Electrical Properties of Sol Gel Derived Lead Titanate ($PbTiO_3$) Thin Films by Dip Coating

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Abstract — Lead Titanate ($PbTiO_3$) thin films derived from metal alkoxide precursor solution through sol-gel method were deposited onto silicon substrates by dip coating. These films were deposited at different withdrawal speeds and different immerse times. The films were then annealed at a fixed temperature of 650°C. The CV measurement and IV characterics were measured using LCR meter and solar simulator respectively. While the structural properties were studied using scanning electron microscope (SEM). From this study, it was found that electrical properties were influenced by the changes in withdrawal speeds and immerse times. The results show that the resistivity of the $PbTiO_3$ thin films decreases as the withdrawal speed increases. Increasing in immerse time result in low resistivity. This result is supported by surface morphology of the thin films which indicated that smaller grain size can be obtained with high immerse time and withdrawal speed.

1. INTRODUCTION

Ferroelectric thin films have attracted the attentions of many researchers in view of their potential application to dynamic random access memories, non-volatile memories and infrared sensors [1]. One of the most promising well-known ferroelectric materials having excellent ferroelectric, pyroelectric and piezoelectric properties is lead titanate [2]. Since lead titanate can exhibit high dielectric constant and low dielectric loss, thus it can results in smaller electrical devices and can potentially be used as a dielectric material for low and high frequency application [3].

This ferroelectric thin film can be prepared using preparation techniques. One of the most widely used techniques is sol-gel. This is due to its ability to allow excellent compositional control and compatible with semiconductor processing techniques. Moreover, this technique is simpler and cheaper compared to other preparation methods [4-8].

Since different parameters of coating technique may result in different film properties, it is therefore necessary to investigate the effect of coating process on the property of sol-gel derived thin films. This paper reports on the structural and electrical properties of lead titanate thin films deposited using dip coating technique on silicon substrates.

2. EXPERIMENTAL

Lead Titanate (PT), $PbTiO_3$ thin films were prepared using sol-gel method. Lead acetate trihydrate, $Pb(CH_3COO)_2{\cdot}3H2O$ and titanium isopropoxide (TI), $Ti[(CH_3)_2CHO]_4$, were used as precursor materials, and 2-methoxyethanol, $CH_3OCH_2CH_2OH$ as a solvent [8].

The solution was prepared by dissolving 7.5868 g of lead acetate trihydrate into 100 ml of 2-methoxyethanol and was stirred heated to around 126°C for almost 48 hours until the solution reduced to 50 ml. Then titanium isopropoxide (2.96 ml) was mixed into the mixture. Another 30 ml of 2-methoxyethanol was added to the solution and heated again at 150°C for 1 ½ hours. The resulted solution was cooled at 80°C for 4 hours. Next, 16.7 ml of 2-methoxyethanol and a mixture of acid nitric and H_2O was added to the stirred alkoxide solution at 80°C. The resulting solution was brown in colour and was kept for 4 hours to mature.

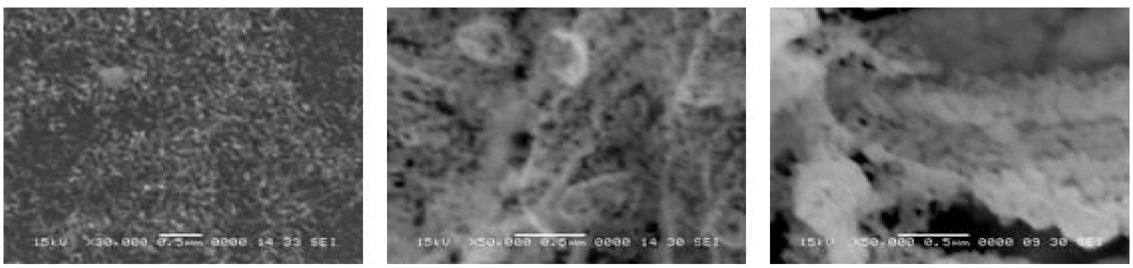
Thin films were deposited on Si substrates by dip-coating. Before deposition, the substrates were cleaned in acetone and methanol and rinsed in deionized (DI) water for 10 minutes. In order to remove the formation of oxide layer on the Si substrates, immersion in HF is therefore necessary.

The deposition process was carried out at different withdrawal speed and immersion time. The samples were baked at 300°C for 0.5 hours. This process was repeated several times to achieve desired film thickness. The films were then annealed for 1 hour at 650°C. The structural properties of the prepared thin films were examined by SEM. The dielectric constant and tan δ were measured at frequencies of 100 to 1000000 Hz using LCR meter (HIOKI 3532-50 LCR HI-TESTER). The electrical conductivity was measured by Spectral Sensitivity Measurement using Solar Simulator.

3. RESULTS AND DISCUSSION

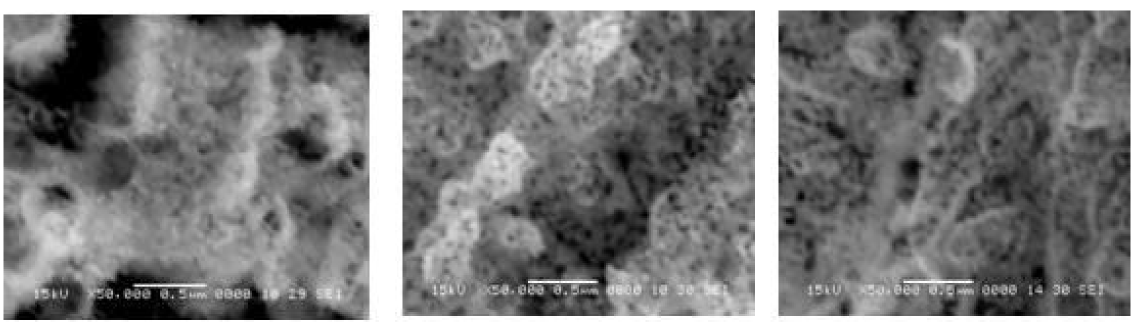
3.1 Scanning Electron Micrographs (SEM)

The microstructural features of PT thin films deposited on <100> Si and annealed at temperature of 650°C by varying withdrawal speeds and immerse times were examined using scanning electron micrographs. The surface micrographs presented in Fig 1 and Fig 2 showed that different withdrawal speeds and immerse times have significant influence on the microstucture and grain size of the films. From the results obtained, it shows that increasing the immersing time resulted in the clustered grain with smaller size. Increasing the withdrawal speed on the other hand improve the uniformity of the films surface.



(a) (b) (c)

Fig 1 SEM images of PbTiO3 thin films at withdrawal speed of 9 mm/s and immerse times of (a) 25s (b) 30s (c) 35s deposited on Si <000> and annealed at temperature of 650°C.



(a) (b) (c)

Fig 2 SEM images of PbTiO3 thin films at immerse time of 35s and withdrawal speed of (a) 5 mm/s (b) 7 mm/s (c) 9 mm/s deposited on Si <100> and annealed at temperature of 650°C.

3.2 Electrical properties

The electrical properties of lead titanate thin films were analyzed by performing IV measurements using Solar Simulator. The measurement used 4-point probe measuring system. This system can be used to measure either bulk or thin film specimen, each of which consists of a different expression. The resistivity was calculated using following equation since the samples are thin films:

$$\rho_{\square}\left(\frac{\Omega}{\square}\right) = \frac{\pi}{ln\,(2)}\frac{V}{I}$$

Where:
ρ = resistivity
V = voltage
I = current
□ = sheet resistance

Figure 3 shows the I-V characteristic of $PbTiO_3$ thin film deposited on silicon substrate. IV characteristics were measured on the sample deposited at various withdrawal speeds and immerse time. From the graph obtained, it could be observed that the most conductive is sample deposited at withdrawal speed of 9 mm/s and immerse time of 35s.

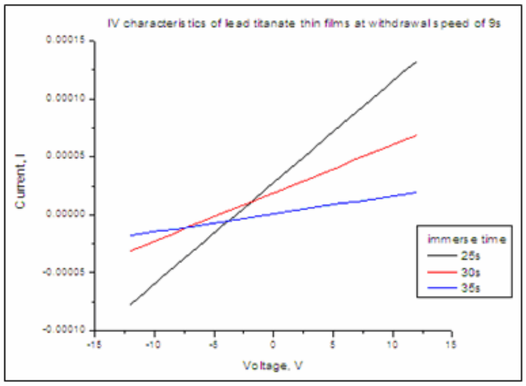


Fig 3 IV characteristics of $PbTiO_3$ thin films deposited by dip-coating at different withdrawal speeds and immerse times.

From Figure 4, it can be seen that the resistivity of $PbTiO_3$ thin films increased as the withdrawal speed decreased. The decreasing in resistivity also has a reciprocal relationship with the immerse time of the sample in the solution i.e the conductivity increased when the immerse time is increased.

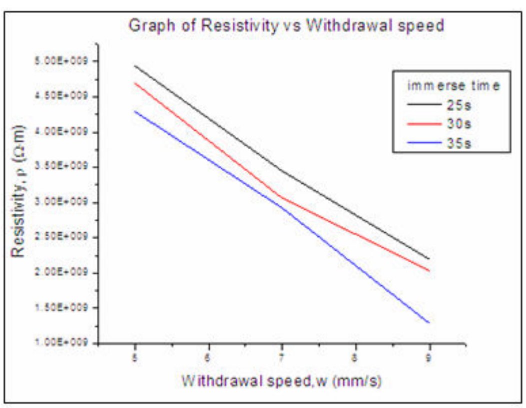


Fig 4 Effect of withdrawal speed against resistivity of $PbTiO_3$ thin films at different immerse times

The decreases in resistivity with withdrawal speeds and immerse times can be explained as follows: the grain size decreases as the withdrawal speed increases; which leads to decrease in grain boundaries and hence resistivity. Smaller grain size will provide higher surface contact between the PbTiO3 and electrode

3.3 Dielectric properties

From CV measurement, the dielectric constant could be determined by manipulating the collection of data using the following equation [9]:

$$\varepsilon_{k}'(\omega) = -\frac{\beta}{\omega C_o\left(\alpha^2 - \beta^2\right)} \qquad C_o = \varepsilon_o S / d$$

where:

α = real impedance
β = imaginary impedance
ω = 2πf
Co = capacitance of empty cells
S = area of electrode
d = distance between electrode

Figure 5 shows the relative permittivity (ξr) of $PbTiO_3$ thin films measured at withdrawal speed of 5s and different immerse times. The relative permittivity is too small compared to the relative permittivity obtained by the previous study [10-11]. From the results obtained, it could be seen that a constant value of ξr could be achieved low frequency.

However, the ξr begin to decrease when the frequency reaches at about 50 kHz. This condition occurred might be because of relaxation mechanism of the prepared lead titanate thin films. The relaxation mechanism causes the dielectric constant of many ferroelectric materials to decrease significantly to a lower value at higher frequencies [4].

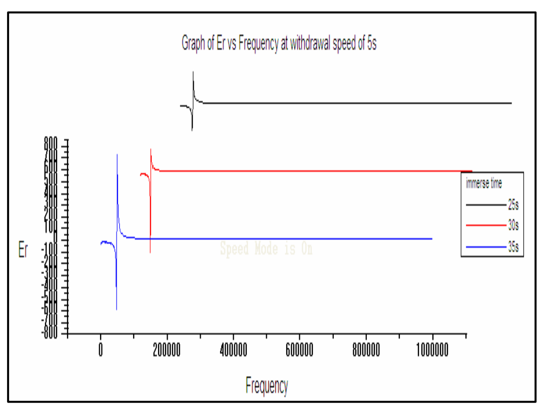


Fig 5 Graph of Er vs Frequency at withdrawal speed of 5s

4. CONCLUSION

Lead titanate thin film was successfully synthesized by depositing sol gel derived $PbTiO_3$ solution onto Si(100) substrates by using dip coating technique. These thin films were then annealed at fixed temperature of 650°C.

For electrical properties, it can be concluded that the resistivity of $PbTiO_3$ thin films decreases as the withdrawal speed and immerse time increase i.e the resistivity of $PbTiO_3$ thin films are inversely proportional to the withdrawal speed and immerse time. The conductivity of $PbTiO_3$ thin film increases as the withdrawal speed and immerse time increase i.e the conductivity is directly proportional to the withdrawal speed and immerse time.

As for the surface topography, the trend of uniformity and cluster formation are increasing as the withdrawal speed and immerse time increase, thus giving the thin film with withdrawal of 9s and immerse time of 35s as the most uniform surface topography. The SEM images illustrate that increasing withdrawal speed and immerse time will produce denser particle formation but too high speed will produce thicker film.

The relative permittivity of $PbTiO_3$ does not provide the pattern that was desired for capacitor application in high frequency. However thin films with the lowest withdrawal speed and immerse time shows a promising trend that might be able to be improved in future. The major observations of this study can be summarized as the withdrawal speed and immerse time clearly affected the properties of $PbTiO_3$ thin films. These changes of properties concluded as due to the growth of grains size of

5. FUTURE DEVELOPMENT

For future development, the outcome of this research could be enhanced by improving the thin films deposition techniques. Other deposition method such as spin coating and CVD could be used to reduce human intervention in the process of preparation of lead titanate thin films. Coating could also be implemented on the substrate before depositing the thin films to obtain better adhesion layer between the substrate and the thin film. The viscosity and concentration of the solution should be taken into consideration as well in order to achieve more precise results.

6. ACKNOWLEDGEMENT

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Reference

[1] K. Saega, (1997), Effect of preparation condition on short circuits in sol-gel derived lead titanate thin films, *Material Science*, (32), pp 5691-5968.

[2] J. Perez, P.M. Vilarinho, Zhao, A.L Kholkin, A. Almeida, (2008), Sol-gel reaction stability studied: Influence in the formation temperature *Materials Research Bulletin* (4239), pp 1-7.

[3] Seong E. M, Eun-Kyoung K., Su-Jae L., Min-Hwan K., Young-Tae K., Han-Cheol R., Won-Jeong K., Tae-Kwun S., (2004), Measurement of microwave dielectric properties of $Pb(Zr_{1-x}Tr_xO_3)$ thin films, *Electroceramics*, (13), pp 257–260.

[4] Vasantha Chivukula, Pak K. Leung Ferroelectric Dielectric for Intergrated Circuit Applications at Microwave Frequencies, U.S Patent, 5 886 867, Mar 23, 1999.

[5] C.J. Brinker, D.E. Clark, D.R. Ulrich, (1984), Better ceramics through chemistry. *Academic Press*, pp 115.

[6] L.L Hench, D.L. Ulrich, (1984), Ultrastucture processing of ceramics glasses and composites, *Wiley-Interscience*, pp 225–230.

[7] J.B. Blum, S.R. Gurkovich, (1985), Sol-gel derived $PbTiO_3$. *Material Science*, (20), pp 4479-4483.

[8] Ko Ko Kwang So, Masaki Maeda, Ikuo Suzuki, (1996), Modifieed sol-gel processing for fabrication of lead titanate thin films. *Physics and Chemical Solids*, Vol 57 (3), pp. 259–266.

[9] Dr. Andrii Golovin, Introduction to dielectric measurements of nematic liquid crystals, presented at Liquid Crystal Institute & Chemical Physics Interdisciplinary Program, University Kent States.

[10] Kunio Saegusa, (1997), Effect of preparation on short circuits in sol-gel derived lead titanate thin films, *Material Science*, (32), pp 5691-5698

[11] H. O. Yadav, (2004), Optical and electrical properties of sol-gel derived thin films of $PbTiO_3$, *Ceramics International*, 30(7), pp. 1493-1498.