Characterization of low-temperature microwave annealed PZT thin films with various thicknesses

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***Abstract*—Ferroelectric lead zirconium titanate (Pb (Zr_xTi_{1-x}) O_3) thin films with various thicknesses were fabricated on Pt/Ti/SiO_2/Si substrates using the sol-gel method with 2.45 GHz microwave energy. Investigations have been made on the crystal structure, surface morphology, dielectric and ferroelectric properties of the films. The thicknesses of PZT film were in the range of 99 to 420 nm, and films were annealed at 450^0C for 30 min. The 99 and 168 nm-thick PZT films have mixed pyrochlore and perovskite phases. Above 168 nm-thick PZT films have complete perovskite phase. The full width at half maximum (FWHM), and the surface roughness were decreased as the film thickness increased. Relative dielectric constant and remnant polarization increased as the film thickness increased, which reflect the difference in crystallinity.**

***Index Terms* —Ferroelectric, PZT, perovskite phase.**

I. Introduction

Recently, ferroelectric thin films have received a great deal of attention in the preparation and application, especially lead zirconate titanate (PZT). Because of its excellent properties, PZT thin film has widely used for preparing ferroelectric, piezoelectric, and pyroelectric devices. Among all the compositions of PZT, Pb (Zr_xTi_{1-x}) O_3 which is near the morphotropic phase boundary (MPB), is the most important because of its excellent ferroelectric properties. Among several methods for deposition of the PZT thin 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 PZT thin films fabricate by the sol-gel technique display a well-saturated hysteresis loop at an annealing temperature of 520^0C [1]. It has been difficult to reduce the annealing temperature of the sol-gel driven PZT film below 520^0C, mainly, due to the pyrochlore phase formation at lower annealing temperature. Such high annealing temperature causes the problem of PZT integration into silicon processing steps and selection of suitable barrier layer, and makes the PZT films unsuitable for high density ferroelectric memory devices.

Microwave processing of ceramics has opened a new venue for materials scientists over the past 15 years. The short durations of time involved when microwaves are used as the energy source for heating have made it quite attractive for ceramic processing. The other advantages of using microwaves when compared to conventional processing include lower power requirements, rapid heating rates, higher toughness of materials and fine grain size. However, no literature reports on low-temperature microwave annealed (<500^0C) PZT thin films with various thicknesses. In this study, the PZT thin films were deposited on Pt/Ti/SiO_2/Si substrate using the single-mode cavity of 2.45 GHz microwave, to obtain good dielectric and ferroelectric properties. The PZT thin films were annealed at 450^0C/30min with various thicknesses. The crystal structure, surface morphology, and electrical properties of PZT thin films were investigated. On the basis of experimental results, we discuss the low-temperature microwave annealed PZT thin films with various thicknesses.

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II. Results and Discussion

A. Electrical properties of PZT thin films

The relative dielectric constant (ε_r) and the dissipation factor of PZT films were investigated as a function of film thicknesses. The measurements were performed at 1 kHz with an impedance analyzer (HP 4194 A) at room temperature. Figure 1 exhibits the dielectric properties of the PZT thin films as a function of film thicknesses. The 168nm-thick PZT film shows lower dielectric constant and higher dissipation factor than the other PZT films, which may be due to the pyrochlore phase as indicated in XRD pattern (Fig. 2). The dielectric constant increases with an increasing of film thicknesses. The dissipation factor decreases as the film thicknesses was increased.

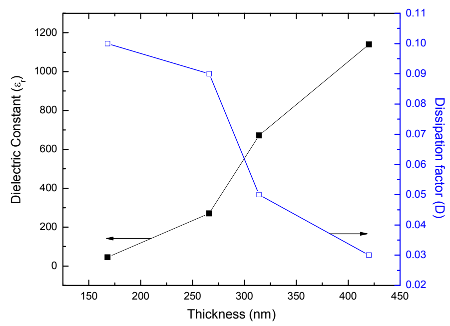

FIG. 1 Dielectric properties of PZT thin films as a function of film thicknesses.

Table 1 P.P.M: Preparation of precursor method, A.M: Annealing method, A.T: Annealing temperature, SG: Sol-gel method, C.A: Conventional annealing, R.T.A: Rapid thermal annealing, F.A + L.A: Furnace + Laser annealing, SG + LA: Sol-gel + laser ablation method, H.P: Hybrid Process, L.A: Laser annealing, M.I: Microwave irradiation, M.A: Microwave annealing,

P. P. M	A.M	Composition	A.T	Thickness (μm)	Pr ($\mu C/cm^2$)	Ec (kV/cm)	Ref.
SG	C.A	PZT(52/48)	520^0C/30min	0.12-0.3	17-19	57.5-74	[1]
SG	C.A	PZT(52/48)	650^0C/30min	3.896	25	28	[2]
SG	R.T.A	PZT(53/47)	550^0C/5min	0.3	32.2	79.9	[3]
SG	F.A+L.A	PZT(53/47)	550^0C/60min	0.17	30.3	123.5	[4]
SG+LA	H.P	PZT(52/48)	650^0C/90min	0.6	23.6	54.8	[5]
SG	28 GHz-M.I	PZT(52/48)	480^0C Input: 2.5kW	001	40	50	[6]
SG	2.45GHz-M.A	PZT(50/50)	600^0C/6min Input: 2kW	0.45	8.4	47.5	[7]
SG	2.45GHz-M.A	PZT(53/47)	450^0C/30min Input: 350W	0.42	46.86	86.25	[this work]

B. Ferroelectric properties

The effects of the film thicknesses on ferroelectric properties of the PZT films were tested using Radiant RT 66A standard test system. Figure 2 presents the remnant polarization and coercive field as a function of the film thicknesses. The P_r value of the films decreases from 46.86 to 36.32 $\mu C/cm^2$ as the film thicknesses decreased from 420 to 266nm due to the crystllinity and grain sizes. The E_c values of the films increases with decreasing of film thicknesses. The average E_c value of a 420 nm-thick PZT film has 86.25 kV/cm, and 266nm-thick PZT film has 215.67 kV/cm. The existence of this internal electric field was often attributed to the space charges, the oxygen defects and the stress. It was admitted that the space charges and the oxygen vacancies were located near the bottom electrode and act as pining centers. Therefore, the maximum of the internal and coercive fields were obtained for very thin films. Scott and co-worker reported that the coercive electric field decrease with an increasing of film thicknesses. The P_r increases and E_c decreases as the film thicknesses increased may be due to the better crystallinity, grain sizes and the reduction of stress under influence of the 2.45 GHz microwave energy.

III. CONCLUSIONS

Using the microwave annealing method, it is possible to obtain 266nm-thick PZT film with high perovskite content at low temperature (450^0C). The pyrochlore phase was observed in PZT films, which were lower than 266nm-thick PZT films. The FWHM decreases with an increasing of film thicknesses. The surface morphology shows that the 420nm-thick PZT film has lower roughness and larger grain size than the other annealed PZT films. Relative dielectric constant and grain sizes of PZT films were increased with an increasing of film thicknesses. As the film thicknesses increases, the remnant polarization increased and coercive filed decreased, which may be due to the better crystallinity, grain sizes, and reduction of stress. The 420nm-thick PZT film shows optimum properties than the other annealed PZT films. These results suggest that the higher thicknesses of PZT films are beneficial for obtaining better properties than the lower thicknesses of PZT films due to the pyrochlore phase and stress.

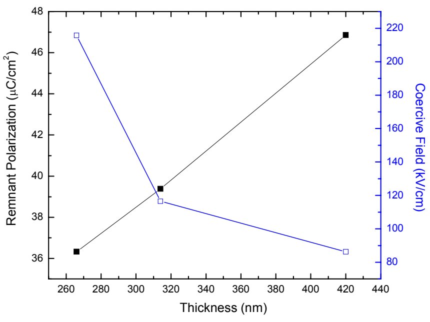

FIG. 2 Remnant polarization and coercive field of PZT thin films as a function of film thicknesses.

REFERENCES

[1] Cho C -R, Lee W -J, Yu B -G, and Kim B -W 1999 Dielectric and ferroelectric response as a function of annealing temperature and film thickness of sol-gel deposited $Pb(Zr_{0.52}Ti_{0.48})O_3$ thin film *J. Appl. Phys.* **86** 2700-11.

[2] Cheng J, Zhu W, Li N, and Eric Cross L 2002 Dielectric properties of (100) textured thick $Pb(Zr_xTi_{1-x})O_3$ films with different Zr/Ti atom ratios *J. Appl. Phys.* **91** 5997-6001.

[3] Tang X G, Jiang L L and Ding A L 2003 The effect of thickness on the dielectric properties of highly (111) oriented $Pb(Zr_{0.52}Ti_{0.48})O_3$ thin films prepared by a simple sol-gel route *Microelectron. Eng.,* **65** 387-93.

[4] Zhu Y, Zhu J, Song Y J, and Desu S B 1998 Laser-assisted low temperature processing of $Pb(Zr,Ti)O_3$ thin films *Appl. Phys. Lett.* **73** 1958-60.

[5] Wang Z J, Karibe I, Maeda R, and Kokawa H 2002 Preparation of lead zirconate titanate thin films derived by hybrid processing: sol-gel method and laser ablation *J. Am. Ceram. Soc.* **85** 3108-10.

[6] Wang Z J, Kokawa H, Takizawa H, Ichiki M and Maeda R 2005 Low-temperature growth of high-quality lead zirconate titanate thin films by 28 GHz microwave irradiation *Appl. Phys. Lett.* **86** 212903 (1-3).

[7] Song S, Fu X, Tan H, Tao M, Chen L, Wang L and Lin C 1997 Microstructure of PZT/Ti thin films prepared by sol-gel process and microwave annealing *Phys. Stat. Sol. (a)* **164** 779-84.