

Deposition of PbTiO₃ thin films by reactive sputtering

Y. S. Ahn,¹⁾ D. S. Lee, E. J. Ahn, and E. Yoon

School of Materials Science and Engineering, Seoul National University, Seoul 151-742, Korea

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Abstract – PbTiO₃ is a promising material with perovskite structure for pyroelectric sensor applications with its superior pyroelectric properties, low dielectric constants, and low piezoelectric constants. Growth of pyroelectric thin films, in general, needs relatively higher temperatures than those of conventional Si semiconductor processing. However, low growth temperature is advantageous for the device integration. We report the low temperature (350°C) growth of PbTiO₃ thin films by 3-gun DC magnetron reactive sputtering. The effects of substrate temperature, Pb-flux, and total pressure on crystallinity and preferred orientation of PbTiO₃ thin films are reported.

I. Introduction

Lead zirconate titanate, Pb(Zr,Ti)O₃ (PZT), and PZT-based solid solutions such as (Pb,La) (Zr,Ti)O₃ (La-doped PZT, PLZT) and (Pb,Nb) (Zr,Ti)O₃ (Nb-doped PZT, PNZT) have been widely investigated for the nonvolatile ferroelectric memory applications. Moreover, these ferroelectric materials can be used for piezoelectric or pyroelectric device applications. Among various ferroelectric materials, PbTiO₃ is one of the promising materials for pyroelectric sensor applications due to its superior pyroelectric properties, low dielectric constants, and relatively low piezoelectric constants [1-2], and the simple composition [3].

Many growth techniques have been used for ferroelectric thin film deposition such as sol-gel deposition, sputter deposition, laser ablation, chemical vapor deposition, multi-magnetron sputter deposition, ion-beam-sputter deposition, and ultrasonic spraying pyrolysis, etc [4-5]. In particular, multi-target magnetron sputter deposition has advantages of easy compositional control of thin films and high growth rate [6].

Pb-based ferroelectric thin films such as PbTiO₃ and PZT, in general, are grown at relatively high temperatures to form perovskite crystalline phases [7]. However, pyrochlore phases or other secondary phases are often formed at high growth tempera-

tures due to the volatility of lead, deteriorating the properties of thin films. Iijima *et al.* reported that the PbTi₃O₇ phase coexisted with the perovskite phase at temperatures higher than 600°C due to volatilization of lead [3, 5]. At temperatures lower than 400°C, however, no perovskite phase was observed [7].

In many applications such as logic devices with ferroelectric nonvolatile memories, it is advantageous to have lower growth temperatures from the point of device integration. In this paper, we report the growth of perovskite PbTiO₃ thin films at 350°C by 3-gun DC magnetron reactive sputter system. The effects of process parameters on properties of PbTiO₃ thin films are reported.

II. Experiment

PbTiO₃ thin films were grown by a 3-gun DC magnetron sputter system as shown in Fig. 1. Metal targets were used in this experiment and high-purity oxygen gas was introduced to form oxide films. The substrate structure was Pt (1500 Å)/SiO₂(3000 Å)/Si and the Pt films were (111)-textured. Substrates were rotated at 10 rpm during deposition to obtain uniformity in thickness and composition of the oxide films. Substrate temperatures were varied from 300 to 450 to investigate the effect of substrate temperature on the formation of PbTiO₃ thin films. The pressure during sputtering was varied from 5 to 15 mTorr. The gas ratio of oxygen to

¹⁾Present address: Samsung Electronic Co.

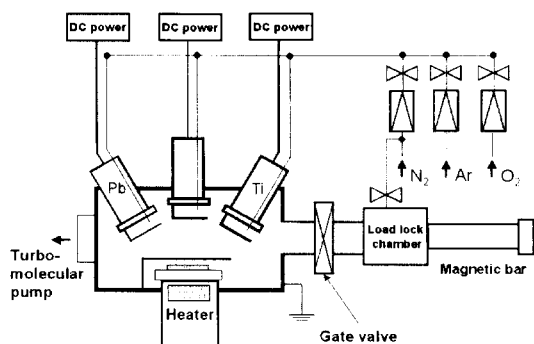


Fig. 1. Schematic diagram of the 3-gun DC magnetron reactive sputtering system.

argon was fixed at one. The power applied to Ti metal target was kept constant at 650 W, whereas that applied to Pb metal target varied from 40 to 80 W to study the changes in composition and phase formation of the films.

The crystallinity of the films were analyzed by X-ray diffraction (XRD) with Cu K α (1.5405 Å) line. The compositions of the films were measured by electron probe micro-analysis (EPMA). The film microstructure was observed by field emission scanning electron microscopy (FESEM). The film thicknesses were measured with a stylus method.

III. Results and discussion.

Composition of the PbTiO₃ thin films changed with increasing substrate temperature due to the volatilization of Pb. Microstructures and film properties were also affected with increasing substrate temperature even in stoichiometric PbTiO₃ thin films. Figure 2 shows the changes in Pb/Ti ratio as the substrate temperature varied from 300 to 450°C. The pressure during sputtering was maintained at 10 mTorr. The power applied to Pb target was fixed at 40 W. High volatility of Pb caused the Pb/Ti ratio of the film to decrease rapidly from 1.07 to zero as the substrate temperature increased. Figure 3 shows the XRD patterns of the deposited films at substrate temperatures of 300, 350 and 400°C. Note that the XRD intensity scale is logarithmic. At 300°C, PbTiO₃ (111) peak, very close to (111) Pt from bottom electrodes, were very strong, however, other peaks were also observed. When the substrate temperature increased from 300 to 350°C, these peaks

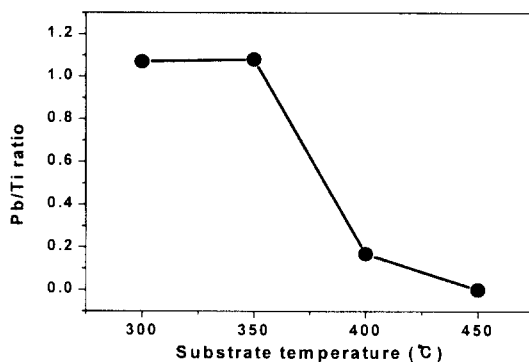


Fig. 2. Pb/Ti composition ratio of the deposited films at various substrate temperatures.

disappeared and the intensity of the PbTiO₃ (111) peak increased further. It is speculated that the enhanced surface adatom mobility at the higher temperature might facilitate the lattice matching of PbTiO₃ films with the (111) Pt bottom electrode. On the other hand, PbTi₃O₇ phase was observed at 400°C, presumably by volatilization of Pb at this temperature. These results were in good agreement with the EPMA data shown in Fig. 2.

It was found that changes in substrate temperature also affected the morphology of the films. Figure 4 shows the FESEM images of the films deposited at temperatures ranging from 300 to 400°C. As the substrate temperature increased from 300 to 400°C, the average grain size increased from 110 to 320 nm. Furthermore, the shape of the grains changed significantly. At 350°C the grain shape was somewhat triangular, similar to the equilibrium shape of PbTiO₃

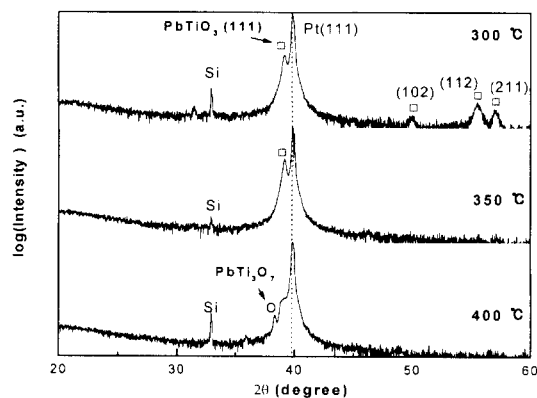


Fig. 3. XRD patterns of the PbTiO₃ films grown on Pt(111)/SiO₂/Si substrates at various substrate temperatures (□ = Perovskite, ○ = PbTi₃O₇).

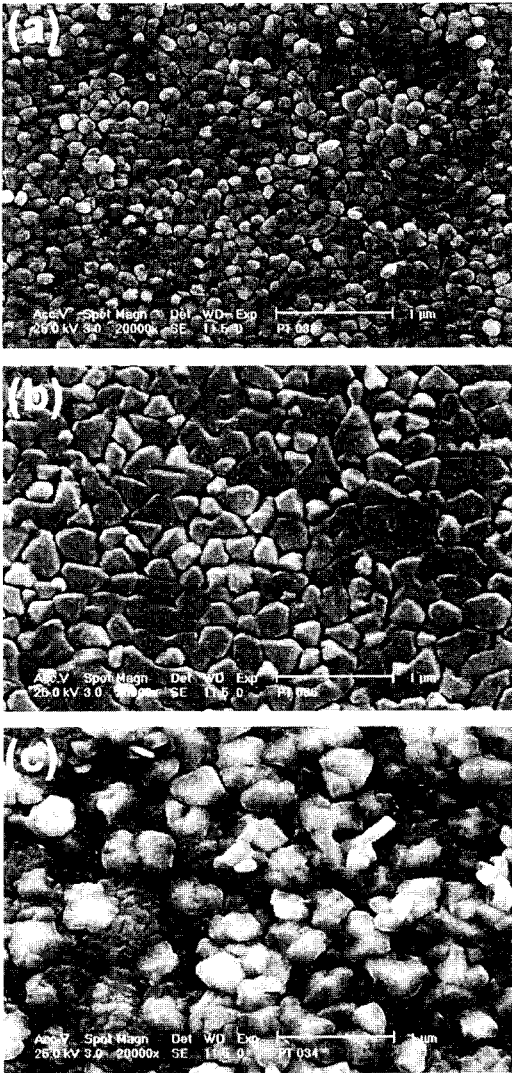


Fig. 4. FESEM images of the PbTiO₃ films grown on Pt(111)/SiO₂/Si substrates deposited at (a) 300°C, (b) 350°C, and (c) 400°C.

grown on {111} planes due to the enhanced growth of the PbTiO₃ {111} planes on lattice-matched Pt (111) plane of the bottom electrode. At 400°C, however, Pb became volatile to form the second phase, resulting in a rough surface and wide dispersion in grain size as shown in Fig. 4(c).

The composition of PbTiO₃ films could be controlled by varying the relative Pb and Ti fluxes in the multi-target sputtering method. It was reported that the Pb/Ti ratio in the PbTiO₃ film could be maintained at a fairly constant level when the Pb/Ti flux

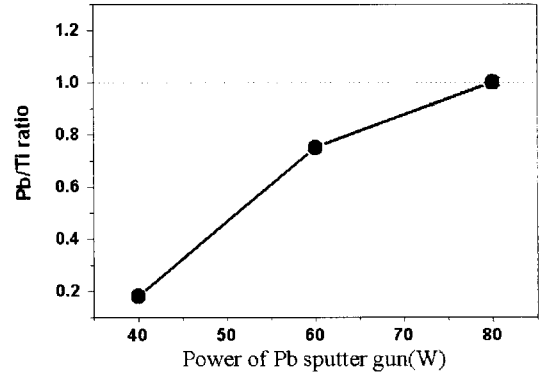


Fig. 5. FESEM images of the PbTiO₃ films grown on Pt(111)/SiO₂/Si substrates deposited at (a) 300°C, (b) 350°C, and (c) 400°C.

ratio exceeded a threshold value, however, the preferred orientations of PbTiO₃ thin films could be changed even though the composition of the films remained almost constant [8]. At 400°C, the power applied to Ti target was fixed at 650 W, and the power applied to Pb target was varied to investigate the effect of Pb flux on the composition and the crystallinity of the films. At this temperature, Pb content in the deposited films was lower than the stoichiometric composition of 1 due to volatilization of Pb at the high temperature. Figure 5 shows Pb/Ti ratio change in the films with power applied to the Pb target. When the power applied to Pb target changed from 60 to 80 W, the Pb/Ti ratios changed from 43/57 at 60 W to 51/49 at 80 W. Note that the Pb/Ti ratio was much lower than the stoichiometric value when the power was less than 60 W. In this case, the stoichiometric PbTiO₃ thin films could be formed at 400°C by increasing the Pb flux to compensate the loss of Pb from the films.

Changes in Pb sputter power changed the film crystallinity and the preferred orientation of the films deposited at 400°C as shown in Fig. 6. By increasing the power from 40 to 80 W, it was possible to suppress the PbTi₃O₇ phase formation and to obtain the film with a single perovskite PbTiO₃ phase. When the power was 60 W, only PbTiO₃ (111) peak was observed. However, when the power was increased to 80 W, other peaks such as PbTiO₃ (101) and (200) peaks were also appeared. In this experiment, we could not observe the changes in orientation and microstructure of the PbTiO₃ films

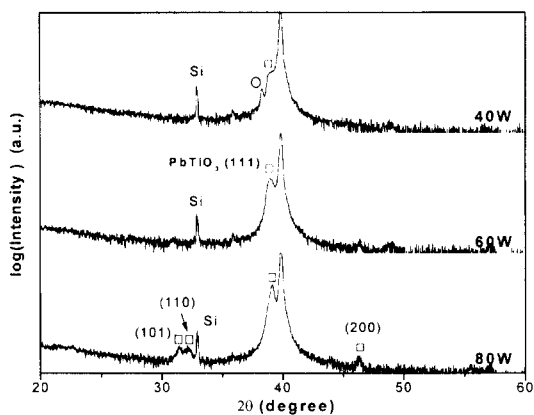


Fig. 6. XRD patterns of the PbTiO₃ films grown on Pt(111)/SiO₂/Si substrates at various substrate temperatures (□ = Perovskite, ○ = PbTi₃O₇).

with varying thickness. Thus, it was believed that the nucleation and growth of PbTiO₃ thin films at the initial stage of deposition determined the orientation and microstructure of the films.

The total pressure during sputtering was also varied to study its effect on the formation of PbTiO₃ thin films. Energy of incoming particles is one of the important process parameters, affecting the film formation mechanism at the initial stage as well as at the later stage. Since the sputtering is a deposition process involving energetic particles, the energy of incoming particles might be affected by gas-phase collision before they arrive at the growth surface and might affect the film formation on the surface. Particles with proper energy might increase the surface mobility of adatoms on substrate, leading to the improved crystallinity of the films, whereas particles of excess energy might generate defects in the films, deteriorating the film crystallinity. The power applied to Pb and Ti targets were fixed at 40 W and 650 W, and the process pressure was varied from 5 to 15 mTorr at 350°C. Intensity of the PbTiO₃ (111) peak was higher at 15 mTorr, as shown in Fig. 7. It is speculated that the crystallinity of the film was improved since less damage was generated, however, more research is needed to understand the details of crystallinity improvement with pressure.

IV. Conclusions

In this report, ferroelectric PbTiO₃ thin films

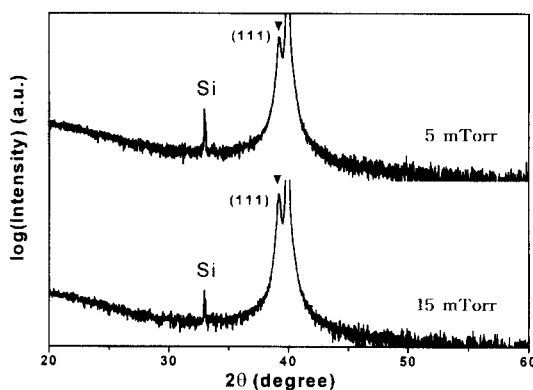


Fig. 7. XRD patterns of the PbTiO₃ films grown on Pt(111)/SiO₂/Si substrates at various total pressures.

could be deposited using 3-gun DC magnetron reactive sputter system at a low substrate temperature of 350°C. At this temperature, stoichiometric perovskite PbTiO₃ thin films could be formed. At temperatures higher than 400°C, non-perovskite phase formation was observed due to volatilization of Pb. However, it was possible to form stoichiometric perovskite PbTiO₃ films by increasing power applied to the Pb target. In addition, the changes in preferred orientation was observed with increasing Pb flux.

Acknowledgment

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