance. Nowadays, capacitor not just only existed by conventional dielectric material, it can become a complex device when ferroelectric materials get involved. This material promotes useful knowledge of their polarization behavior which contains switching element that premier contribution for memory storage applications. The present study demonstrates the potential of amorphous PbTiO3 thin films as nanodielectric layer for high performance capacitor at low voltage applications. This unique characteristic of amorphous structure performs such incredible high dielectric constant value about ~100 and tangent loss of 4-5%, measured at 1 kHz. The PbTiO3 films also involve other electrical measurement like P-E hysteresis loop.

Keywords: Lead titanate thin films; dielectric property, ferroelectric behaviour, metal-ferroelectric-metal capacitor

1. Introduction
Lead titanate (PbTiO3) is a perovskite structured ceramic family that has ferroelectric behaviour. This comes across to the attention that the energy storage elementary in memory device has been influenced by this factor. Thus, as pointed out by Haertling et al in her extensively literature on ferroelectric ceramic overview; ferroelectric behaviour is the reason to gain high dielectric constant of thin films [1]. This highlights to the significant of PbTiO3 ferroelectric ceramic material to be used in a broad range of device application, for example metal-ferroelectric-metal (MFM) capacitor [2], metal ferroelectric semiconductor (MFS) transistor [3], [4], and non-volatile random access memories (NVRAMs) [5]. Various processing methods have been used to prepare PbTiO3 thin films, such as metal organic chemical vapour deposition [6]–[8], radio frequency magnetron sputtering [9]–[11], and sol-gel processing [12]–[16].
The films preparation by sol-gel processing has attracted many researchers because of its ability to deposit large area as well as being cost effective production in line with industrial needs. It also produces such a various structural property which depends on the effect during deposition process. Crystalline PbTiO$_3$ films with purely perovskite structure were obtained in most studies preferred using platinised silicon substrate with titanium adhesion, with contribution of highly rapid annealing treatment up to 650–800°C [17]–[19]. This however gives impact on mass production cost, where low synthesis temperature could be the best alternative to be implemented for the preparation of ceramic films on soda lime glass substrate. In [20], Cheng et al had successfully prepared nanocrystalline PbTiO$_3$ films on glass substrate and spent most of his time to value the films potentialities through electrical measurement. In this study, we purposely prepare amorphous films of PbTiO$_3$ in order to investigate its property mainly for high performance capacitor applications.

2. Experimental Method

Preparation of thin films PbTiO$_3$ using indium doped tin oxide; ITO glass substrate is most preferable for metal-ferroelectric-metal, MFM capacitor due to high conductivity behaviour of ITO itself. This study presents an experimental investigation on the potentiality of purely amorphous PbTiO$_3$ films under sub-100nm thickness at low processing temperature. Among various techniques in chemical solution deposition, spin coating technique shows interesting way in approaching sub-100nm scaled film thickness with high films densification controlled. Basically the technique promotes homogeneity of multilayer coating which also covering large and very complex area. Thus zero defect films could yield to high performance thin films capacitor devices.

2.1. PbTiO$_3$ solutions

The PbTiO$_3$ precursor solutions were made through polymerization at open ambient 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%). A mixture of lead powders and solvent were mixed in 50ml beaker glass and stirred at 100°C for about 1hour. The stirring heat then were reduced to 60°C, while quickly added the titanium isopropoxide into the solutions and continuously stirred for the next 30minutes. The process at this stage was handled in very quick movement so that the alkoxide solution will not vaporized quickly with humidity at room temperature. Then, the prepared solutions were added with an appropriate amount of lead powder that sufficient to avoid lead compensation during annealing treatment. After that, the solutions were gone through ageing process about 24–36 hours with tight sealed beaker.

2.2. PbTiO$_3$ films processing

Sol-gel transformations will be completed by deposition of light yellowish color of PbTiO$_3$ solutions onto cleaned ITO layer of glass substrate. First and for most, the cleaned and clear substrates were dried at 150°C in hot furnace before proceed to the solutions deposition. The reason behind this is to promote such homogenous films developed on top of ITO surface, thus reduced out the existence of interfacial layer problem. About 20minutes before deposition, PbTiO$_3$ solutions were sonicated moderately in ultrasonic bath at 50°C of sonication temperature. The spin coater was set at 3000rpm, 30s of deposition time and the films was coated in five repetitions layer. The heat treatment involved repetition of drying process at 200°C and annealing process at 550°C for 10minutes and 1hour respectively.

2.3. Films Characterizations

The prepared sol-gel derived spin coated PbTiO$_3$/ITO glass thin films at sub-100nm thickness were characterized in both structural and electrical properties. Surface morphological study of the films were observed through field emission scanning electron microscopy (FESEM-JEOL) while to investigate the films uniformity by topological study were performed by atomic force microscopy,
AFM (Park System XE-100). Electrical characterization of PbTiO$_3$ thin films were carried out for ferroelectric and dielectric property which is measured by P-E hysteresis loop measurement (Radiant Technology, Precision LC) and impedance spectroscopy (Agilent 4294A). For this purposes, aluminium (Al) was deposited on the films as top metal contact by thermal evaporation based on Al/PbTiO$_3$/ITO/glass configuration.

3. Results and Discussions

3.1. Nanostructural PbTiO$_3$ thin films

PbTiO$_3$ films surface morphology were observed at x50,000 magnification, 5.0kV and 10.4μA of emission power as shown in figure 1. The films demonstrate noncrystalline structure, provided by the formation of multisize flakes and grains formation. Even though the films were in nonuniform structure, thus having such high densification films without existence of microcrack surface films would be the premier contribution for ceramic thin films capacitor. This is in agreement with Bao et al that mentioned denser films gives the best impact on the dielectric properties [21]. Furthermore, EDX analysis as shown in figure 1b indicates that Pb element facilitate high binding energy performance due to the fact that the films were at influenced of 10mol% Pb excess.

Figure 1. FESEM result of PbTiO$_3$ thin films, (a) surface morphology and (b) EDX analysis

![Figure 1](image1.png)

Figure 2. AFM result of PbTiO$_3$ thin films, (a) planar view and (b) 3-D view

Study on the films surface roughness that is topographical source is important to acknowledge at, thus, ushering the smooth electronic conduction when applying source. The films surface topology
were observed by using AFM as shown in figure 2, set by planar view and 3-D view of the films. The
details of the scanning parameters were set at localized 10µm² scanning area, 2.50 servo gain and
1.50Hz scan rate. Films surface topology indicates the average surface roughness and average grain
volumes were achieved about 8.905nm and 1.2x10⁻³μm³ respectively.

3.2. Electrical Measurement

3.2.1. Ferroelectric behaviour. The ferroelectric behaviour of PbTiO₃ films are demonstrated by the
plot of P-E hysteresis loop at various dc bias which are 30, 75, 100, and 150V as shown in figure 3.
Plus, the details of spontaneous polarization (Pₛ), remanent polarization (Pᵣ), and coercive field (Eₖ)
value of are tabulated in table 1. The area of the films according to sandwich-type MFM
configurations that measured by using surface profiler is about 1.08x10⁻⁵cm² and the thickness is
139.47nm.

![Figure 3. Plot of P-E hysteresis loop of PbTiO₃ thin films measured at various dc bias](image)

### Table 1. Ferroelectric properties at various dc biases obtained at 500Hz

| DC value (V) | Spontaneous Polarization, Pₛ (μC/cm²) | Remanent Polarization, Pᵣ (μC/cm²) | Coercive Field, Eₖ (kV/cm) |
|--------------|--------------------------------------|------------------------------------|--------------------------|
| 30           | 0.13                                 | 0.58                               | 450                      |
| 75           | 4.95                                 | 0.32                               | 500                      |
| 100          | 7.51                                 | 3.05                               | 800                      |
| 150          | 11.25                                | 2.62                               | 500                      |

Ferroelectricity behaviour in this study shows the P-E loops were meeting the agreements where
the spontaneous polarization and electric field source are approximate to each other. This is due to the
fact that the ferroelectric polarization happened between two conductive plates and creates the
hysteresis which is caused by the application of an external voltage on the internal electric dipoles. The P-E result in this study is about 12.5\(\mu\)C/cm\(^2\) at 2MV/cm obtained at very high electric field applications due to the performance of amorphous structured PbTiO\(_3\) films. It was found that Many studies had impressively prepared the films on crystalline Pt/Ti/Si substrate as reported by Wang et al in his tremendous literature review on ferroelectric behaviour of lead based titanate films [22]. Closest reference made by Cheng et al, claimed that highest spontaneous polarization could be obtained with such ITO glass substrate as indicated in his study [20].

3.2.2. Dielectric measurement. The measurement was conducted as same parameter (area and thickness) as done in ferroelectric measurement based on MFM configuration. The analyzer was set up with 500mV ac signal and performed in range of 40Hz to 100 kHz frequencies as shown in figure 4. The k value is having constantly space charge moment about ~99 with tolerance of ±7% measured at 1kHz frequencies complimented with low dissipation energy about 4 to 5%. Whereas, above than 10kHz, the dielectric polarizations were dropped drastically to a specific value indicated dipole moment polarizations. Hence, the films are believed in well suited for DC power application when there highlight significant k value approached to the lowest frequency. High densification films brought by the addition of Pb excess as shown in Figure 1 are in addition to demonstrate such high dielectric constant which is in agreement with studies reported by Bao et al in [21].

![Figure 4. Plot of dielectric versus frequency of PbTiO\(_3\) thin films](image)

The measured capacitance density, (F/cm\(^2\)) is related to the dielectric permittivity according to following express:

\[
\frac{C}{A} = \frac{\varepsilon_r \varepsilon_0}{d}
\]

(1)

Where, \(A\), \(\varepsilon_r\), \(\varepsilon_0\), and \(d\) comprises of films area, relative permittivity of dielectric material, free space permittivity, films thickness respectively. Thus, the capacitance density is about ~0.63\(\mu\)F/cm\(^2\) with ±7% tolerance that is quite interesting to acknowledge at sub-100 nm thickness films.
4. Conclusions
Using sol-gel spin coating method with low synthesis temperature, amorphous nanostructured PbTiO$_3$ thin films were obtained. The plots of P-E hysteresis loop and dielectric versus frequency were successfully performed on Al/PbTiO$_3$/ITO glass at remarkable ~140nm thickness. For various dc bias applications on ferroelectric measurement, it demonstrates approximate relation between spontaneous polarization and dc source. In this study, the ferroelectric behaviour of the films were not affected by the increase of electric field that generated by dense films. Furthermore, high dielectric constant with low dissipation energy presented in this study shows that the PbTiO$_3$ thin films are potential as nanodielectric films for future multilayered nanoscaled ferroelectric capacitor device applications.

Acknowledgement
The author would like to thank for the financial support of Ministry of High Education, Malaysia (MOHE).

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