Effects of Deposition Temperature and Annealing Process on PZT Thin Films Prepared by Pulsed Laser Deposition

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The effects of substrate temperatures and annealing temperatures on the microstructures and ferroelectric properties of $PbZr_{0.52}Ti_{0.48}O_3$ (PZT) thin films prepared by pulsed laser deposition (PLD) were investigated. For this purpose, the PZT films were deposited at various substrate temperatures (400~600℃) with post annealing process in oxygen atmosphere. The single perovskite phase was formed at the deposition temperature of 500 to 550℃ without post annealing and the PZT films deposited below 500℃ formed the single phase with post annealing at 650℃. The grain size of the films increased and the grain boundary of the films was clearly defined as the substrate temperature increased from 400 to 550℃. The remnant polarization (Pr) and the coercive field (Ec) of the films deposited at 550℃ and annealed at 650℃ were 34.3 $\mu C/cm^2$ and 60.2 kV/cm, respectively.

Keywords : PZT thin films, Pulsed laser deposition, Post annealing, Remnant polarization

1. INTRODUCTION

Recently, ferroelectric thin films are utilized for microelectronic applications and lead zirconate titanate (PZT) thin film is one of the various promising materials for many applications such as ferroelectric random access memory (FRAM), dynamic random access memory (DRAM), high value capacitors, infrared devices, SAW delay lines, sensors, actuators, electro-optic displays, and ferroelectric field-effect transistors, etc. The PZT thin films have been fabricated by many method such as sol-gel process[1], metal organic chemical vapor deposition (MOCVD)[2], metal organic decomposition (MOD)[3], chemical vapor deposition (CVD)[4], evaporation[5], sputtering[6], pulsed laser deposition (PLD)[7-10] and others. Especially, PLD is considered as outstanding method to obtain high quality thin films.

Pulsed laser deposition (PLD) is one of the deposition method and considered as outstanding methods to obtain high quality thin films. The advantages of PLD are that good stoichiometric control is maintained easily and the energy source that creates the plume of ejected laser is independent from the deposition system. Thus complex multilayer films can be produced within a single system by moving various targets into and out of the beam focal point. And due to the high energy density, deposition rate is very fast and films can be crystallized into pure phase without post annealing. Parametric studies are still necessary to establish optimum process condition. In this paper, the effect of deposition temperatures on ferroelectric properties of the PZT films prepared by PLD method was investigated.

2. EXPERIMENTAL PROCEDURE

Ceramic target of $PbZr_{0.52}Ti_{0.48}O_3$ (PZT) composition was prepared by conventional solid state reaction method. Excess PbO of 10 wt% was added to compensate for lead and oxygen loss during deposition and post annealing process. The KrF excimer laser (Lambda Physik, wavelength 248 nm) was used to ablate the PZT target in the deposition chamber. The laser beam fluence and repetition frequency of the laser beam were 1.8 J/cm^2 and 5 Hz, respectively. The target was rotated and oscillating scanned to decrease surface roughness, nucleating second phases and misoriented grains[11] The distance from target to substrate was 4.0 cm. The chamber was initially pumped down to a base pressure of 5× 10^{-7} mTorr, and oxygen ambient gas pressures was fixed as 300mTorr. The PZT films were deposited at various temperatures in the range of 400 to 600℃ and then annealed at 650℃ in furnace under oxygen atmosphere.

Phase and crystalline state analyses of the PZT films were investigated by X-ray diffraction (XRD) with Cu K radiation, and the microstructure of the PZT films was observed using scanning electron microscopy (SEM, Hitachi, S-4200). Hysteresis loop (polarization vs. electric field) and fatigue curve (retained polarization vs. switching cycles.) were measured using RT 66A (Radiant Technologies, ver. 2.3) measuring system. A high voltage source unit on HP4155A was used to measure leakage current density.

3. RESULTS AND DISCUSSION

Figure 1 shows the XRD patterns of the PZT films deposited on the substrates heated from 400 to 600℃. The orientations of PZT films were indexed as (100), (110), (111), (200) and (211). As the deposition temperature increased, the relative intensities of the (100), (110) increased, and (111) increased to 550℃ and then decreased. The PZT films deposited below 450℃ had pyrochlore phases without perovskite phase. In case of as-deposited film at 400℃, Pb oxides-related peak observed at 2θ of 29.36. Peaks at 33.96, 48.96, and 58.12 correspond to $PbTi_3O_7$ (Ti-rich phase). C. V. R. Vasant Kumar et al. reported that $PbTi_3O_7$ is easily formed even when Pb/Ti ratio is greater than 1[12]. As increasing the deposition temperature Pb oxides-related peak and $PbTi_3O_7$ peaks vanished. When the PZT films were deposited over 500℃, formation of the perovskite single phase was observed, and crystallinity was improved at the deposition temperature of 550℃. The PZT film deposited at 600℃ had a Pb oxides-related peak again.

Figure 2 shows XRD patterns of the PZT thin films deposited at different temperatures with post annealing at 650℃. The PZT films deposited at 400 and 450℃ were annealed to crystallize into perovskite. To compare with deposition temperature, the PZT film deposited at 550℃ were annealed. With the post annealing process, the PZT thin films deposited below 450℃ also crystallized into pure perovskite. As the deposition temperature increased, the relative intensity of the (110) and (111) were increased.

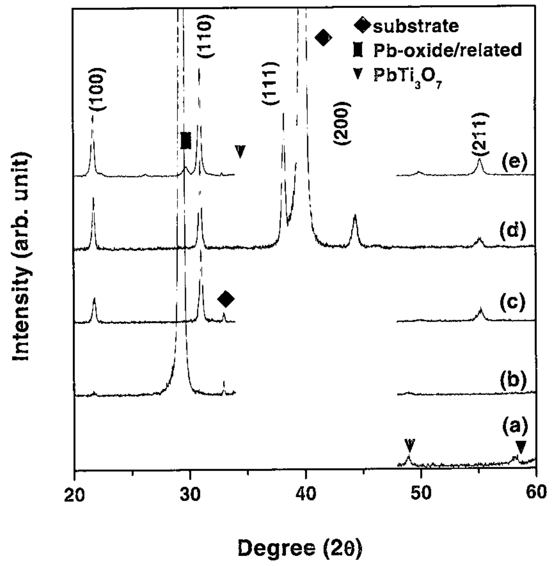


Fig. 1. XRD patterns of PZT films deposited at various temperatures; (a) 400, (b) 450, (c) 500, (d) 550, (e) 600℃.

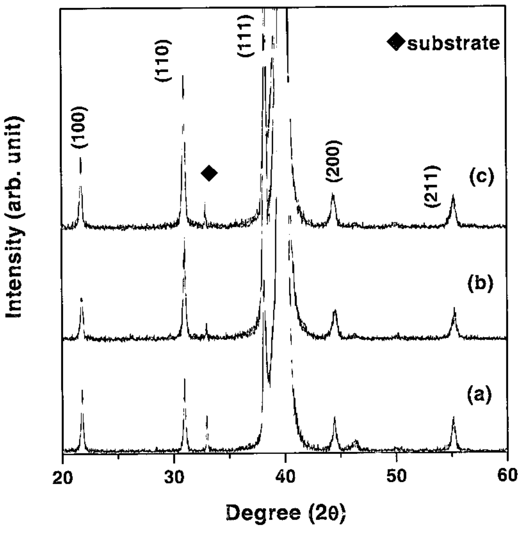
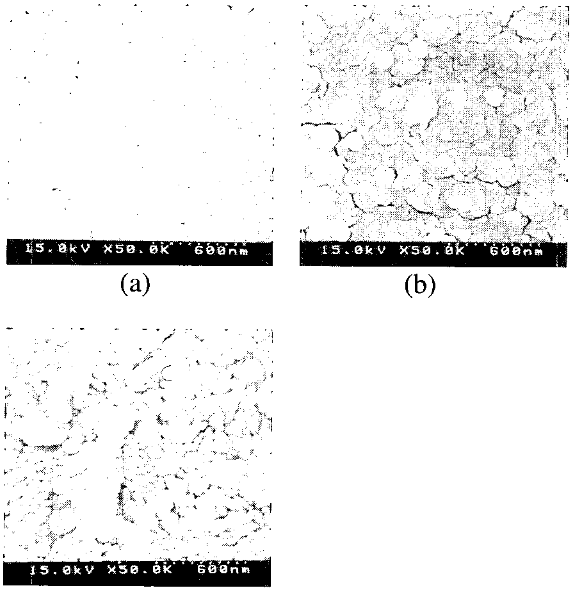


Fig. 2. XRD patterns of the PZT thin films at various temperatures with post annealing; (a) 400, (b) 450, (c) 550℃.

Figure 3 shows surface microstructure morphology of the films deposited at 400, 450, and 550℃ with post annealing process at 650℃. With an increase of deposition temperature, grain size was increased. The PZT film deposited at 400℃ showed very small grain of 50 nm and the film deposited at 450℃ showed micro-cracks because of shrinkage during annealing process.



(a) (b) (c)

Fig. 3. SEM photographs of the PZT films deposited at various temperatures, with post annealing; (a) 400, (b) 450, (c) 550℃.

However, the film deposited at 550℃ showed grain growth and clearly defined grain boundary

Figure 4 shows hysteresis loops of the PZT films deposited at 550℃ and annealed at various temperatures. A typical behavior of ferroelectric properties was obtained at 250 KV/cm. There was a tendency to change ferroelectric properties with an increase of the limited post annealing temperature. Remnant polarization (Pr) increased from 27.6 to 34.3 μ C/cm^2 with increasing post annealing temperature from 600 to 650℃ and then reduced from 34.3 to 25.1 μ C/cm^2 with increasing from 650 to 750℃.

Figure 5 shows the Hysteresis loops of a Pt/PZT/Pt (111) capacitors deposited at different temperatures with post annealing at 650℃. As shown in Fig. 2 and Fig. 3 the PZT film deposited at 400℃ and post annealed at 650℃ had small relative intensities of the (100) and (110), and small grains. Therefore these films had small Pr of 12 μ C/cm^2. The PZT film deposited at 450℃ had Pr of 28.0 μ C/cm^2 but some areas were shut because of shrinkage shown in Fig. 3. The PZT films deposited at 550℃ and post annealed at 650℃ had Pr of 34.3 μ C/cm^2 and Ec of 60.2 KV/cm.

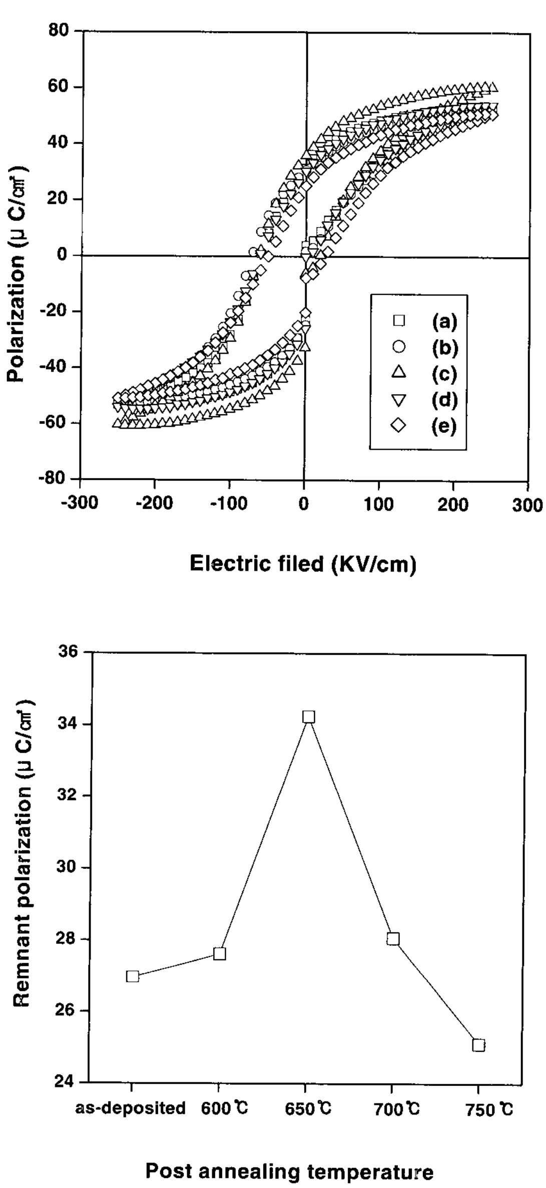


Fig. 4. Hysteresis loops and remnant polarization values of Pt/PZT/Pt(111) capacitors deposited at 550℃; (a) as-deposited and after annealing at (b) 600, (c) 650, (d) 700, (e) 750℃.

4. CONCLUSION

According to the variation of substrate temperatures with annealing process, crystallization and ferroelectric properties of $PbZr_{0.52}Ti_{0.48}O_3$ (PZT) thin films deposited by pulsed laser deposition were investigated. The single perovskite phase was formed at the deposition temperature of 500 to 550℃. With post annealing process at 650℃, the PZT thin films deposited at 300mTorr and 550℃ showed an optimum process condition. It was crystallized into perovskite single phase with uniform morphology, and had the remnant polarization and coercive field of 34.3 μ C/cm^2 and 60.2 KV/cm, respectively.

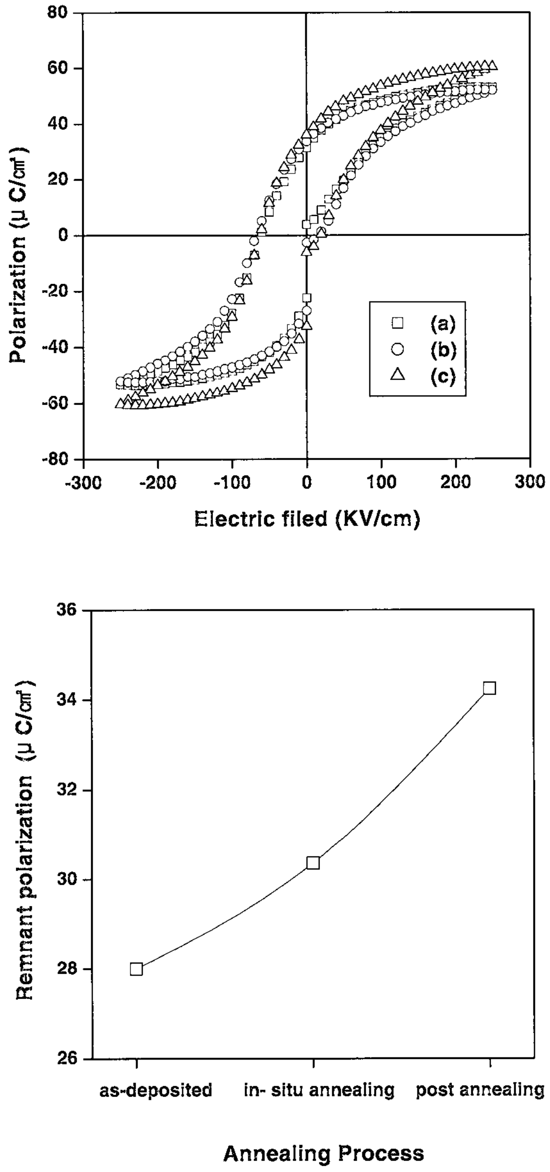


Fig. 5. Hysteresis loops and remnant polarization values of Pt/PZT/Pt(111) capacitors deposited at 550℃; (a) as deposited, after (b) in-situ annealing, and (c) post annealing at 650℃.

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