# PREPARATION OF $Pb(Zr,Ti)O_3$ THIN FILMS SPUTTERED FROM A MULTI-ELEMENT METALLIC TARGET

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**Abstract:** PZT thin films have been grown on $Pt/Ti/SiO_2/Si$ substrates by the reactive RF-magnetron sputtering deposition method using a multi-element metallic target. The $ABO_3$ perovskite structure in the thin films sputtered at a substrate temperature of 250 $^0C$ was formed through various intermediate phases by annealing at 650 $^0C$ for 1 hour in the air or an oxygen gas ambience. The film compositions were estimated by Electron Probe Micro-Analyzer (EPMA). The surface morphology observed by Atomic Force Microscopy (AFM) showed a densely packed grain structure with no rosettes structure. The remanent polarization value of the thin film with a thickness of 500 nm was 1.37 $\mu C/cm^2$.

## 1. Introduction

Over the last 20 years, thin films of lead zirconate titanate, $Pb(Zr,Ti)O_3$ (PZT), have been attracted much attention due to their applications in nonvolatile memory and MicroElectroMechanic Systems (MEMS) devices[1,2]. Most of works have been concentrated on the compositions of the Morphotropic Phase Boundary (MPB) at around Zr/Ti=50/50 compositional ratio, at which the piezoelectric and ferroelectric properties show their maximum values. Various technical solutions proposed for obtaining the thin films of PZT such as sol-gel method, pulsed laser ablation, sputter deposition, and ion beam sputtering have been employed. Among them, the sputtering method has been most widely used for obtaining high quality PZT films because of its relatively simple fabrication process.

One of the most important factors in the preparation of PZT thin films is the control of the correct perovskite phase formation in order to obtain the desired electrical properties. Mostly, in the as-deposited films there have been no perovskite phase. So post-deposition annealing treatments at high temperatures, typically in the range 600-700 $^0C$ for 1 hour or more, are necessary to crystallize the film into perovskite structure.

In this study, PZT thin films were fabricated by the reactive RF-magnetron sputtering method. The perovskite phase crystallization of PZT films was investigated in term of the effects of annealing time and heat treatment ambience by X-Ray Diffraction (XRD). The surface morphology and electrical properties of the films were also reported.

## 2. Experimental procedure

An Alcatel SCM-400 13.56MHz RF-magnetron sputtering system was used to deposit the PZT thin films on $Pt/Ti/SiO_2/Si$ multiplayer substrates. During sputtering process, the substrates, as bottom electrodes, were heated at 250 $^0C$. The sputtering target was multi-element metallic, the design of which is shown in Fig. 1. This was composed of individual sectors of Pb, Zr, and Ti metals with Pb/Zr/Ti:2/7.5/8.5 compositional ratio. Prior to the deposition, the sputtering chamber was pumped down to a base pressure of $10^{-6}$ mbar. Subsequently, gas mixture of Ar and $O_2$ with $Ar/O_2$:60/40 ratio was introduced to a pressure of $2x10^{-2}$ mbar. An RF-power was fixed at 200 W. The selected sputtering conditions for the deposition of bottom electrodes and PZT thin films are summarized in Table 1.

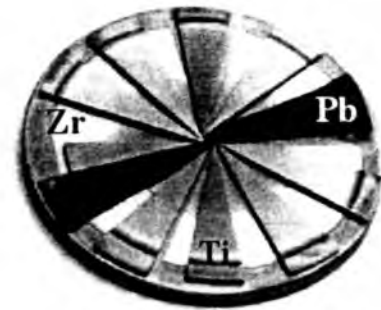


*Fig. 1.* The multi-element PZT metal target (after sputtering)

**Table 1.** The conditions for preparation of bottom electrodes and the PZT(51/49) thin films.

| | *Bottom electrodes* | *PZT thin films* |
|---|---|---|
| RF- power | 200 W | |
| Base pressure | ~$10^{-6}$ mbar | |
| Substrate | $SiO_2/Si$ | $Pt/Ti/SiO_2/Si$ |
| Target | Ti<br>Pt | Pb/Zr/Ti |
| Working pressure | $3x10^{-3}$ mbar | $1x10^{-2}$ mbar |
| Ambience gas | Ar | $O_2/Ar$:40/60 |
| Substrate temperature | $T_{Room}$ | 250 $^0C$ |
| Deposition time | Ti: 5 min.<br>Pt: 30 min. | 4 hours |
| Film thickness | Ti: 20 nm.<br>Pt: 100 nm | 500 nm |

The PZT film thickness was determined about 500 nm by the grazing incident X-Ray Reflection (XRR), as illustrated in Fig. 2. The Zr/Ti:51/49 compositional ratio of the PZT films was analyzed using Electron Probe Micro-Analyzer (EPMA). In order to crystallize perovskite phase, the as-deposited films were annealed using

conventional furnace at 650$^0$C fixed temperature in the air and an oxygen ambience for 30, 60, 90, 120 min., respectively. Phase and crystalline behavior analyses of PZT films were performed using X-Ray Diffractometer with the CuK$_\alpha$ source ($\lambda$=1.5405 Å). Surface morphology and grain size were investigated using Atomic Force Microscopy (AFM). The ferroelectric property of PZT thin films were also measured using RT66A standardized hysteresis tester (Radiant Technology).

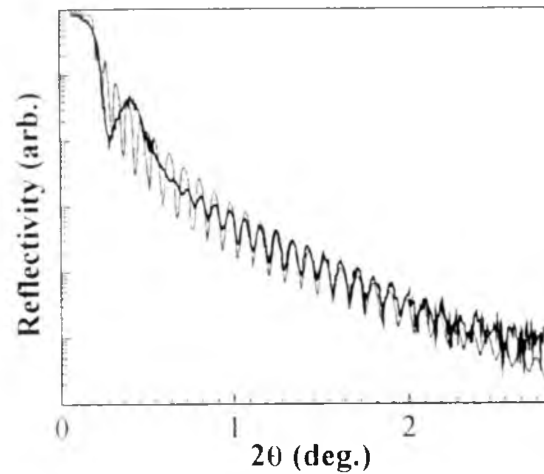


*Fig. 2.* The XRR pattern of the PZT thin film annealed at 650$^0$C for 60 min

## 3. Results and discussion

### *Crystallographic structure*

The crystal structure of the as-deposited and annealed PZT thin films was examined by XRD patterns in comparison with crystallographic information reported earlier on PZT films and ceramics. This part may shed light on the optimum annealing time and ambience required for the perovskite PZT formation. The XRD patterns of the films annealed for the various times in the air are given in Fig. 3.

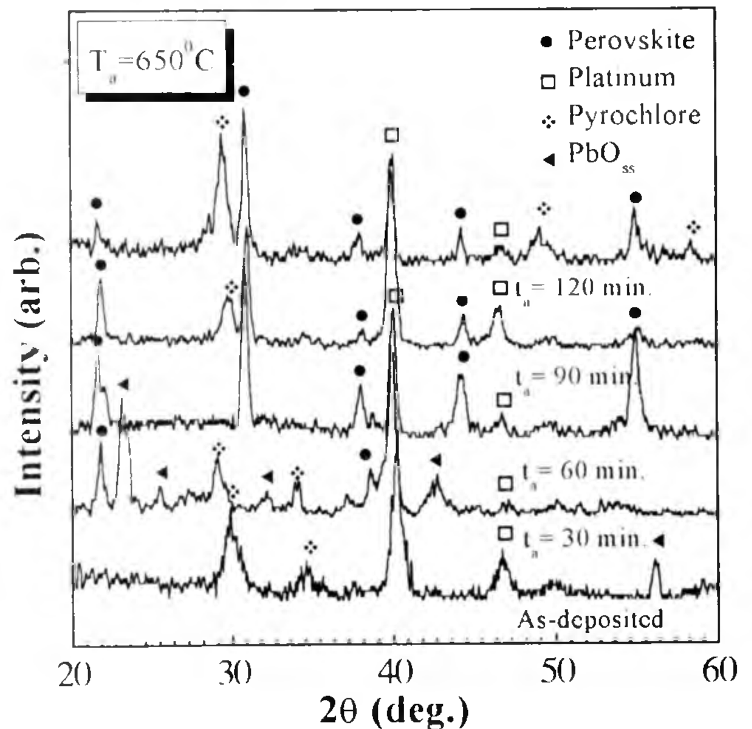


*Fig. 3.* The XRD pattern of PZT thin films annealed for various annealing times

It can be seen from the figure that all of films always show two peaks at $2\theta$=40$^0$ and 46.55$^0$ corresponding to the Pt polycrystalline phase.

In case of the as-deposited film, there are two peaks at 29.6$^0$ and 34.15$^0$ depicting non-ferroelectric pyrochlore, $Pb_2Ti_2O_6$ cubic oxygen deficiency phase at low temperature. A peak at 56.24$^0$ is identified $\alpha$-$PbO_2$ structure. Mean while it is possible that $ZrO_2$, $TiO_2$ are presented in an amorphous form because whole Pb, Zr, Ti were oxidized in sputtering process simultaneously.

When the film was annealed for 30 min., $\alpha$-$PbO_2$ transferred to the lead-rich phases $PbO_{ss}$ that are observed at $2\theta$ of $23.2^0$, $25.45^0$, $32.1^0$, and $42.4^0$. Their relative high intensity may show the excess contents of Pb and $O_2$ in the thin film[3]. The peaks at $29.05^0$ and $33.94^0$ match with the pyrochlore monoclinic $AB_3O_7$ phase, which is normally caused by a deficiency in lead due to an evaporation at high temperature. In this work, the pyrochlore phase appears even when lead-rich $PbO_{ss}$ compound presented in accordance with [4]. It has revealed that the formation of $AB_3O_7$-type was favored over $ABO_3$-type even when the Pb/Ti ratio was greater than one and $AB_3O_7$ phase seemed to be an intermediate phase before the PZT films crystallized into the $ABO_3$ perovskite phase. The peaks at $21.75^0$ and $38.55^0$ perform the perovskite struture. It is confirmed that the PZT films deposited at the substrate temperature $250^0C$ can be converted into the perovskite crystalline structure at the annealing temperature 650 $^0C$ with a sufficient annealing time.

Increasing the annealing time to 60 min., complete perovskite crystallization occurs. Besides the former peaks, the others at $30.77^0$, $44.15^0$, and $54.85^0$ according to the perovskite phase appears. The ratio of intensity between the peaks show that the structure of the PZT thin film is polycrystalline (like PZT ceramic)[5]. However, the (110) intensity peak at $30.77^0$ is largely superior to the others, thus it is considered that the thin films has a preferred-(110) orientation.

The trend suggests that these films may be converted into the single perovskite phase by increasing the annealing time or annealing temperature. Nevertheless, the annealed films for more than 60 min. are diphase with pyrochlore and perovskite coexistence. The pyrochlore peaks reappear that proves Pb loss. The deficiency of Pb is understandable by considering its high volatility for a long annealing time at a high temperature. After the annealing time reaching 120 min., the non-ferroelectric pyrochlore phase is predominating with strong and sharp peaks.

To investigate the effect of annealing ambiences, the PZT thin films were annealed for 60 min. at 650 $^0C$ in the air, an oxygen and an argon gas ambience and the results are depicted in Fig. 4. As above discussion, the thin film, which was heated in the air, has the polycrystalline perovskite structure with predominated (110) orientation. The film annealed in the oxygen ambience has still the correct perovskite structure but (100) orientation is preferred. It may be caused by the influence of oxygen content on PZT orientations. It has been reported that the oxygen partial pressure is an important factor in determining the Pb valence state in the PZT films, which dictates the kinetics of the pyrochlore-perovskite phase transformation[6]. A low Pb valency state enhances the kinetics of transformation, whereas a high Pb valence state suppresses the kinetics of transformation leading to incomplete transformation of the pyrochlore to perovskite phase. The growth of PZT(100) on $Pt/Ti/SiO_2/Si$ wafers attributed to the formation of crystalline PbO(001)

during prolysis. PbO has good lattice matching with PZT(100) orientation; this lowers the interfacia energy and promotes the nucleation of PZT(100). On the contrary, for the PZT film annealed in the argon ambience the pyrochlore phase dominates completely.

Although PZT films were annealed for different times in various ambiences, the (110) or (100) orientation is mainly observed. These results imply that PZT essentially has natural preference to grow in (110) or (100) directions at temperatures less than 700 $^0$C[7].

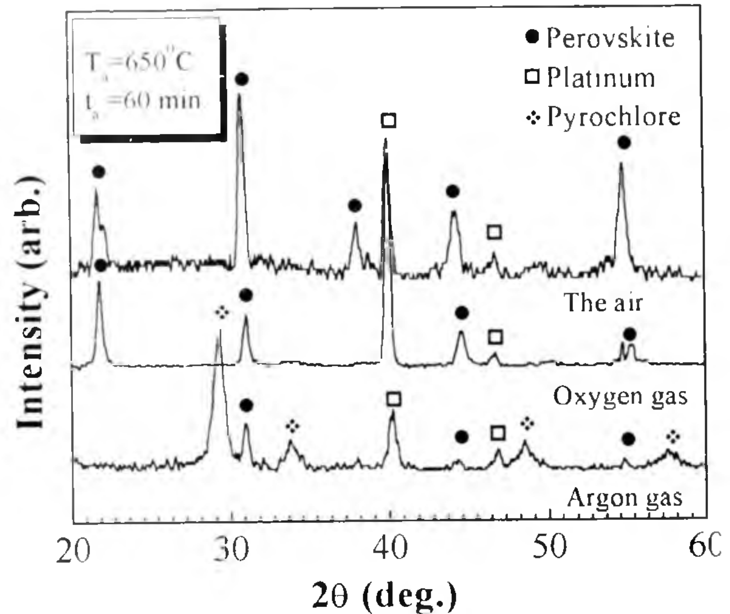


*Fig. 4.* The XRD pattern of PZT thin films annealed in various annealing ambiences.

On the basic of this information, the crystallization of sputterd PZT thin films was stucied. The as-deposited film shows peaks due to $\alpha$-$PbO_2$ and $A_2B_2O_{7-x}$ crystalline while $ZrO_2$ and $TiO_2$ are amorphous. After annealing, lead-rich $PbO_{ss}$ and lead-deficient $AB_3O_7$ phases were found as the intermediate phases and they reacted each other to form the perovskite structure during post-deposition heat treatments. In order to obtain the correct perovskite crystal structure the PZT thin films need to be annealed for 60 min. at 650 $^0$C in the air or the oxygen ambience.

### *Surface morphology and grain size*

The surface morphological investigation on the sputtered PZT thin film annealed at 650 $^0$C for 60 min. in the air was shown in Fig. 5. The film has a relative smooth surface with no microcrack, a dense structure, and fine grain distributing homogeneous. Agreeing well with AFM result, the average grain size is also estimated to be 50 nm by using Sherrer's equation with the half-width of the (110) diffractive peak observed at $2\theta$=30.77$^0$ in the XRD pattern in Fig. 4.

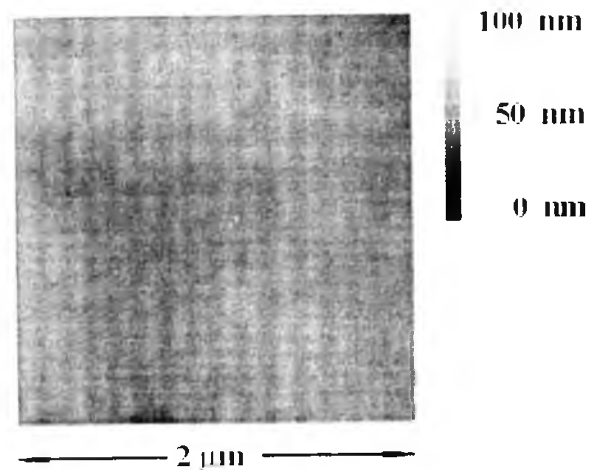


*Fig. 5.* The AFM micrograph of PZT thin film annealed at 650$^0$C for 60 min. in the air

***Ferroelectric property***

Ferroelectric behavior of the PZT film annealed at 650 $^0$C for 60 min. in the air was studied by a plotting P-E hysteresis loop and is shown in Fig. 6.

The remenant polarization $P_r$ of the PZT film is about 1.37 μC/cm$^2$. The film exhibits the characteristic "elliptic" shaped ferroelectric response of a hard ferroelectric. This shape is common for film referred to as "lossy" or "leaky", which is not good insulator. The loop has shifted toward the negative side. This asymmetry also observed by many workers was attributed to the difference in interfacial states between top electrode/PZT interface and PZT/bottom electrode interface[8] due to the electrodes were prepared in completely different conditions.

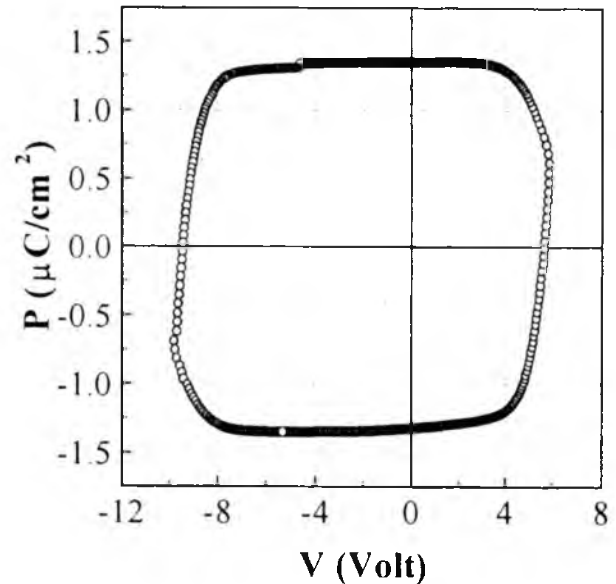


*Fig. 6.* The P-E pattern of the PZT thin film at 650 $^0$C for 60 min. in the air

## 4. Conclusions

PZT thin films were prepared on platinized silicon substrates by RF-magnetron sputtering method using a multi-element metallic target. Lead-rich $PbO_{88}$ and lead-deficient $AB_3O_7$ phases were discussed as immediate phases in the $ABO_3$ correct perovskite crystallization. The complete perovskite structure could be obtained at the optimized condition being at 650 $^0$C annealed temperature for 60 min. in the air or the oxygen ambience.

## References

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