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Electrical Characteristics and Preparation of Nanostructured $Pb(Zr_{0.5}Ti_{0.5})O_3$ Ferroelectric Films by Spray Pyrolysis

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Abstract —Nanostructured ferroelectric thin films of $Pb(Zr_{0.5}Ti_{0.5})O_3$ on $Pt/Ti/SiO_2/Si$ substrates are prepared by spray pyrolysis and thermal annealing. The crystal structure of the as-sprayed films transformed from amorphous, pyrochlore, multiple phases of pyrochlore and perovskite, to a single phase of perovskite as the annealing temperature is increased up to 500°C. The physical characteristics of the resultant films show the dielectric constant of 400, remanent polarization of 30.0μC/cm^2 and coercive field of 70.0kV/cm, respectively.

***Keywords* —**Ferroelectric film, spray pyrolysis, remanent polarization, coercive field, dielectric constant, perovskite

1 Introduction

It is well known that PZT film has been resulted in a considerable attention due to their potential applications microelectronic, piezoelectric and pyroelectric devices. The physical characteristics of $Pb(Zr,Ti)O_3$ (PZT) and $(Pb_{1-x}La_x)(Zr_yTi_{1-y})O_3$(PLZT) films include high permittivity, high photosensitivities, pyroelectric, and large spontaneous polarization. Therefore, a PZT film is suitable for potential applications in dynamic random access and nonvolatile random access memories capacitors[1].

Up to day, a variety of techniques have adopted to prepare the high-quality PZT and PLZT films. These include physical vapor deposition such as rf-sputtering[2], and chemical vapor deposition of metalorganic deposition[3], spray pyrolysis[4], and so on. Spray pyrolysis[5] is an economic and convenient process and has been used on the fabrication of inorganic films[6-7]. However, literatures on the fabrication and electrical characteristics of PZT and PLZT thin films by spray pyrolysis are very few[8]. It reported the preparation of PLZT films on substrates by spray pyrolysis and demonstrated a highly homogeneous and amorphous PLZT films on the oriented silicon[8].

This paper investigates the preparation and ferroelectric characteristics of the perovskite single-phase PZT films on $Pt/Ti/SiO_2/Si$ via spray pyrolysis of solution.

2 Experiment Procedure

Ferroelectric films with the composition of $Pb_{1.1}(Zr_{0.5}Ti_{0.5})O_3$ prepared by spray pyrolysis and thermal processing. The metal stoichimetric ratios of the precursor solutions are Pb : Zr : Ti of 1.1 : 0.5 : 0.5. 2-methoxyethanol and ethylene glycerol used as the solvents for titanium isopropoxide and metal nitrates. The mixed solution of nitrates is heated up to 120°C under stirring. The dehydrated solution was cooled down to 70°C, and then mixed with solvent of titanium isopropoxide. 2-methoxyethanol is poured into dehydrated solution, which follow with reflux and stirring until a clean and transparent solution is obtained.

The combination of spin-on and spray pyrolysis is applied to fabricate the ferroelectric PZT films. The precursor solution is spin-coated and dried on the Pt, Ti-coated thermal oxidized Si wafer. The as-sprayed films are formed on the $Pt(1000A)/Ti(100A)/SiO_2(2000A)/Si$ with spin-coated film by spraying precursor solution using a spray gun and heated up at 300°C. The as-sprayed films are thermal annealed at temperatures of 400-700°C for 10min for the preparation of ferroelectric film with high dielectric constant. The phase identification of the as-prayed and resultant film carried out by X-ray diffractometer.

For the ferroelectric properties measurement, a multi-frequency impedance analyzer is employed. The polarization versus electric field hysteresis is observed by using a Sawyer-Tower circuit at 1 kHz. I-V characteristics are measured by HP-4145.

3 Results and Discussion

Figure 1 shows XRD patterns of the as-sprayed(a) and PZT resultant films which are annealed at the temperatures of 400-700°C(b)-(e) for 10 min. Pyrochlore phase appeared in the as-sprayed film when annealed temperature is 400°C and disappears when film annealed at temperature of 500°C. Perovskite phase with characteristic peaks of (110) and (111) formed in the film annealed temperature at 400°C and relative intensity of characteristic peaks gradually increase with increasing annealing temperature while (100) characteristic peak appears in the film annealed at 600°C. The perovskite phase of PZT exhibits ferroelectric properties while the pyrochlore phase of PZT does not show ferroelectric characteristics. Mixed phases of perovskite and pyrochlore are merely observed in the film annealed at temperature of 400°C and single phase of perovskite observed in the annealed at temperature above 500°C. From the XRD patterns, we can infer to the formation of single phase of perovskite PZT occurs at annealing temperature over 500°C.

Figure 2 shows the typical polarization versus electric field(P-E) hysteresis loops, at applied voltage of 5V, of the $Pb(Zr_{0.5}Ti_{0.5})O_3$ resultant films which annealed at temperatures of 500°C and 700°C for 10mins. With the low applied voltage, hystersis loop does not exhibit a sufficiently

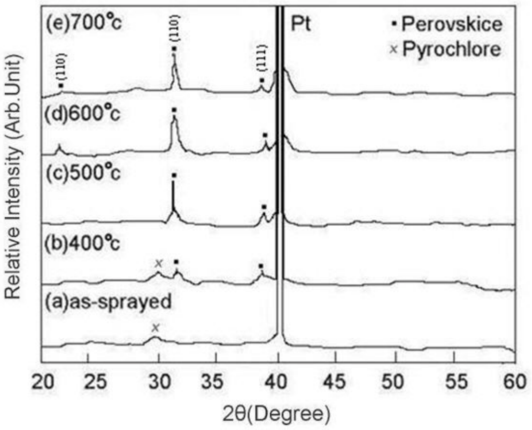

Figure 1 shows the XRD patterns of the as-sprayed(a) and PZT films which were annealed at temperatures of 400°C(b), 500°C(c), 600°C(d) and 700°C(e) for 10 min.

and perfectly saturated shape, but in the case of the applied voltage of 5V, the oval-like shape of the hysteresis loops are improved and show a better ratio between remanent polarization and saturation polarization. However, the hystersis characteristics of film annealed at 500°C for 10min is better than that of film annealed at 700°C for 10min. Therefore, the optimal annealing temperature significantly affects the hysteresis characteristics of the PZT films.

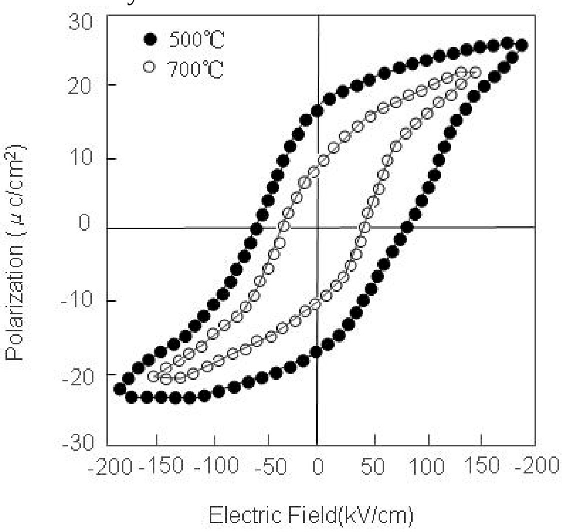

Figure 2 shows typical polarization versus electric field hysteresis loops of PZT films which annealed at 500°C and 700°C for 10min.

Figure 3 shows annealing temperature dependence of the remanent polarization and coercive field for PZT films which annealed at different temperatures for 10min. The remanent polarization of the resultant film annealed at 500°C for 10min is larger than that of the film annealed at 400°C and 700°C for 10min. The same as remanent polarization, the coercive field of the resultant films also initially increase and then decrease with increasing annealing temperatures. The coercive field of the PZT film annealed at 500°C for 10mins is larger than that of the film annealed at 400°C and 700°C for 10mins which indicates that the maximum value of 2Pr and Ec appear in the resultant film annealed at 500°C and is consistent with the result of XRD pattern.

Figure 4 show the annealing temperature dependence of the dielectric constant and dissipation factor for the PZT resultant films. Dielectric constant increases and tangent loss decreases with increasing annealing temperatures. The

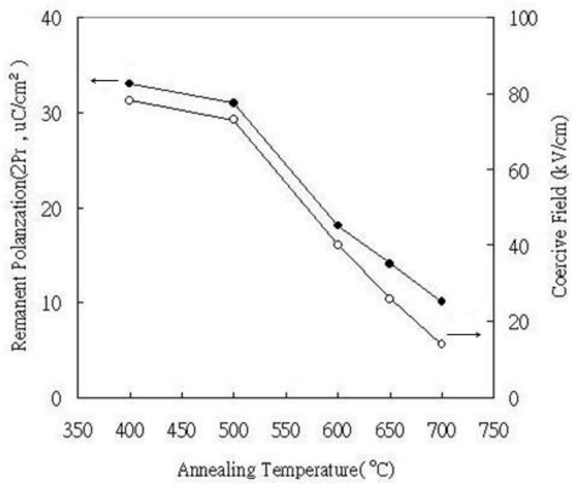

Figure 3 shows the annealing temperature dependence of the remanent polarization and coercive field for the PZT resultant films which annealed at different temperatures for 10min.

variation of dielectric properties is attributed to the change in grain structure and size because the grain morphologies are related to the domain region in the resultant film.

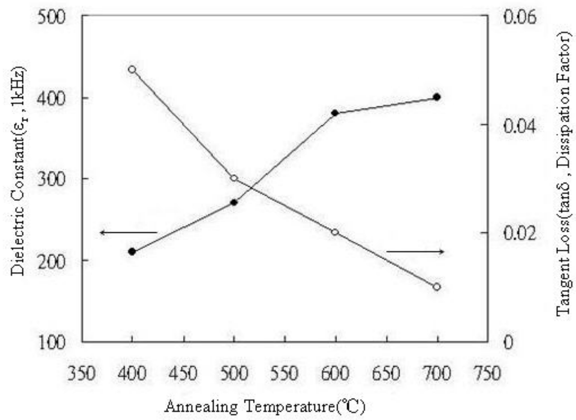

Figure 4 shows the annealing temperature dependence of the dielectric constant and dissipation factor for the PZT films.

4 Conclusion

PZT film on $Pt/Ti/SiO_2/Si$ substrates prepared by processing of spray pyrolysis and thermal annealing. The resultant films show the dielectric constantof 400, remanent polarization of 30μC/cm² and coercive field of 70kV/cm, respectively.

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