FABRICATION AND EVALUATIONS OF PZT THIN FILMS BY RF REACTIVE SPUTTERING USING SOLID OXYGEN-SOURCE

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Abstract: PZT films were prepared on $Pt/Ti/SiO_2/Si$ substrate by RF reactive sputtering apparatus using metal-oxide composite $ZrTi+PbO_2$ powder and pellet targets. The main sputtering conditions are as follows: sputtering gas is argon and oxygen, gas pressure is $1*10^{-2}$Torr, O_2/Ar flow rate is 0% and 4.2%, substrate temperature is 200 (unintentionally heated), 450 and 550°C. PbO_2 target occupation is 30%. It is confirmed that PbO_2 pellet target has the potential to be the oxygen-source during the deposition with a high deposition rate. Perovskite PZT peak was observed in XRD measurement for film grown with PbO_2 pellet target without introducing any oxygen gas and with a small target occupation during deposition.

Keywords : PZT, RF Reactive Sputtering, Solid oxygen-source, Deposition rate, Pellet target

INTRODUCTION

PZT ($Pb(Zr,Ti)O_3$) or Lead Zirconate Titanate is a promising ferroelectric material for memory devices [7] such as Ferroelectric Random Access Memory (FeRAM) [2], Dynamic Random Access Memory (DRAM), piezoelectric and pyroelectric devices. Various deposition techniques have been developed, such as sputtering [4], Metal Organic Chemical Vapor Deposition (MOCVD) [6], Sol-Gel and laser ablation [9]. Low temperature preparation for compatibility with VLSI process, higher deposition rate and stability on mass production, benefits for environment and cost performances are demanded.

Among those techniques mentioned above, RF sputtering has been widely used because of the relatively simple fabrication process and it is compatible with various device processing steps. It is well known that in reactive sputtering, there is a nonlinear relationship between the deposition rate and the reactive gas flow rate ratio as shown in Figure 1. The range of reactive gas flow rate in which the target is not completely oxidized (A-B) is called the metallic mode and the range which the target is completely oxidized (D-C) is called oxide mode which deposits metallic and oxide films respectively. We have been developing an RF reactive sputtering technique using a new target system, where oxide films were deposited in metallic mode using a metal-oxide composite target (ZrTi + PbO) [5], which we called the quasi-metallic mode [1].

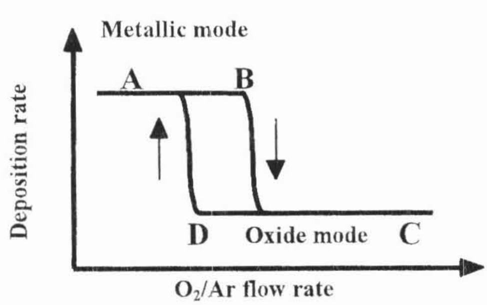


Figure 1: Reactive Sputtering Hysterisis Loop

The specialties of the quasi-metallic mode are that the PZT thin films can be deposited in a very small oxygen flow rate that lead to high deposition rate [3] . Furthermore we have revealed that the PbO pellets act as the oxygen-source in this mode [8]. We have discovered that PbO_2, which contains more oxygen than PbO, also can be an effective oxygen-source. It is confirmed that PbO_2 powder target supplies more oxygen than that of PbO powder target during deposition [5]. However, the deposition rate using powder target is low. Since we managed to fabricate PZT thin films with high deposition rate using ZrTi + PbO pellet target, ZrTi + PbO_2 pellet target are expected to produce the same result. This paper focuses on the differences of PbO_2 powder target and pellet targets concerning the deposition rate, oxygen gas ratio during the process and composition of the deposited films.

MATERIALS AND METHODS

A non-magnetron RF sputtering apparatus was used in the experiment. The target is as shown in Figure 2. Z is a 100mm in diameter and 5 mm in thickness zirconium-titanium composite metal (ZrTi alloy) plate which was mechanically clamped to a water-cooled copper electrodes. For PbO_2 powder target, P are PbO_2 powder placed in $\Phi 13 \times 2$mm holes made on the ZrTi alloy, whereas for PbO_2 pellet target, P are$\Phi 13 \times 2$mm pellets placed on top of the ZrTi alloy. The target composition is defined as ZrTi + xPbO in which x is defined as area ratio of target surfaces $S_{PbO2}/(S_{PbO2} + S_{ZrTi})$, where S_{PbO2} is the total surface area of PbO_2 powder or pellet targets and S_{ZrTi} is the uncovered surface area of ZrTi alloy target.

Table 1: Sputtering conditions

Substrate	Pt/Ti/SiO_2/Si
Target	ZrTi + 30%PbO_2 powder & pellet
Power	200W
Sputtering pressure	10mTorr
Substrate temperature	200 to 550° C
Sputtering medium	Ar and O_2
O_2/Ar flow rate	0.0 to 4.2%

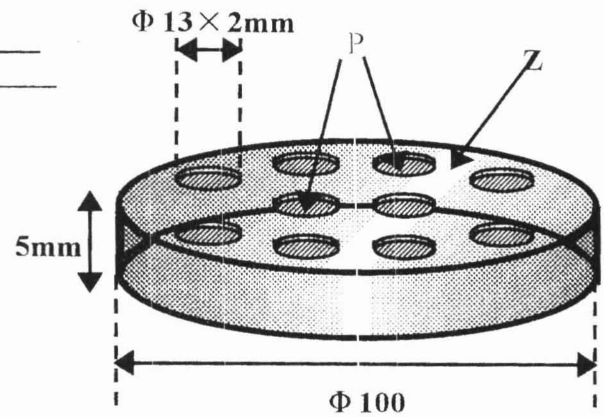


Figure 2: Schematic diagram of the metal-composite target

Typical sputtering conditions are tabulated in Table 1. The sputtering chamber was evacuated to a background pressure less than 4×10^{-6} Torr. Argon gas was introduced the chamber keeping the flow rate constant at 6.94sccm (std.cm3/min) by a mass-flow controller. A small amount of oxygen gas was introduced into the chamber to create a reactive environment and the flow rate was controlled by another mass-flow controller. The pressure 10 mTorr was held by throttling the main valve. Target was pre-sputtered with a shutter closed for 45 min before and 15 min after oxygen gas introduced into the chamber in order to eliminate contamination. The substrate was heated and the temperature was measured by a chromel-alumel thermocouple on the surface of the substrate.

The films deposited was analyzed by an X-ray diffraction (XRD) using Cu-Kα radiation. A conventional surface roughness detector with a stylus (Dektak3) was used to determined the film thickness. The oxygen gas pressure during the deposition process was measured by micropole gas analyzer.

RESULTS AND DISCUSSIONS

Figure 3 shows the deposition rate dependences on O_2/Ar flow rate and temperature for films deposited sing ZrTi + 30%PbO_2 powder and pellet targets. Deposition rate is obtained by dividing the film hickness with the deposition period. From the figure it can be seen that the deposition rate for pellet targets are higher than that of powder targets. The deposition rate for deposition without any oxygen gas introduced, or 0% of O_2/Ar flow rate, was higher than that of deposition with 4.2% of O_2/Ar flow rate at 450 and 500°C.

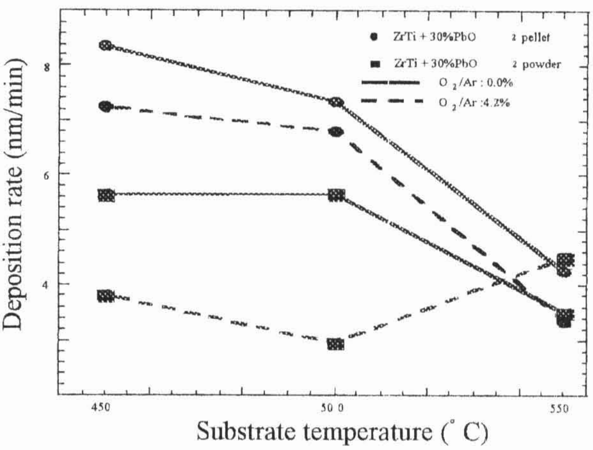


Figure 3: Deposition rate dependences on O_2/Ar flow rate and substrate temperature

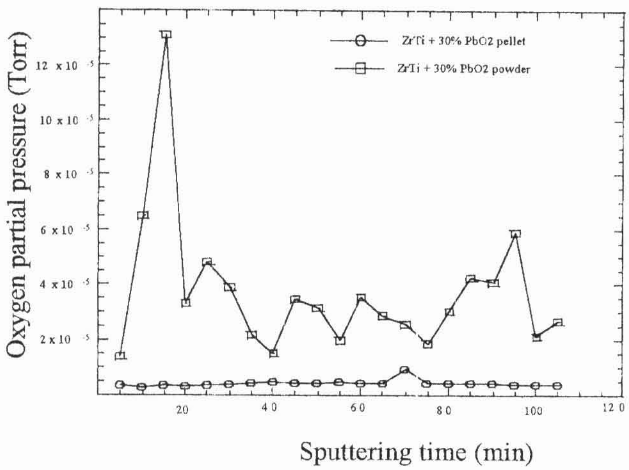
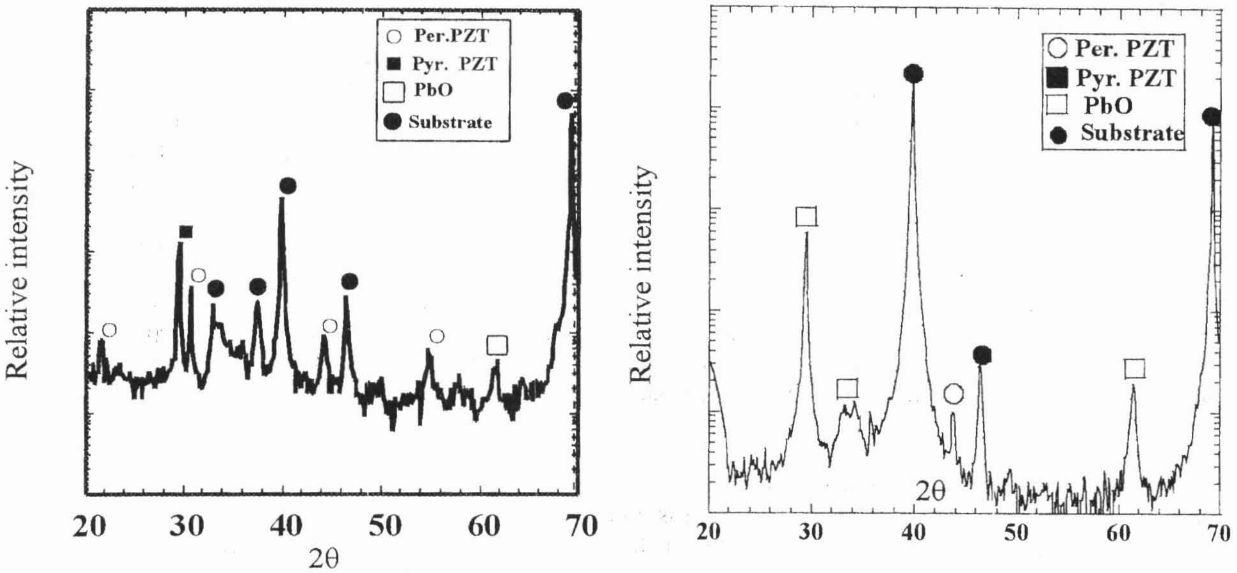


Figure 4: Oxygen partial pressure during deposition

As stated in the introduction, in reactive sputtering, deposition rate will fall due to the increasing O_2/Ar flow rate, or the deposition rate will decrease as the oxygen in the chamber during the deposition increase. The result in Figure 3 shows the same phenomenon. Moreover, in the deposition with 0% of O_2/Ar flow rate, the deposition rate for pellet target is higher than that of powder target in all conditions, thus it can be said that PbO_2 powder targets released more oxygen than that of pellet targets. However at 550°C, it can be observed that the deposition rate of ZrTi + 30%PbO_2 powder target in 4.2% O_2/Ar flow rate is the highest.

Figure 4 shows the oxygen partial pressure during deposition measured by the micropole gas analyzer. The deposition was carried using ZrTi + 30%PbO_2 powder and pellet targets respectively without introducing any oxygen gas during the process so that the oxygen pressure measured was purely the oxygen that was released by the targets. From the graph it can be seen clearly that the oxygen partial pressure measured during the deposition by powder target is higher than that of pellet target. It is confirmed that PbO_2 powder target released more oxygen than PbO_2 pellet target.

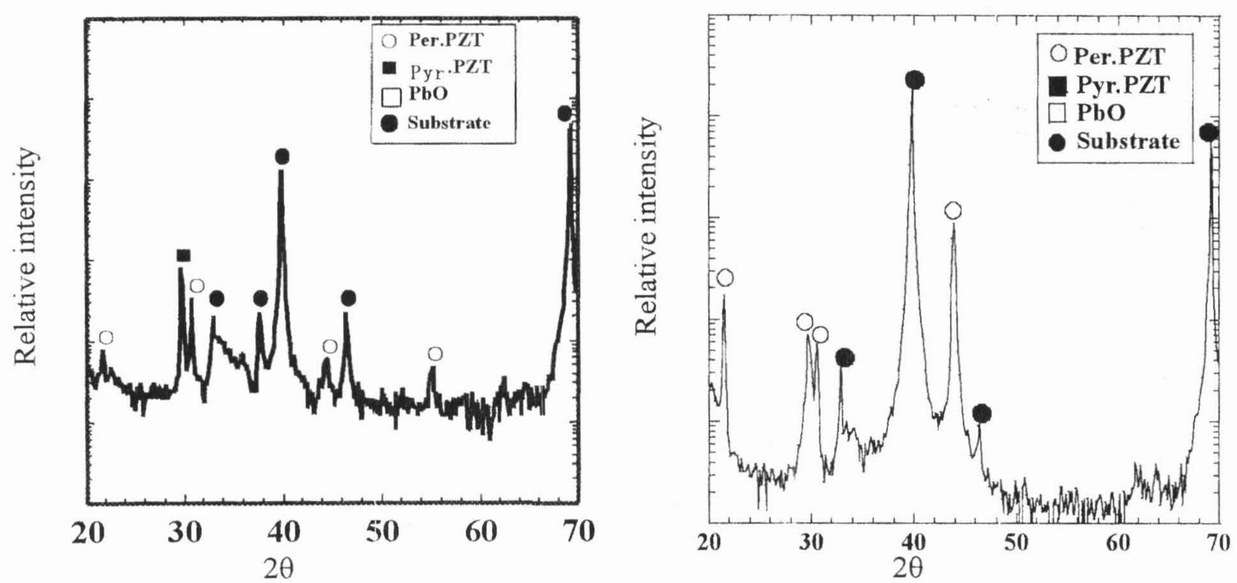
Figure 5 shows the XRD results of the films deposited at 550°C on Pt/Ti/SiO_2/Si substrate under 4.2% O_2/Ar flow rate by ZrTi + 30%PbO_2 powder and pellet targets respectively. The left figure is the result of film deposited using ZrTi + 30%PbO_2 powder target and the right figure is that of ZrTi + 30%PbO_2 pellet target. Both results show that no pure perovskite PZT was obtained. Thin film deposited using the ZrTi + 30%PbO_2 pellet target exhibits strong PbO peaks mixed with perovskite PZT peak, but thin film deposited using ZrTi + 30%PbO_2 powder target shows strong perovskite PZT peaks however with a second phase of pyrochlore PZT and PbO. The existence of PbO peaks in both results indicate that there were access PbO supplied during the deposition, and the pyrochlore PZT peak exhibit the lack of oxygen supply.



ZrTi + 30%PbO_2 powder target

ZrTi + 30%PbO_2 pellet target

Figure 5: XRD analysis of films deposited at 550° C and 4.2% O_2/Ar flow rate



ZrTi + 30%PbO_2 powder target

ZrTi + 30%PbO_2 pellet target

Figure 6: XRD analysis of films deposited at 550° C and 0% O_2/Ar flow rate

This results also explain the phenomenon occurred in the deposition rate result where at 550°C, the deposition rate of ZrTi + 30%PbO_2 powder target is higher than that of pellet target. PZT thin film with high evaporation temperature were formed in the case of powder target but PbO were deposited in the case of pellet target. PbO will be re-evaporated more easily than PZT. Thus the thickness of the thin film obtained by ZrTi + 30%PbO_2 powder target will be thicker than that of pellet target, that leads to high deposition rate.

Thin films were deposited under the same conditions as above except that the O_2/Ar flow rate is 0%, or without any oxygen introduced during the deposition. The XRD result of the films were depicted in Figure 6. The left figure is the result of film deposited using ZrTi + 30%PbO_2 powder target and the right figure is that of ZrTi + 30%PbO_2 pellet target. From the results it can be seen that pure perovskite PZT can be obtained from the film deposited by ZrTi + 30%PbO_2 pellet target, but perovskite PZT peaks mixed with a pyrochlore PZT peak can be observed in the result of film deposited by ZrTi + 30%PbO_2 powder target. The existence of pyrochlore PZT peak in the result of the film deposited using ZrTi + PbO_2 powder target indicates the lack of oxygen supply in the film, whereas the oxygen supply in the film deposited by ZrTi + 30%PbO_2 pellet target was sufficient. This does not mean that pellet target supplies more oxygen than that of powder target base on the deposition rate and oxygen partial pressure results where it is confirmed that powder target released more oxygen than that of pellet target. Thus it can be said that PbO_2 pellet target plays the role as the oxygen-source more efficient than PbO_2 powder target.

As the conclusions, we have discovered that PbO_2 powder target released more oxygen than PbO_2 pellet target. Deposition rate for PbO_2 pellet target is higher than PbO_2 powder target. Pure perovskite PZT was obtained by deposition using ZrTi + PbO_2 pellet target without any oxygen introduced during the process. The role of PbO_2 pellet as an effective solid oxygen-source is highly appreciated.

REFERENCES

1. Kim, J.D. Kawagoe, S. Sasaki, K. and Hata, T. Target for Pb(Zr,Ti)O_3 Thin Film Deposited at Low Temperature using a Quasi-Metallic Mode of Reactive Sputtering. *Japanese Journal of Applied Physics*. 38 : 6882-6886

2. Gotoh, K. , Hirotaka, T. , Takauchi, H. and Yoshida, A. Pt/PZT/n-$SrTiO_3$ Ferroelectric Memory Diode *Japanese Journal of Applied Physics*. 35: 39-43

3. Sasaki, K. , Zhang, W. and Hata, T. Origin of oxygen in Pb)Zr,Ti)O_3 films prepared by metal-oxide combined target. 51: 661-664

4. Krupanidhi, S.B. , Hu, H. and Kumar, V. Multi –ion-beam reactive sputter deposition of ferroelectric Pb(Zr,Ti)O_3 thin films. *Japanese Journal of Applied Physics*. 71:376-388

5. Sukreen, H., Kaneta, R., Saparin, N., Sasaki, K. and Hata, T. A new PZT thin film preparation technique using solid oxygen-source target by RF reactive sputtering. *Proceedings of IEEE International Conference on Semiconductor Electronics 2002 (ICSE2002)* pp: 378-382

6. Asakura, T. , Ishikawa, K , Sato, A. and Okada, M. Preparation and Pyroelectric Characteristics of Pb(Zr,Ti)O_3 Thin Films Grown by Metalorganic Chemical Vapor Deposition *Japanese Journal of Applied Physics* . 35: 4886-4889

7. Nakamura, T. , Fujimori, Y. , Izumi, N. and Kamisawa, A.Fabrication Technology of Ferroelectric Memories. *Japanese Journal of Applied Physics* . 37: 1325-1327

8. Zhang, W. , Sasaki, K. and Hata, T. Low temperature fabrication of Pb(Zr,Ti)O_3 films by RF Reactive Sputtering using Zr/Ti + PbO target. *Japanese Journal of Applied Physics*. 34: 5120-5123

9. Wang, Z.J. , Kikuchi, K. and Maeda, R. Effect of Pb Content in Target on Electrical Properties of Laser Ablation Derived Lead Zirconate Titanate Thin Films. *Japanese Journal of Applied Physics*. 39: 5413-5417