Effect of Dry Process on Dielectric Properties of PZT Thin Films Prepared by Sol-Gel Process

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Properties of lead zirconate titanate ferroelectric thin films prepared by rapid thermal annealing/direct insertion thermal annealing were investigated. The remnant polarization (Pr), saturation polarization (Ps), and coercive force (Ec) of typical samples annealed by rapid thermal annealing (RTA) are about 13.7 μ C/㎠, 27.1 μ C/㎠, and 55.6 ㎸/㎝, respectively. The dielectric constant of the sample is about 786, the dielectric loss tangent is about 2.4 % at 1 kHz. Furthermore, ferroelectric, conduction, and piezoelectric properties of the thin films annealed by RTA process and the direct insertion thermal annealing (DITA) process were compared. The influence of temperature in the dry process on the above properties was also investigated.

Keywords : Ferroelectrics, PZT, Sol-Gel, RTA, DITA

1. INTRODUCTION

$Pb(Zr,Ti)O_3$ is a well known material having excellent ferroelectric, pyroelectric, and piezoelectric properties. There have been some proposals for its application to various electronic and piezoelectric devices such as infrared pyroelectric sensors, ultrasonic transducers, nonvolatile memories, and etc. For more than a decade, there have been several attempts to prepare PZT thin films using RF magnetron sputtering, metal organic chemical vapor phase deposition (MOCVD), laser ablation, or sol-gel method, and so on[1-5]. Among several methods for deposition of the PZT films, the sol-gel process has received considerable attention because it has a variety of advantages, including easier composition and film homogeneity, easier fabrication of large area thin films, low cost, and a short fabrication cycle. The properties and qualities of the film deposited by the sol-gel process depends on the dry process and the annealing process[7-9].

In this paper, the effect of the annealing process and the dry condition on the properties of $Pb(Zr_{0.52}Ti_{0.48})O_3$ (PZT) thin films were investigated in order to explore the optimum heat treatment process in the sol-gel deposition method.

2. EXPERIMENTAL

The preparing process of PZT films is shown in Fig. 1 The starting materials for preparing stock solutions were lead acetate ($Pb(CH_3COO)_2 3H_2O$), zirconium (Ⅳ)n-propoxide($Zr(OCH_2CH_2CH_3)_4$), and titanium (Ⅳ) is o-propoxide($Ti(OCH(CH_3)_2)_4$). Methoxyethanol ($CH_3C_2H_4$-OH) and HNO_3 were chosen as a solvent and catalyst. Each homogeneous, clear solution was prepared at 125 ℃ by mixing solvent and lead acetate, zirconium(Ⅳ) n-propoxide, and titanium(Ⅳ) iso-propoxide, respectively. The volume of the final hydrolyzed solution was then adjusted to give the 0.4 M PZT stock solution with excess PbO of 10 mol%. PZT films were prepared by a multi-layer spin coating the hydrolyzed solution onto Pt(100nmt)/Ti(50nmt)/ SiO_2(100nmt)/Si substrates of 2 inch diameter at 3000 rpm for a duration of 20 s.

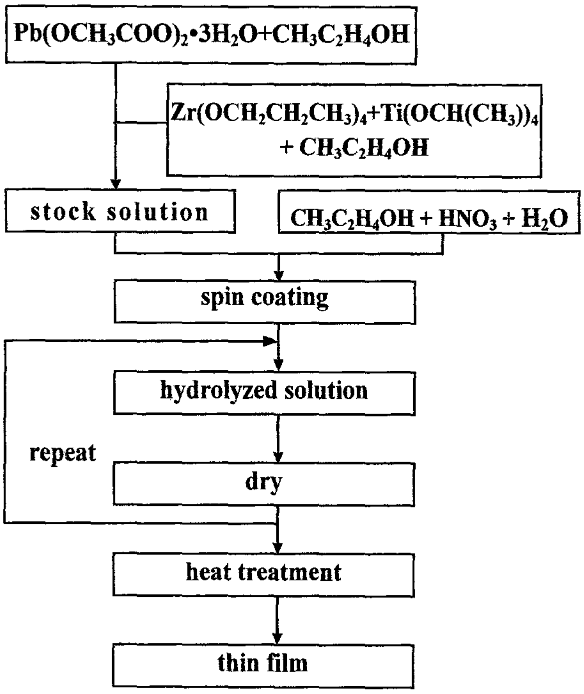


Fig. 1. Process flow diagram for PZT thin films.

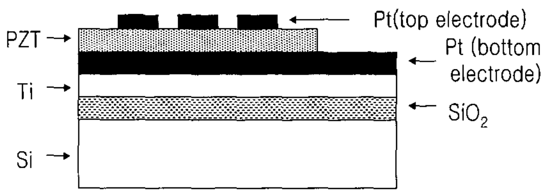


Fig. 2. Structure of PZT films.

Each layer was dried at 250, 300, 350, or 400 ℃, respectively for 5 minutes. The films were consisted of 4, 6, and 8 layers, respectively, to control the thickness of the PZT films. The films were finally annealed at 650 ℃ for 3 minutes by RTA or at 650 ℃ for 30 minutes by the direct insertion thermal annealing process.

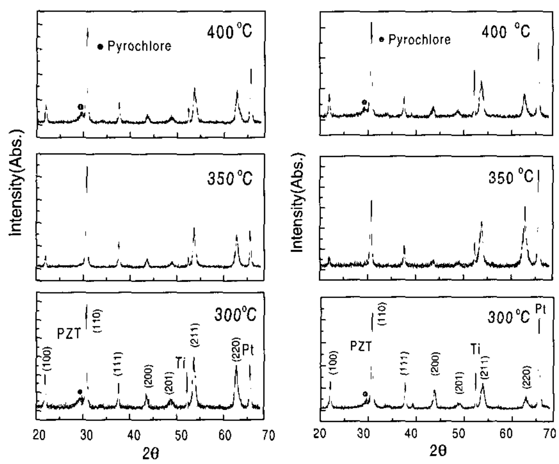
The shape of the prepared films is shown in Fig. 2. The hysteretic properties were measured with the sawyer-Tower circuit (RT66A). The dielectric properties were measured with an Impedance Analyzer (HP4194A). The I-V properties were measured with a computerized system that consists of an electrometer, a voltage source, and a computer. The film crystal structure was determined by X-ray diffraction (XRD). The piezoelectric properties were measured with the Berlincourt d33 meter (Channel Product Co.) after poling at 150 kV/cm, 120 ℃, for 10 minutes.

3. RESULTS AND DISCUSSION

Figure 3 shows the X-rays diffraction patterns of the films dried at different temperatures and annealed through different processes. For films dried at 300, 400 ℃ and annealed by both processes, the pyrochlore phase and the perovskite phase appeared. However, the pyrochlore disappeared at $2\theta \cong 29.6^{o}$ in the films dried at 350 ℃. Pt peaks ($2\theta \cong 66^{o}$) in the films annealed by RTA were weaker than that annealed through DITA. This indicates that the Pt electrode layer is strongly affected to form the crystalline phase of PZT in DITA rather than in RTA.

Figure 4 shows P-E hysteresis loops of films dried at different temperatures and annealed by different processes. The remnant polarization (Pr) and coercive force (Ec) of each films deduced from Fig. 4 are shown in Fig. 5 . For the films annealed through RTA, Pr and Ec are 12.5 ~13.7μC/cm^2, 55~64 kV/cm, respectively. Comparing with those of the films annealed through DITA, RTA annealed films show larger Pr and lower Ec.

Among them, 350 □ dried films show the largest Pr and the lowest Ec. These results can be explained by the microstructure and crystalline structure of the films. It is noted that the films dried at 350 □ and annealed through RTA show the highest content of the perovskite phase among the samples.



(a) RTA (b) DITA

Fig. 3. XRD pattern of PZT dried at different temperatures and annealed by different processes.

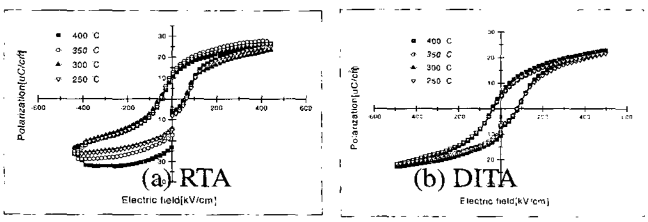


Fig. 4. P-E hysteresis loop of PZT thin films.

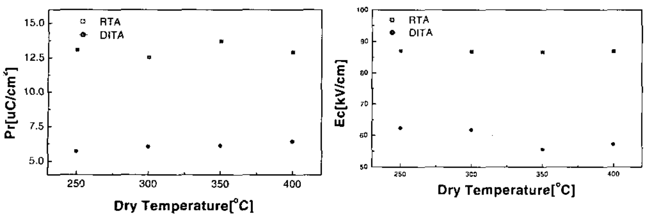


Fig. 5. Pr and Ec for PZT thin films.

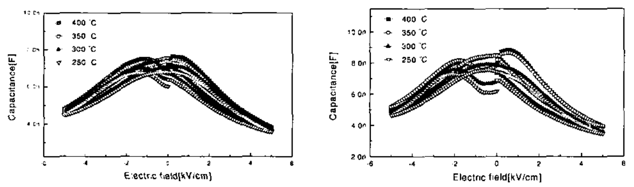
Figure 6 shows DC bias voltage dependence of capacitance of the films. The C-V curve in the films annealed through RTA shows more symmetry than that in the films annealed by DITA. Asymmetry in the C-V curve results from nonswitching in spontaneous polarization and structual defects [6, 8].

The frequency dependence of capacitance of the films are shown in Fig. 7. The films dried at 350 ℃ and annealed through RTA show the highest dielectric constants, 758 at 100 Hz. The dielectric loss factor of this film shows the lowest value, about 2.4 % at 100 Hz, though not present in this paper.

The fatigue characteristics of the samples are shown in Fig. 8. A 20 kHz sin wave of a 10 V amplitude was used to fatigue the PZT thin films. From 10^4 cycles to 10^9 cycles, the normalized switching polarization dropped logarithmically to 78~82 % of the initial value. From the results, fatigue measurements showed that the films dried at 350 ℃ and annealed through RTA were stable up to 10^9 cycles.

The characteristics of I-V of the films are shown in Fig.9. The leakage current in RTA thin films is about 10 nA/cm^2, but the leakage current in DITA films is about 30 nA/cm^2. The breakdown strengths are 0.8 MV/cm in DITA film 12 MV/cm in RTA film. From the results, the RTA film is assumed to have good insulation properties. Figure 10 shows voltage response induced by mechanical forces in the poled PZT films. The voltage response is increased linearly with increasing mechanical force.

The piezoelectric strain constant can be deduced from the slopes in this figure. The results are shown in Fig. 11 The piezoelectric constants are 50~200 pC/N. The constant



(a) RTA (b) DITA

Fig. 6. DC bias voltage dependence of capacitance of PZT films annealed by different processes.

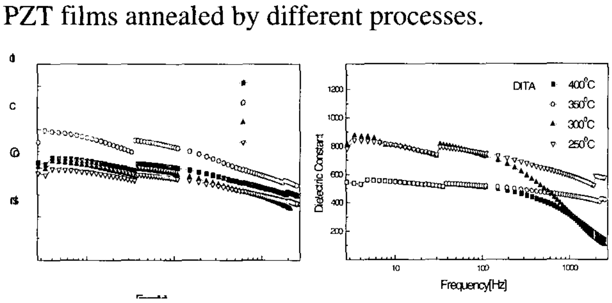


Fig. 7. C-f characteristics of PZT thin films.

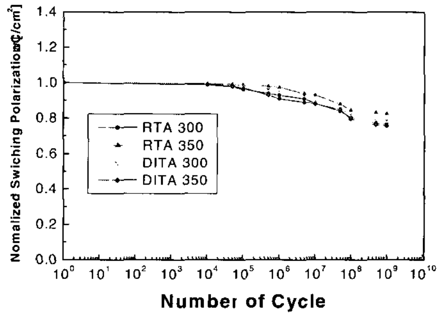


Fig. 8. Characteristics of fatigue in PZT thin films.

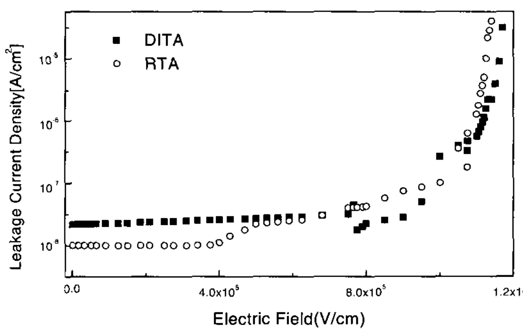


Fig. 9. I-V characteristics of PZT thin films.

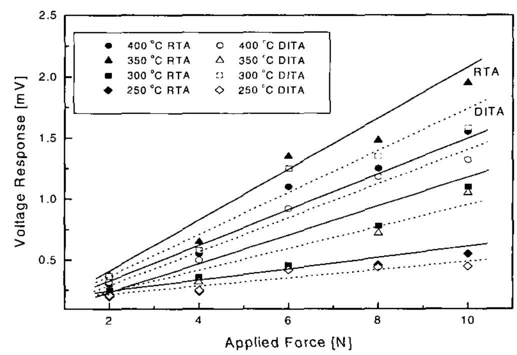


Fig. 10. Voltage response induced by mechanical forces in poled PZT thin films.

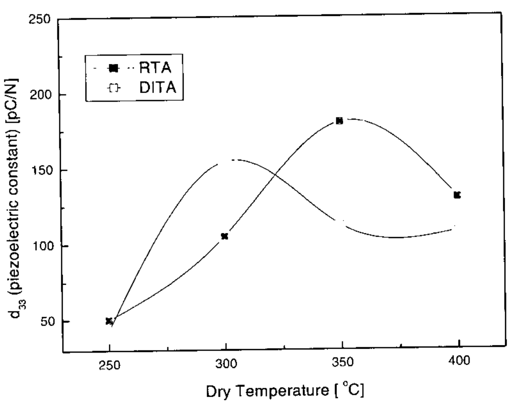


Fig. 11. Piezoelectric constant of PZT thin films.

in the films dried at 350 ℃ and annealed through RTA have a comparable value to bulk PZT. The results in Fig. 11 can be understood through the microstructure and crystalline structure of the films as mentioned previously

4. CONCLUSION

$Pb(Zr_{0.52}Ti_{0.48})O_3$ ferroelectric thin films on the Pt/Ti/SiO2/Si substrate were fabricated by the sol-gel multi-layer spin-coating. The thin films were dried at 250~400 ℃, and were annealed through RTA / DITA process. The dielectric, ferroelectric, conduction, and piezoelectric properties of the PZT thin films were measured. From the results of the XRD pattern, the pyrochlore disappeared at $2\theta \cong 29.6^o$ in the films dried at 350 ℃. Pt peak ($2\theta \cong 66^o$) in the films annealed through RTA were weaker than films annealed through DITA. RTA annealed films have a smaller coercive field Ec and a larger remnant polarization Pr than those of DITA annealed film. For the films dried at 350 ℃ and annealed through RTA, Pr reaches the maximum value of 13.7 μ C/cm^2, and Ec is shown as the lowest value of 55 kV/cm. DC bias voltage dependence of the capacitance curve in the films annealed by RTA shows more symmetry than that in the films annealed by DITA. This means that the film annealed by RTA have less components of spontaneous polarization nonswitching and structural defects than that of DITA annealed film. The fatigue measurements show that the film dried at 350 ℃ and annealed by RTA was stable up to 10^9 cycles. The films dried at 350 ℃ and annealed by RTA shows the highest dielectric constants, 758 at 100 Hz. The dielectric loss factor of this film shows the lowest value. about 2.4 % at 100 Hz. From the current – voltage curve, the RTA annealed films are assumed to have good insulation properties. The piezoelectric strain constants are 50~200 pC/N, especially the constant of the film dried at 350 ℃ and annealed through RTA which reaches a largest value of 200. The experimental results of ferroelectric, dielectric, and conduction properties depend strongly on the microstructure and crystalline structure. As the results of the above experiments, we considered that the ferroelectric PZT thin film dried at 350 ℃and annealed through RTA is applicable to electronic devices such as, FRAM and the piezoelectric transducer.

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