# Effects of Annealing Process on Dielectric Properties of Sol-gel Derived Lead Titanate Thin Films

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*Abstract*-**This paper reports on the effects of annealing process on the electrical properties of lead titanate ($PbTiO_3$) thin films. The thin films have been deposited on silicon substrates using sol-gel spin coating method. The dielectric properties of the thin films annealed at different annealing temperatures and times were then investigated. The dielectric properties and resistivity of the film was measured using HIOKI 3532-50 LCR meter and four point probe respectively. The dielectric constant exhibits inverse relationship with dielectric loss and strongly affected by annealing time and temperature. Annealed at 700°C resulted in dielectric constant and loss of 44 and 0.1 respectively. The resistivity of the films was measured to be $1.34 \times 10^4$ Ωm.**

***Keywords:* lead titanate(PT), sol-gel, electrical properties**

## I. INTRODUCTION

Due to the emergence of microelectronic technology, smaller electronic devices are highly in need. This can be achieved by either using thin dielectric layer or high dielectric constant material. Since thin dielectric layer will result in high leakage current using high dielectric constant material is therefore the best solution.

Recently, several studies have been carried out to investigate the performance of ferroelectric materials as the alternative insulator. This is maybe due to their high dielectric constant properties. One of the most promising ferroelectric materials is lead titanate ($PbTiO_3$) thin films. Since electrical and dielectric properties of thin films are highly dependent on frequencies, it is therefore essential to investigate the performance of these films in a wide range of frequency.

Lead titanate has been known as the perovskite-type material that has good ferroelectric and pyroelectric properties [1]. Since lead titanate is a well known ferroelectric material, it has been demanded for being use in various functional devices including non-volatile memories [2], IR sensors [3] and micro-electromechanical systems (MEMS) [4]. Lead titanate thin films could posses higher dielectric constant compared to other dielectric materials such $SiO_2$ ($\varepsilon_r$ = 3.9) and $Si_3N_4$ ($\varepsilon_r$ = 6.0-7.5) [5].

Several deposition techniques can be employed to prepare the lead titanate thin films such as flash evaporation, radio frequency magnetron sputtering [6], chemical vapor deposition [7], chemical solution deposition [8], pulsed laser deposition [9], sol-gel method [10] and others. Of the various techniques, sol-gel method has been widely used. This is due to its ability to allow excellent compositional control and compatibility with standard semiconductor processing technique. Moreover, this technique is cheap and permits uniform film homogeneity at low temperature. In the sol-gel method, metal alkoxide precursor solution is initially prepared followed by coating process. Several parameters may influence the properties of the prepared thin films. One of them is annealing temperatures and times.

In this paper, the effects of annealing temperature and annealing time on dielectric properties of lead titanate thin films are presented.

## II. METHODOLOGY

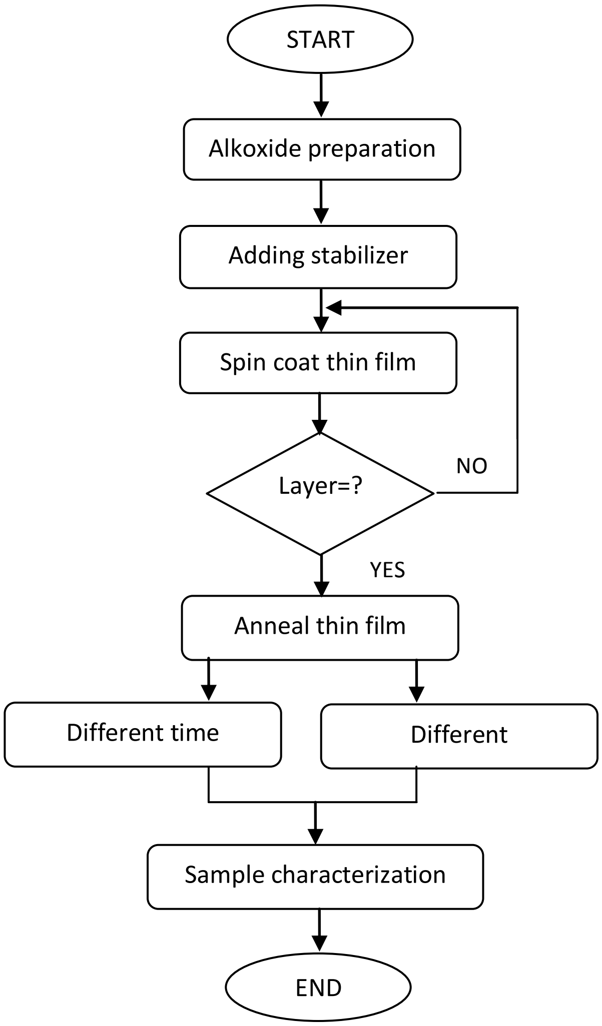



Figure 1. Flow chart illustrating solution preparation process.

Lead titanate (PT) thin film were fabricated by sol-gel spin coating deposition technique using titanium isopropoxide and lead acetate trihydrate as precursor. There are two steps in preparing the sol, alkoxide preparation step and adding stabilizer step as shown in Fig. 1. In alkoxide preparation step, the sol was prepared by dissolving 11.3802 g of lead acetate trihydrate in 150 ml 2-methoxyethanol.

The solution was then stirred and heated at 126°C using hot plate magnetic stirrer until the solution was dehydrated until 100 ml. As the solution reaches 100 ml, the temperature was reduced to 60°C and kept for 2 hours. Then, 5.92 ml titanium(IV) isopropoxide and another 50 ml of 2-methoxyethanol were then added and stirred at 150°C for another 3 hours. After cooling to room temperature, a mixture of nitric acid, deionized water, and 2-methoxyethanol was mixed into the alkoxide solution.

To adjust the concentration of final solution, another amount of 2-methoxyethanol was added to the mixture. The solution was then slowly stirred and heated at 80°C for 4 hours to mature and ready for deposition process.

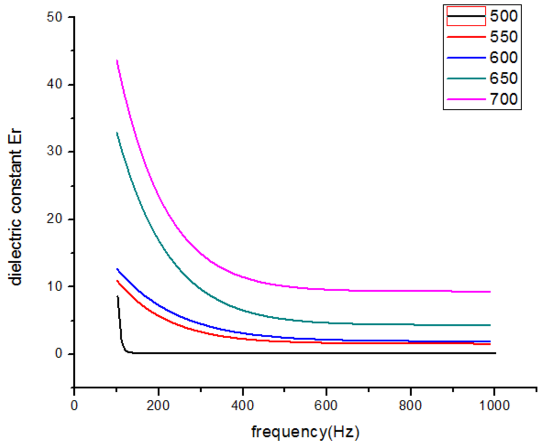
Ten samples were used and divided into two parts. First part consists of five samples, were used to investigate the effect of annealing temperature whereas the remaining samples were used to investigate the effect of annealing time. All samples were deposited on silicon substrates using spin coating method. The spinning process was carried out for five times. After each layer, the films were baked at 150$^{o}$C for 15 mins. The dielectric properties measurements were carried out using HIOKI 3532-50 LCR meter. The resistivity of the prepared thin films was measured using four-point-probe measurement.

## III. RESULT AND DISCUSSION

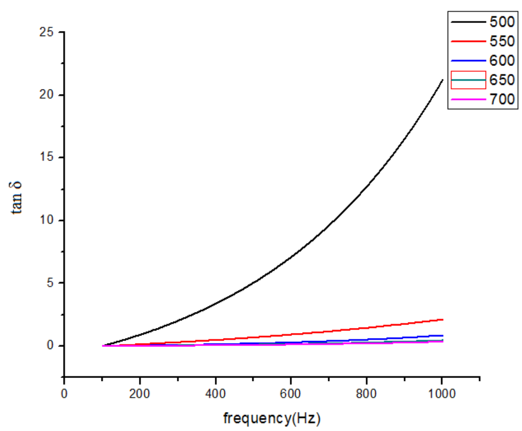
### *A. Dielectric properties of lead titanate thin film annealed at different temperature.*

Fig. 2(a) shows the effects of annealing temperature on the dielectric properties of the lead titanate thin films. The dielectric constant was measured at different frequencies in a range of 100 Hz to 1 kHz. As can be seen from the graph, increasing the annealing temperature resulted in the increase of dielectric constant. The dielectric loss on the other hand decreases at high annealing temperature as shown in Fig. 2(b). This is may be due to the improvement of film crystallinity which then leads to the improvement of dielectric properties of the thin films as reported by K. Byun *et. al* [11].

The film annealed at 700$^{o}$C shows the highest dielectric constant which is approximately 44 and dielectric loss of 0.1 at 100 Hz. the dielectric constant obtained is slightly higher than current industry standard dielectric materials ($SiO_2$ ($\varepsilon_r$ =3.9) and $Si_3N_4$($\varepsilon_r$=6.0-7.5)) which have been discussed earlier. The thin films annealed at 500$^{o}$C on the other hand, exhibit the lowest dielectric constant. This is possibly due to the imperfection of films crystallinity annealed at low temperature.




(a)




(b)

Figure 2. Plot of (a) dielectric constant and (b) tangent loss versus frequency at different annealing temperatures.

Fig. 3 shows the dielectric constant of the films measured at elevated atmospheric temperature at frequency of 100Hz, 10 kHz, and 1 MHz. As can be observed, the dielectric constant at 100 Hz is relatively high which is approximately 23. However, the dielectric constant decreases with increasing atmospheric temperature. At applied frequency of 1 MHz, the dielectric constant is relatively small of approximately 0.1 and slightly decreases as the temperature increases. The same pattern was observed on the sample at applied frequency of 10 kHz.

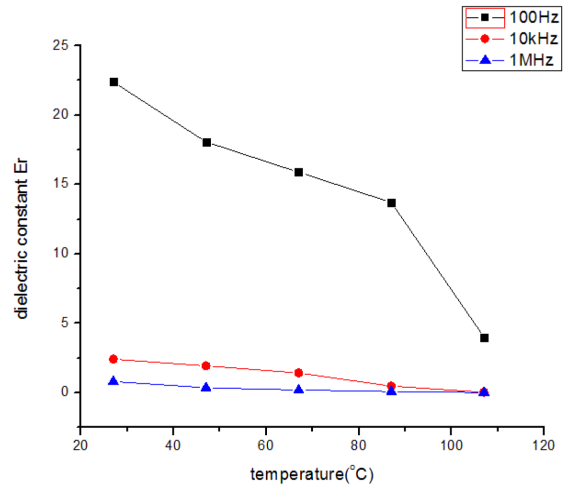



Figure 3. Plot of dielectric constant versus atmospheric temperature at different frequencies.

The interaction between resistivity with annealing temperature is illustrated in Fig. 4. As can be seen, the resistivity increases exponentially as annealing temperature increases. The highest resistivity is obtained when the lead titanate thin films were annealed at 700°C which is approximately $1.34 \times 10^4$ Ωm whereas annealed at low temperature resulted in the lowest resistivity.

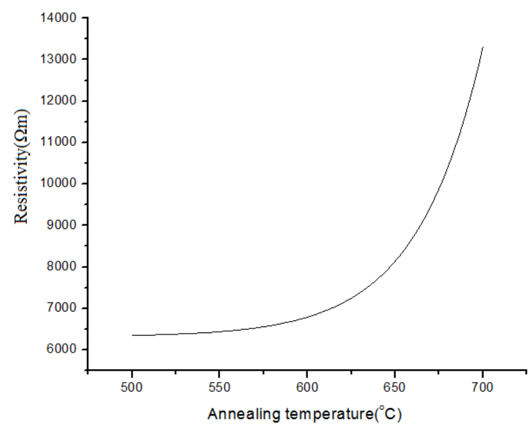
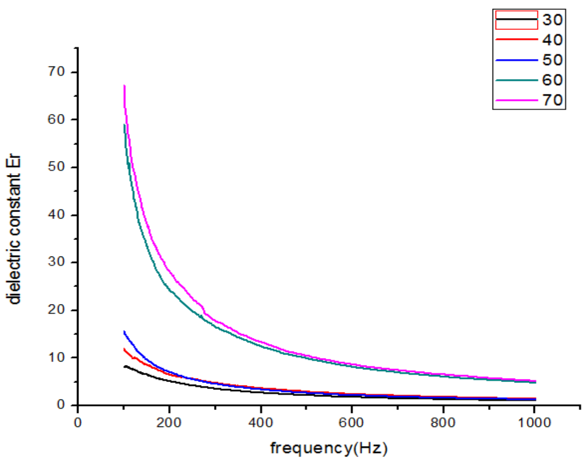



Figure 4. Plot of resistivity versus annealing temperatures.

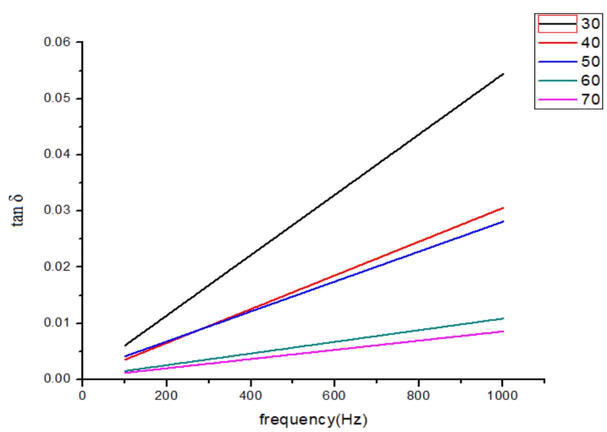
### *B. Dielectric properties of lead titanate thin film annealed at different time.*

Fig. 5(a) shows the relationship between dielectric constant and frequency annealed at five different annealing times. As demonstrated in the graph, the dielectric constant increases with increasing annealing time from 30-70 min. The films annealed at 500°C for 30 mins exhibit low dielectric constant. Increasing the annealing time on the hand resulted in the increase of the dielectric constant. Therefore, longer annealing time contribute to the higher dielectric constant. As can also seen from the graph, the dielectric constant decreases with increasing frequency.

Fig. 5(b) shows the effect of annealing time on dielectric loss at frequency in the range of 100-1 kHz measured at room temperature. It is observed that the dielectric loss decreases with increasing annealing time in a range of 30-70 min. Since the dielectric loss is inversely related with dielectric constant, thus the dielectric loss linearly increases as the frequency increases. This trend shows similar results for the sample annealed at different temperature.




(a)




(b)

Figure 5. Plot of (a) dielectric constant and (b) loss tangent versus frequency for lead titanate thin films annealed at different annealing times.

Fig. 6 shows the effects of atmospheric temperature on dielectric constant of lead titanate thin films at frequency of 100 Hz, 10 kHz, and 1 MHz. Based on the result, the dielectric constant can be affected by the ambient temperature. This case similar to the research reported by Ming Jen Pan *et. al* [12]. The dielectric constants reduce when the temperature increase from 27 to 107$^o$C. As discussed earlier, the dielectric constant is frequency dependence, hence results in lower dielectric constant ($\varepsilon_r$= 0.5) at frequency of 1 MHz compared to dielectric constant at 100 Hz which results in higher dielectric constant, $\varepsilon_r$ =18.

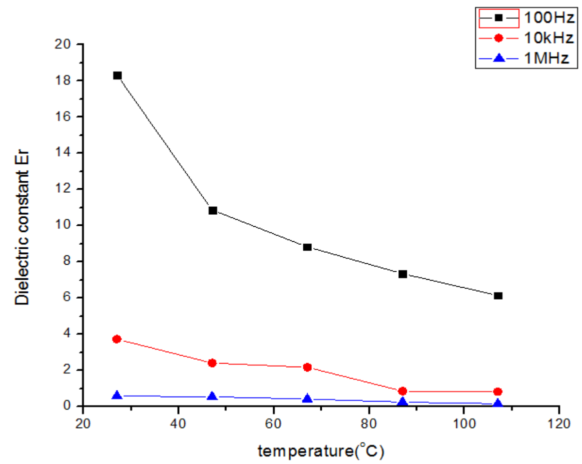



Figure 6. Plot of dielectric constant versus atmospheric temperature at different frequencies

The relationship between resistivity and annealing time of lead titanate thin films is depicted in Fig. 7. The resistivity of the film is increases with increase in annealing time. This behavior is similar with the dielectric constant of the film as shown in Fig. 5(a). At 70min, resistivity of the film is higher which is approximately 1.6x10$^5$ Ωm compared to the resistivity of the sample annealed at different annealing temperature. Thus, longer annealing time resulted in higher resistivity thin films. However, the resistivity of current industry dielectric materials such as silicon oxide ($SiO_2$) and silicon nitride ($Si_3N_4$) are 10$^{14}$ and 10$^{12}$ Ωm respectively which are higher than resistivity of the film in our research.

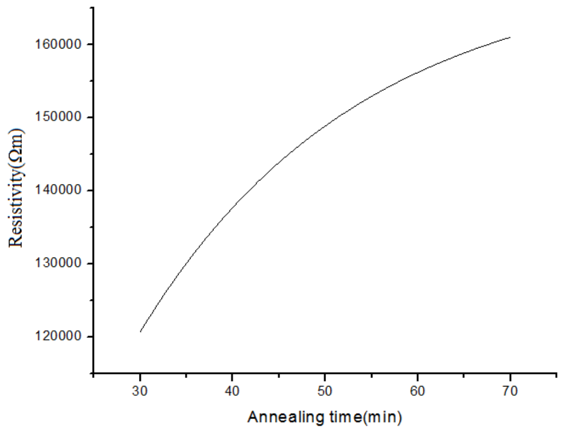



Figure 7. Plot of resistivity versus annealing time

## IV. CONCLUSION

Lead titanate (PT) thin films were prepared using sol-gel spin coating deposition. The effects of annealing time and temperature were investigated. The results showed that the thin film films annealed at high temperatures and times resulted in high dielectric constant and low dielectric loss. The resistivity of the thin films was found to be increased with annealing times and temperatures.

## V. FUTURE DEVELOPMENT

With the development of Integrated Circuit (IC) technology, dielectric thin films which have high dielectric constant are required for various types of electronic applications. For further research, lead titanate thin films were suggested to be modified by doping with other ions including Ca, Zr, La, Ba, Eu, Ce and so on to obtain other lead-based titanate thin films. Since the dielectric constant and resistivity of lead titanate thin films in our research is not high enough, hence modification of the films is the better alternative in order to improve electrical properties of the films.

## ACKNOWLEDGEMENT

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