

Fabrication of Bilayer Structure Hybrid PbTiO₃/PVDF-TRFE for Metal-Insulator-Metal Thin Films Capacitor

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Abstract: Combination of polymer and ceramic material would satisfy high dielectric permittivity and high dielectric breakdown strength of these materials. The motivation of this study is to produce high capacitance device with long life cycle. This study had found such improvement in dielectric value (ϵ_r) from 150-220 for single layer to bilayer structure, respectively. This emphasizes different perspective in capacitor theory where layers of films presents as in series connection which resulted in reduced of capacitance value. Therefore, this study explores the significant contribution of each layer by associating the capacitance (frequency dependent) with the effect of varying thickness. The fabricated bilayer structured film was structurally characterised and electrical measured based on capacitor application.

Key words: Lead titanate, poly (vinylidene fluoride-trifluoroethylene), bilayer films, dielectric property, surface morphology, C-V characteristic

INTRODUCTION

Capacitor is a passive device that can store high energy density with high dielectric permittivity. The material used for thin film capacitors were first reported using oxide material such as multilayered SiO₂ films which poses high dielectric permittivity at that time, in 1976 (Bailey and Nevin, 1976). However they having a difficulty in aligning with the nanotechnology trends in which scaling down to sub nanometer thickness is a requirement. Thus, finding the dielectric material that has high dielectric permittivity became significant in nano-device performance. Ferroelectric ceramic material with outstanding dielectric polarization was first discovered in 1824, as stated in the extensive literature (Haertling, 1999). In fact, realization after hundreds years, capacitor device has evolved with the development of BaTiO₃ as an active dielectric layer of high dielectric constant ($k > 1200$). Subsequently, k value is consistent for tetragonal phase BatiO3 (k value dropped to 17 at amorphous phase, as stated in page 4 in ref (Roy, 2010).

However, this is in contrary with the effect of PbTiO₃ where the k value was found to be ten times more (even in amorphous phase). Many have discovered the potential use of PbTiO₃ which has ferroelectric behavior and favorable as charge storage capacitor, non-volatile random access memory, sensor and transducers (Poyato *et al.*, 2001; Kim and Lee, 2005; Tang *et al.*, 2007; Sidorkin *et al.*, 2010). Eventually, it was discovered that ceramic based materials were brittle in structure and that it would be the challenge in to prepare thin ceramic films. Thus, modification of the ceramic films such as introduction of porous-like surface with notable films thickness in order to avoid cracking was made (Kim *et al.*, 1999). Nevertheless, breakdown strength performance was affected due to the thin ceramic films. Therefore, this brings forward the interest of polymer layer that is prepared as a top layer on PbTiO₃ in order to encapsulate the porosity and yet improve breakdown strength. As far as it concern, the combination of polymer and ceramic material provides a synergy between high breakdown strength in polymer and high dielectric

constant in ceramic, important properties for device especially for processing thin films. For large capacitance device applications, poly (vinylidene fluoride) and its copolymers, trifluoroethylene (PVDF-TrFE) exhibit high dielectric permittivity ($k \approx 12$) but high loss factor ($\tan(\delta) < 1.8\%$) amongst other polymers (Rabuffi and Picci, 2002). There were several studies on nanocomposited PVDF-TrFE with various fillers loadings such as $\text{Pb}(\text{Zr}, \text{Ti})\text{O}_3$ (Zak *et al.*, 2011), PbTiO_3 (Wang *et al.*, 2002), BaTiO_3 (Kobayashi *et al.*, 2008) that are typically ferroelectric in behavior. The preparation of these PVDF-TrFE nanocomposites can be best produced by either spin coating or solvent casting (Nguyen *et al.*, 2014). In our case, thin films of PVDF-TrFE as a top layer is the most preferable. The film is sufficient enough to conceal any porous PbTiO_3 surfaces. It is done by coating process using various spinning speed. The present study proposes new surface characteristic of $\text{PbTiO}_3/\text{PVDF-TrFE}$ that is controlled by top layer thickness for Metal-Insulator-Metal (MIM) capacitor.

MATERIALS AND METHODS

In this study we fabricated Bilayer (BL) films based hybrid composited MIM capacitor by sol-gel spin coating method. The fabrication process consists of two steps: Single Layer (SL) PbTiO_3 thin films as the first ceramic layer and PVDF films as the second layer.

Single layer PbTiO_3 deposition procedure: The starting materials were lead acetate trihydrate [PbAc ; 99% purity], titanium isopropoxide [TIP; 97% purity] and 2-methoxyethanol (as solvent) were purchased from Sigma Aldrich. The solutions were prepared in the presence of Glacial Acetic Acid (GAA) which acts as a stabilizer agent. This was used to control the alkoxide solutions as it being prepared in a humid environment (Zainal *et al.*, 2013; Shi *et al.*, 2010; Wu *et al.*, 2000). The PbTiO_3 solutions were prepared with 0.4 mol L^{-1} molar concentration. The prepared solutions were then deposited on top of ITO glass substrate at room temperature using spin coating technique with the defined parameters of 3000 rpm and 30 sec, spinning speed and time, respectively. The films were dried and coated several times in order to produce the optimized thickness. Then, annealed at 550°C for 30 min in a hot furnace. The prepared PbTiO_3 films known as SL- PbTiO_3 ready for second layer deposition.

Bilayer $\text{PbTiO}_3/\text{PVDF-TrFE}$ deposition procedure: The PVDF-TrFE powder of ratio 70:30 mol% was obtained from Piezotech. The powder mixed in the solvent of methyl

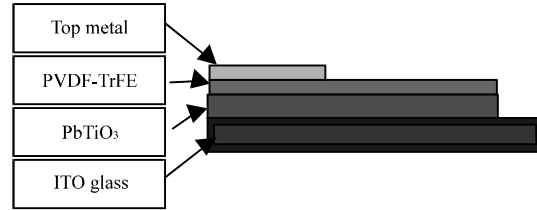


Fig. 1: Bilayer configuration of $\text{PbTiO}_3/\text{PVDF-TrFE}$ prepared for MIM capacitive measurements

ethyl ketone [MEK, 97% purity], purchased from Sigma Aldrich. The solution of concentration 30 g L^{-1} was prepared at room temperature by stirring continuously for 24 h. PVDF-TrFE solutions went through ultrasonication process in order to disperse any inorganic phase in the solutions, as conducted by previous studies (Nguyen *et al.*, 2014; Hadji *et al.*, 2012). Then, a layer of PVDF-TrFE was deposited on top of the coated PbTiO_3 layer by spin coating technique at various spin speeds (1500-6000 rpm) for 90 sec. the prepared samples were named as BL00, BL15, BL30, BL45 and BL60. The prepared bilayer structure films were air dried (60°C , 10 min) and annealed (120°C , 10 min) in hot furnace.

Electrical and structural characterization methods: The characterization of SL and BL films in this study includes their structural and electrical performances. In electrical measurement, an approximate of 60 nm thickness of aluminum metal contact was deposited on the films surface using steel mask via thermal evaporation method (area: 0.09 cm^2). The bilayer configuration can be described using illustration in Fig. 1. The films surface was observed by field effect scanning electron microscopic [FESEM, Jeol] and atomic force microscopic [AFM, Park System XE-100]. Meanwhile, dielectric property was measured by impedance spectroscopic [Agilent 4194A] and capacitance behavior of fabricated device was measured by C-V measurement [Keithley Model 82].

RESULTS AND DISCUSSION

Microstructural property: The FESEM surface micrograph of SL PbTiO_3 is shown in Fig. 2. The crystal growth of SL films indicates multiple grain size and nano-holes at the grain boundaries. In average, the grain size is approximately 60-70 nm diameter while the nano-holes size is about 20-30 nm. From the EDX analysis, shown as inset, the ratio of lead and titanium Pb:Ti element content is almost similar which highlights lead deficiencies can be avoid. Figure 3 presents the FESEM surface micrographs of entire BL films along with cross

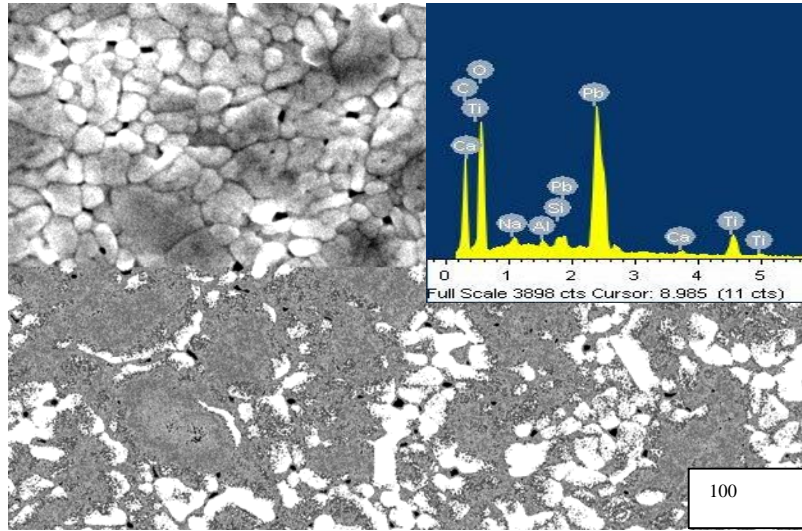


Fig. 2: Surface morphology of SL films, inset: EDX analysis

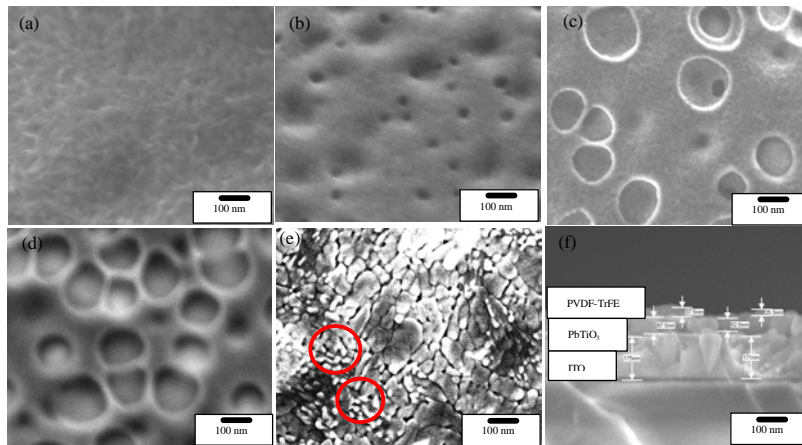


Fig. 3: Surface morphology of BL samples, a) Bloo, b) BL 15, c) BL 30, d) BL 45, e) BL 60 and f) cross sectional view of BL 60 sample

sectional BL films prepared at 6000 rpm speed. The solvent casted samples, BL00 showed an almost perfect PVDF-TrFE surface with no apparent porous structure. On the other hand, there is a certainty of porous surfaces in samples prepared at speeds from 1500-6000 rpm. The BL15 sample showed small porosity with average pore size about 58 nm diameters. The pore size was four times larger at 3000 rpm and six times larger at 4500 rpm for BL30 and BL45 samples, respectively. Meanwhile, BL60 samples showed different structural behavior where almost entire surface diminished. What was left was the penetrated PVDF in nano-holes provided by origin of PbTiO₃ surface. The diameter size of PVDF penetration is about 15-18 nm, almost similar size to the nano-holes size mentioned in Fig. 1. Furthermore, Fig. 2f shows the

BL60 samples, a cross sectional view of PbTiO₃/PVDF-TrFE that proves that the films thickness achieved a sub-100 nm, i.e., 57.5 nm PbTiO₃ layer and 37.5 nm PVDF-TrFE layer. The grain structure of PbTiO₃ surface films could be much influenced by ITO surface, as substrate is the template for nucleation growth. Thus, producing multiple grain size that are not aligned may contribute to the factor of producing nano-holes surfaces. This is very important to ensure uniformly oriented particles that are polarized when electric fields are applied. Thus, many researchers have used platinum (Pt) coated SiO₂/Si substrate to meet this objective (Fu *et al.*, 2000; Kim *et al.*, 1998; Khan *et al.*, 2008; Moon *et al.*, 1997).

The FESEM image in Fig. 3a presents elongated structure of film surface that can suggest a β -phase PVDF

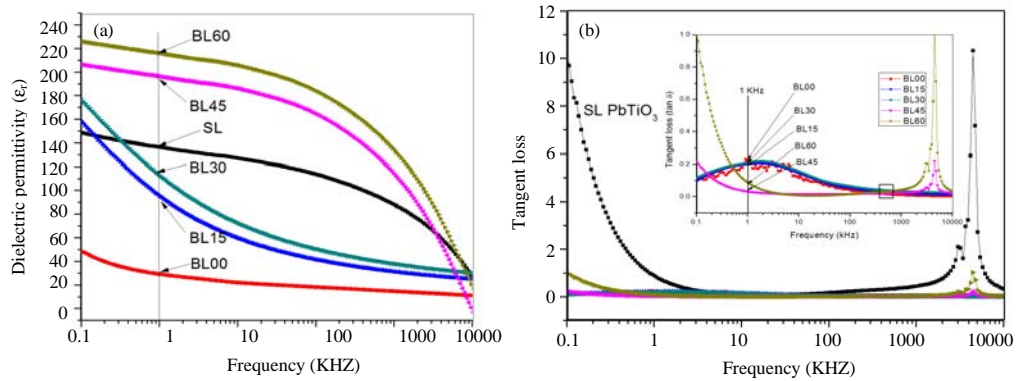


Fig. 4: Dielectric property of entire films at various spinning speeds, a) dielectric permittivity, ϵ_r and b) tangent loss, $\tan(\delta)$ taken in range of 100 to 100 MHz frequency measurement

with ferroelectric behavior (Hafiz *et al.*, 2013). Ho *et al.* (2010) in her review on capacitor evolutions stated that a single layer of PVDF and its co-polymer would exhibit high dielectric constant, up to 12 and loss $\tan(\delta)$ in range 1.8% (Ho *et al.*, 2010). Although, PVDF-TrFE is quite well-known as ferroelectric polymer, this study will not focus on ferroelectric property of the electrical part. In Fig. 2b-e, the surface films experienced porous behavior due to the highly hydrophilic PVDF-TrFE property affected during high speed coating (Liang *et al.*, 2013). Furthermore, the wet films were air dried which may have created weakening of the bonding, resulted in larger pore size. For polarization activity of single PVDF-TrFE layer to occur, the opposition side of H (+) and F (-) atoms charge must align in order to produce the polarity (Tascan 2014). This is quite impossible for sample BL15, BL30 and BL45 where porosity of BL sample is hard to control and might cause failure in polarization. The BL60 films have a far perspective to be acknowledged at where almost 90% of molecular structure of PVDF-TrFE was segregated beneath the porous surface of PbTiO_3 . The cross sectional view of this sample can be found at approximate to 95 nm thicknesses, notably new sub-100 nm dielectric films bilayer approaches

Dielectric property: The plot of dielectric property for both SL and BL is shown in Fig. 4, measured at 0.5 mV ac signals, room temperature. The frequency measurement was taken in range 100-10 MHz for dielectric permittivity, ϵ_r and tangent loss, $\tan(\delta)$ in Fig. 4a and 4b, respectively. The dielectric permittivity value of SL PbTiO_3 films obtained was about 150 at initial 100 Hz and decreased slightly to 113. Then, it drastically dropped to 29 at 100 kHz and 10 MHz respectively. The films prepared at low spin speed such as BL00, BL15 and BL30 achieved lower dielectric permittivity than SL films, about 18, 42

and 50, respectively at 100 kHz frequency. Although, these (BL15 and BL30 samples) had initially obtained high dielectric response, the dielectric value was constant at high frequency, i.e., 100 kHz. The drastic dropped at low frequency (1 kHz) somehow show conductive response of these samples. However, BL45 and BL60 were of contrary response, determined by the dielectric permittivity that constant at 165 and 184, respectively below than 100 kHz. This is believed that BL samples produced at speed higher than 3000 rpm were remarkably improved. Furthermore, SL films obtained $\tan(\delta) = 10.08$ shows quite high dielectric loss films, thus, indicates low dielectric breakdown. Meanwhile, BL samples obtained about 0.11, 0.10, 0.16, 0.22 and 0.99 for BL00-BL60, respectively. These values were obtained at initial operating frequency ($f = 100$ Hz) and was found to be scattered.

In general, dielectric permittivity is the ability of dielectric material to be polarized upon application of an electric field. It was found that samples prepared at lower spinning speed (BL00, BL15 and BL30) have space charge polarization at 1 kHz. It is justified that the typical range for this type of polarization is about 10^{-3} to 10^3 Hz as stated by Lu thesis). Another reason was due to the heterogeneous system of the multi-component which is the hybrid property of PbTiO_3 and PVDF-TrFE layer. It is ensured the layer thickness of PVDF-TrFE (d_p) is greater than ceramic PbTiO_3 layer (d_c) which is influenced by the decrease in dielectric permittivity value. Furthermore, space charge accumulation arising from the oxygen vacancies would be the possible answer to the conductive response in dielectric permittivity of these samples as mention earlier (Osada and Sasaki, 2012). However, other sample, SL, BL45 and BL60 performed notable finding where the dielectric behaviour exhibited was due to dipole polarization above than 1 MHz frequencies. This may be cause by the microstructural

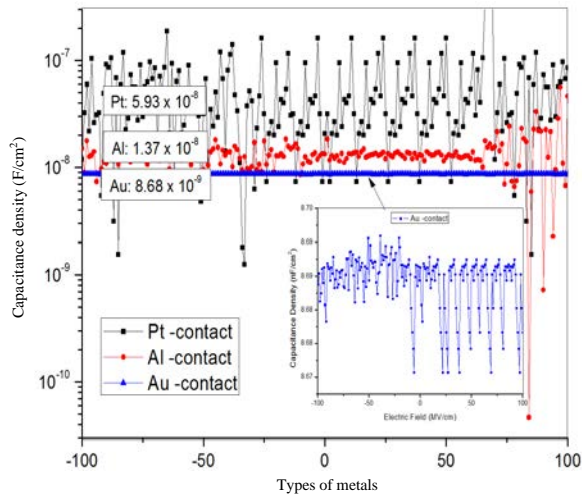


Fig. 5: Capacitance versus voltage measurement of optimized BL60 sample with different type of metal (Pt, Al and Au)

features which provided to determines the relaxation process happened at high frequency (Han *et al.*, 2011). Furthermore, the significant contribution by thinner PVDF-TrFE layer (35 nm and 55 nm for BL60 and BL45, respectively) becomes dominant to the highly polarized PbTiO₃ films. Thus, creates the contrary judgement to the bilayer structure that exhibits higher dielectric permittivity than bulk composite (Dang *et al.*, 2012). In previous study, Wang *et al.* (2003) proved that the bilayer construction decreased from 63-20 dielectric value. Although, in theory, it is established that the bilayer films permits low capacitance value than the series, the thin films produced by spin coating provides such flexibility that can offer various electrical characteristic.

Capacitance-voltage measurement: Capacitance characteristic of BL60 samples were measured using C-V measurement with different types of electrodes (Pt, Al, and Au) as shown in Fig. 5. The measurement of sub-100 nm thickness was plotted for capacitance density (F/cm²) versus electric field (MV/cm) measured at 1 kHz. The entire BL60 samples performed no hysteresis (linear electrical response) at sweeping bias voltage of -10 to +10 V. The average capacitance density value of each device was about 5.93×10^{-8} , 1.37×10^{-8} and 8.68×10^{-9} F/cm² for sample Pt, Al and Au, respectively. There are several factors that would affect the performance of capacitance behavior and electrodes are one of these factors. Many studies had performed various types of metal electrodes, i.e., LNO, SrTiO₃, RuO, Pt, Ni, Au, Al, etc. Pt electrodes were fondly prepared by many studies because of the good bond of elementary cell size between

the dielectric films and the electrodes (Sidorkin *et al.*, 2010; Khan *et al.*, 2008; Thomas *et al.*, 2002). This study presents highly fluctuated straight line of sample prepared with Pt electrodes, yet this sample device exhibited very high capacitance density value.

This suggested that modification between films and Pt electrodes is important. Han and Lee (2000) remarkably used different metal oxide as buffer layer between films and Pt electrodes to act as a sink for oxygen vacancy, thus reduced fatigue rate. Besides that, the films prepared with Al electrodes yield almost uniform measurement at increased positive dc bias. It is very conductive metal and has been used commonly for metallization on polymer surface film. This electrode has the ability to go through self-healing process where surface polymer suffers pin holes or micro flaws (Tewari, 2009; Reed and Cichanowski, 1994). This will help the capacitor to keep on functioning with high reliability even though with reduced in capacitance value. Although, Au metal is more conductive than Al, yet the oxidation level can be quite hard. Concisely, it is believed that deposition of different electrodes could create much interest for different range of device applications. Our study had committed that Al electrodes was the appropriate electrode to meet the required thin films polymer-ceramic device.

CONCLUSION

The study had prepared SL PbTiO₃ and BL PbTiO₃/PVDF-TrFE on ITO glass substrate through simple spin coating method with various spinning speeds of PVDF-TrFE layers. The electrical characteristics of the thin films devices are much influenced by microstructural behavior of the top layer depositions. We had exclusively captured a new finding on sub-100 nm thickness of BL PbTiO₃/PVDF-TrFE prepared at optimized speed of 6000 rpm that notably enhanced in dielectric performance ($\epsilon_r = 220$, $\tan(\delta)$ at 1.5%). The C-V measurement had demonstrated BL60 films with Al metal contact obtained such reliable capacitance density of 1.37×10^{-8} F/cm² which is truly denoted for new finding of bilayer structured MIM capacitor device. It is as expected that the development of pure capacitor characteristic is affected by the thin films processing technique. Thus indicates that layer-by-layer deposition could present the transition of series to parallel capacitor theory.

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