Effects of Two-Step Annealing Process on the Pulsed Laser Ablated Lead Zirconate Titanate Thin Films

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Abstract - Lead zirconate titanate (PZT) thin films were fabricated by the pulsed laser ablation deposition (PLAD) method onto Pt/Ti/SiO2/Si substrates. Crystalline phases as well as preferred orientations in PZT films were investigated by X-ray diffraction analysis (XRD). The well-crystallized perovskite phase and the (101) preferred orientation were obtained by two-step annealing at the conditions of 650 ℃, 1 hour. It was found that the temperature for the pulsed laser ablated PZT films annealed via a two-step annealing process can be reduced 200 ℃ compared to that of the conventional three-step annealing temperature profile for enhancing the transformation of the perovskite phase. The remanent polarization and the coercive field of this film were about 20 μC/cm2 and 46 kV/cm, while the dielectric constant and loss values measured at 1 kHz were approximately 860 and 0.04, respectively. The interesting phenomena of this film, such as vertical shift in hysteresis curve, are also discussed.

Keywords: pulsed laser ablation deposition(PLAD), lead zirconate titanate(PZT), preferred orientation, perovskite phase, ferroelectric properties, dielectric properties

1. Introduction

Ferroelectric lead-zirconate-titanate(PZT) ceramics in the form of thin films have been studied intensively for various applications over the past few years. Electrical and electromechanical properties, such as the remanent polarization, piezoelectricity and pyroelectricity offer a wide variety of applications in microelectronics and micromechanics. Composition of $Pb(Zr_xTi_{1-x})O_3$ near the morphotropic phase boundary with $x\approx0.5$, which denotes an abrupt structural change with composition at constant temperature in a solid solution range, provides an increased capability of polarization and a high electromechanical coupling coefficient [1]. These properties are utilized in nonvolatile memory and piezoelectric micromovement actuator applications [2,3]. On the other hand, films with compositions of x>0.7 are found to be sensitive in pyroelectric sensors [4]. Several different deposition methods including chemical vapor deposition [5], sputtering technology[6], spin coating of sol-gel derived PZT solutions [7] and pulsed laser ablation deposition(PLAD) [8] have been used to prepare PZT thin film structures. The PLAD technique is suitable for the deposition of a large variety of materials and its advantages are good reproducibility of a multicomponent target composition in the films and the capability to evaporate materials having a high melting point. The main disadvantages are nonuniform thickness distributions and generation of large particulates.

In the multiplayer capacitor structure the electrical properties of the PZT thin film are also affected by the substrate material and different processing conditions during the fabrication steps. In particular, the difference of thermal expansion coefficients between the substrate and film during the heat treatment at temperatures above 500℃ can lead to formation of hillocks or cracking in the case of high compressive and tensile stresses, respectively. Stresses in the thin films are typically considered to be biaxial, affecting only the plane of the film and relaxed in the deposition perpendicular to the substrate surface. For example, on the silicon substrate both in the sputtered platinum electrodes and in the PZT films, deposited by the sol-gel technique, the stresses are found to be tensile of the order of 1 GPa and 100 MPa, respectively [9]. Typically, the remanent polarization decreases and the Curie temperature were increased with increasing the stress.

In this study, laser ablated Au/PZT/Pt capacitor structures have been made on thermally oxidized silicon substrate. Proper ablation-process parameters and thermal heat-treatment procedure for the deposition of both platinum and PZT thin films were determined. Structural and compositional analyses of the capacitor structures are given

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2. Experiment

2.1 Laser Apparatus

Fig. 1 shows the pulsed laser ablation system, which is composed of a laser source, and a deposition chamber with a three-inch wafer substrate holder. A pulsed KrF eximer laser beam with wavelength 248nm, pulse repetition rate of 10Hz and energy of 600mmJ was focused through Quartz SUPRASIL II window.

The pumping system is composed of rotary and molecular pumps and the chamber could be evacuated to 10^{-7} Pa at room temperature. A fast atom beam source(Ion Tech Ltd., FAB110) was also available for substrate cleaning and atoms were supplied during deposition. Chamber pressure during FAB treatment was 1×10^{-3} Pa and applied voltage was 0.55 kV. The corresponding current was 10 mA. The distance between target and substrate was about 5 cm and both were rotated during deposition to improve the uniformity of thickness. The laser beam fluence was 1.2 J/cm^2 and the beam size was about 1×3 mm^2.

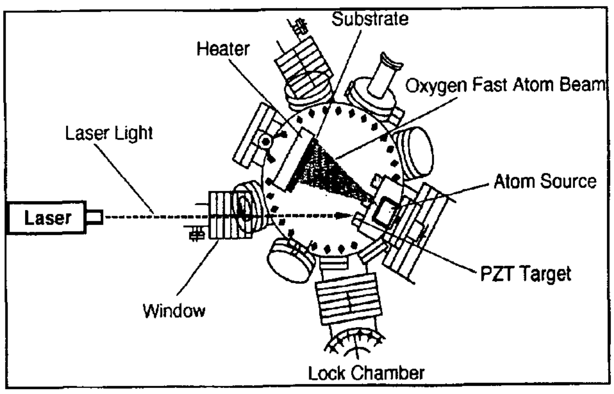

Fig. 1 Pulsed laser ablation deposition system

2.2 Specimens, Process and Measurement

A commercially available three-inch Si wafer was adopted for the substrate material. This is an *n*-type semiconductor of (100) orientation. The target material was also commercially available PZT (Furuuchi Co. PZR F-13, reported value of relative permittivity 1800 and piezoelectric constant d31 and 180, respectively) of morphotropic region of $Pb(Zr_{0.52}Ti_{0.48})O_3$. The target was 20 mm in diameter and 5 mm in thickness.

The PZT thin films were fabricated onto Pt(111)/Ti/SiO_2/Si substrates using the PLAD method. These substrates were prepared by sputtering 0.05 μm of titanium onto an oxidized(1.8 μm of SiO2) silicon substrate, and then sputtering 0.15 μm of platinum.

For the ferroelectric PZT film deposition, a laser-beam fluence of 1.2 J/cm2 was found to be proper to produce a film with nearly stoichiometric composition and good morphology [10]. The thicknesses of the pulsed laser ablated PZT films were about 0.8 μm. The deposition rate was measured by a surface roughness meter (Ulvac Co., Dektak 3) and calculated as 1.6 μm/hr. Deposition was done under irradiation of oxygen FAB (oxygen gas pressure of 0.06 Pa, 1 kV, 30 mA). After deposition, two-step annealing was done at atmospheric pressure with the temperature range of 600–750°C and the holding time of 1–4 hours. In this two-step annealing process, two electric ovens are prepared for rapid increasing of temperature. First, the as-deposited films were put into the first oven set at 300°C and secondly, after pre-heating at 300°C the specimens were taken from the first oven and put immediately into the second oven. The annealing conditions of the deposited PZT films are as summarized in Table 1.

Finally, the top electrodes of Cr/Au (total thickness of 100 nm) were formed by evaporation.

Fig. 2 shows the temperature profile of the previously carried three-step annealing process [11], and Fig. 3 shows the profile of the two-step annealing proposed here.

X-ray diffractometry (Rigaku RINT-2500) was used for analysis of the crystallographic structure of the deposited films. The P-E hysteresis loops of these films were measured using a standardized ferroelectric test system (Radiant Technologies RT-6000) which employs the principle of the

Table 1. Annealing conditions of the samples

Sample	Temperature (°C)		Holding Time, T_h(hr)	
	1st stage	2nd stage	1st stage	2nd stage
A	300	600	0.5	1
B	300	650	0.5	1
C	300	700	0.5	1
D	300	750	0.5	1
E	300	600	0.5	2
F	300	600	0.5	4

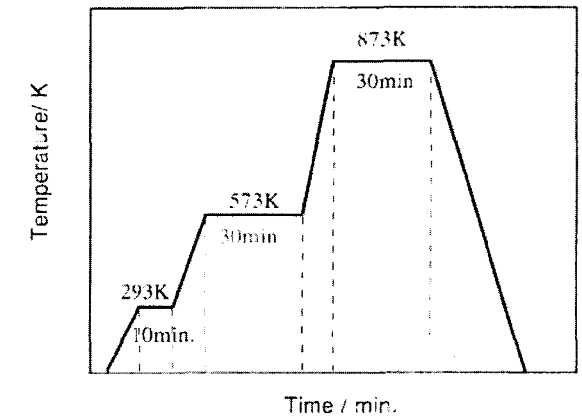

Fig. 2 Temperature profile of three-step annealing [11]

Sawyer-Tower circuit. The dielectric constant and loss tangent values of these films were measured at 1 kHz using an LF impedance analyzer system(Hewlett-Packard HP4192A).

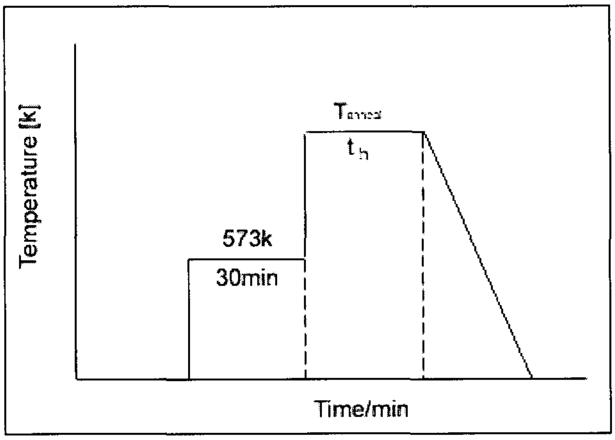

Fig. 3 Temperature profile of two-step annealing

3. Results and Discussion

Some applications require an oriented or epitaxial film with its polar axis perpendicular to the substrate. Previous studies report that the final heat treatment temperature is quite effective for crystallization and epitaxy of ferroelectric PZT films deposited by the PLAD [12].

Fig. 4 shows the XRD patterns for laser-ablated PZT films on $Pt/Ti/SiO_2/Si$ substrates annealed at each condition. The films annealed at temperatures above 650°C reveal the peaks of (101) planes of perovskite phase at $2\theta = 30.9°$, as shown in Fig. 4. On the other hand, the films annealed at 600°C show no perovkite phase in spite of increasing holding times from 0.5 to 4 hours. The PZT layers deposited at room temperature have been reported to have an amorphous structure [13], while after annealing at 750°C the perovskite structure was found to have some pyroclore phase. An annealing temperature of 750°C is rather higher since such high temperature induces the peal off of the deposited layer because of large thermal elongation. In this study, by changing the annealing temperature profile from the conventional three-step to the proposed two-step, the annealing temperature can be reduced to 650°C without the need for additional multi-layered structure of PZT/PbO for obtaining perovskite phase at a lower annealing temperature.

The electrical properties of PZT thin films are typically found to be somewhat moderate compared with the properties of the bulk ceramics [3]. The values of the dielectric constant and the remanent polarization in the thin films are lower and the loss angle higher than in the bulk material. The dielectric constant and loss value measurements for

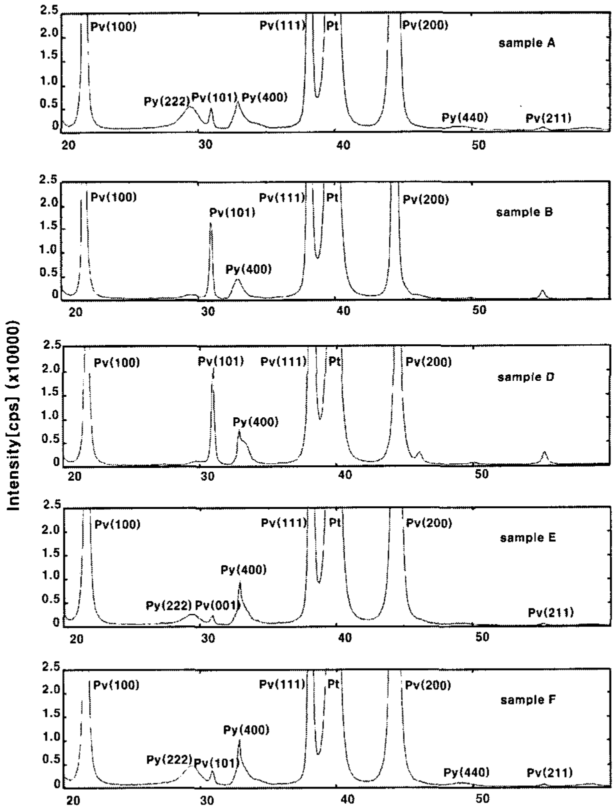

Fig. 4 XRD patterns for pulsed laser ablated PZT films annealed with different conditions

the pulsed laser ablated PZT were carried out at a frequency of 1 kHz using an impedance analyzer. The room temperature dielectric constants in the films annealed at 600°C (1 hr), 650°C (1 hr), 750°C (1 hr) were about 300, 850, 930, and loss values were about 0.09, 0.04 and 0.04, respectively. In the case of films annealed at 600°C, the measured value of the dielectric constant was unsatisfactory, meanwhile, the values for the case of annealing temperatures of above 650°C reveals comparably higher values with respect to other published data [3].

Ferroelectricity was investigated by observing the polarization hysteresis loop. Fig 5 shows the results of the ferroelectric properties among PZT films annealed at each condition. The remanent polarization of 23 $\mu C/cm^2$, 20 $\mu C/cm^2$ and 20 $\mu C/cm^2$ were found in the sample films of A, B, and C, respectively. The values of coercive field were that of 48 kV/cm, 46 kV/cm, and 46 kV/cm, respectively. The D-E hysteresis loop exhibited a conspicuous voltage shift toward the negative-bias field and its magnitude were examined to be 12.6 kV/cm, 16.1 kV/cm, and 15.4 kV/cm, respectively. According to Okamura et al. [14], space charges due to defects such as lead and oxygen vacancies were easily moved by the electric field generated by spontaneous polarization during the cooling process because of

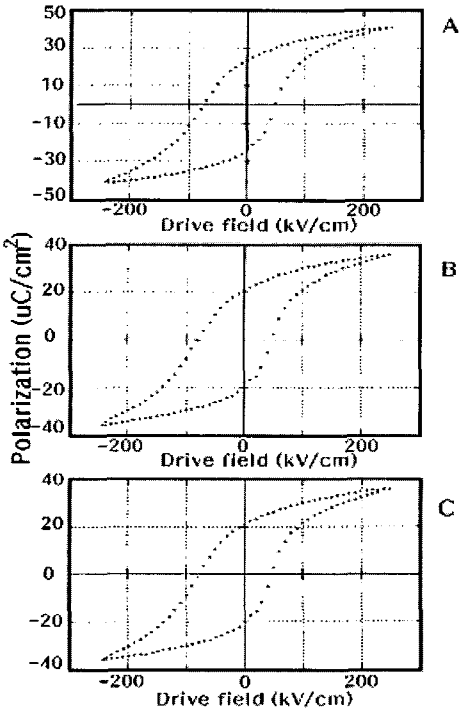

Fig. 5 Polarization hysteresis loops of PLAD PZT films for annealed at three different conditions.

the high temperature. These defects were trapped at the interfaces between the electrodes and the film, grain boundaries, or domain walls at room temperature. Then, they generated an internal bias field directed from the top to the bottom. The internal bias field led to the conspicuous voltage shift in the D-E hysteresis loop. At present state, it is unclear why the spontaneous polarization aligned downward.

Due to thin films' large surface to volume ratio, the electrode-film interfaces produce states of electrical degradation breakdown at relatively low electric fields, as a consequence of the increase with time of the leakage currents under a field stress. This contribution can be large enough to mask the ferroelectric charge, giving rise to the disappearance of the ferroelectric hysteresis loop. Among the major contributions to the leakage currents on ferroelectric thin films, the Schottky injection is the most reported. It is asymmetric (depending on the sign of the applied voltage) due to the different nature of the two film-electrode interfaces and it involves different electric charge quantities for both signs of the electric field, thus producing a vertical shift of the Sawyer-Tower hysteresis loops.

4. Conclusion

PZT($Pb(Zr_{0.52}Ti_{0.48})O_3$) films were fabricated by PLAD method and the effects of two-step annealing process on these films with different conditions were investigated. The perovskite phases can be detected for the specimens deposited at room temperature after annealing even at 600°C. The value of dielectric constant annealed at 650°C was measured as about 850 and the loss value was about 0.04. A conspicuous voltage shift can be observed in the D-E hysteresis loop toward a negative-bias field in polycrystalline PZT films fabricated by the PLAD method. It can be concluded that the voltage shift was caused by an internal bias field due to asymmetric space-charge distribution. In the PZT thin films, spontaneous polarization appeared with alignment downward naturally below the Curie temperature. The asymmetric space-charge distribution was induced by the aligned spontaneous polarization during the cooling process. However, it is still not clear why the spontaneous polarization aligned naturally.

Conclusively, annealing temperature for the PLAD PZT films can be lowered as much aso 200°C by the two-step annealing process compared with the traditional three-step annealing process.

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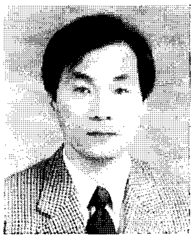

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