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# Preparation of $Pb(Zr, Ti)O_3$ Thin Films on $(Pb, La)TiO_3$ Buffer Layer by Multi-Ion-Beam Sputtering

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Ferroelectric lead-zirconate-titanate (PZT) thin films were successfully fabricated by multi-ion-beam sputtering technique in an oxygen ambient at a low substrate temperature of 415 °C. By insertion of lead-lanthanum-titanate (PLT) buffer layers between substrates and PZT films, the perovskite-PZT thin films could be epitaxially grown on (100)MgO, (100)Pt/MgO and (111)Pt/Ti/$SiO_2$/Si substrates. These films, even in thickness as thin as 600Å, showed excellent ferroelectric properties with a remanant polarization of 20 $\mu C/cm^2$, coercive field of 200 kV/cm, and a relative dielectric constant of 675.

## INTRODUCTION

Recently the fabrication of $Pb(Zr,Ti)O_3$ (PZT) thin films has been widely investigated since their ferroelectric properties and dielectric constant are very suitable for applications in nonvolatile random access memories (NVRAMs) or dynamic random access memories (DRAMs). Considering these applications, very thin and high quality PZT films must be prepared under low processing temperatures below 500 °C because of the compatibility with the semiconductor process.

In this work we have succeeded in fabricating excellent PZT thin films less than 1000Å using a multi-ion beam sputtering technique at a low substrate temperature of 415 °C. This technique has several advantages in synthesizing high quality thin films, such as (i) deposition under high vacuum, (ii) prevention of the damage from plasma, and (iii) flexibility of the composition of a thin film. Although some attempts to fabricate PZT thin films using such a technique have been already reported[1,2], it has been still difficult to obtain perovskite-PZT thin films with sufficient crystallinity and electric properties at low processing temperatures. In the present work, in order to fabricate high quality PZT thin films, $(Pb,La)TiO_3$ (PLT) buffer layer was deposited on the substrate prior to the deposition of PZT film. With a help of the PLT buffer layer, successively deposited PZT films could be epitaxially grown in perovskite phase. This report describes the preparation and properties of very thin PZT film on PLT buffer layer fabricated by multi-ion-beam sputtering technique.

## EXPERIMENTAL PROCEDURE

Figure 1 shows the schematic illustration of the multi-ion-beam sputtering apparatus. Four bucket type ion-sources which generate $Ar^+$ ions, are arranged toward individual metal targets of Pb, La, Zr and Ti. The typical sputtering conditions are listed in table I. The deposition chamber was evacuated by the cryo-pump to a background pressure less than $1x10^{-6}$ Torr. The sputtering rate of each target was controlled by the $Ar^+$ ion beam current, monitored by quartz crystal resonators mounted over individual targets. In order to oxidize the sputtered species, $O_2$ gas was introduced near the substrates at an oxygen partial pressure of approximately $1x10^{-4}$ Torr, and the total pressure was 2 - 3 x $10^{-4}$ Torr. The substrates used were (100)Pt/MgO and (111)Pt/Ti/$SiO_2$/Si, which were coated by Pt about 700Å in thickness as bottom electrodes, as well as single crystal (100)MgO. They were clamped to a copper holder and heated at 415 °C during the deposition. The substrate temperature was evaluated using a thermocouple attached at the surface of MgO substrate.

Cross-sectional view of the deposited film was illustrated in Fig. 2. First, Pb, La and Ti targets were simultaneously sputtered to form PLT buffer layer on the substrates before PZT deposition. The thickness of the PLT buffer layer was approximately 50Å and the concentration of La was La/(Pb+La) = 20 mol%. The stoichiometric PZT thin films, whose Zr/Ti ratio was

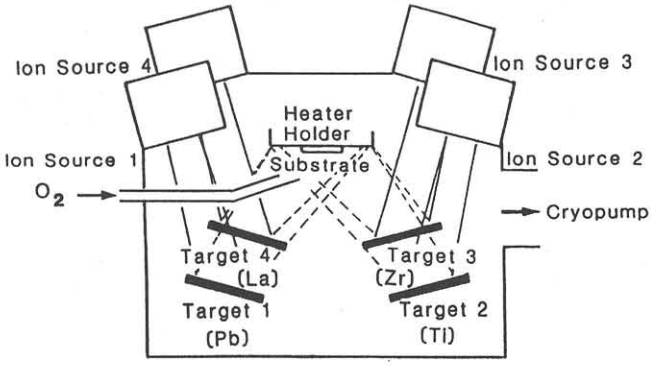


Fig.1. Schematic illustration of multi-ion beam sputtering system.

Table I. Typical sputtering conditions

| | |
|---|---|
| Substrate | (100)MgO, (100)Pt/MgO, (111)Pt/Ti/$SiO_2$/Si |
| Substrate temperature | 415 °C |
| Targets | Pb, La, Zr and Ti metals (3 inches) |
| Ion source-target distance | 17cm |
| Target - substrate distance | 25cm |
| Gas flow | Ar: 2.0 x 3 sccm<br>O2: 7.5 sccm ($1.0 \times 10^{-4}$ Torr) |
| Total pressure | 2.0 - 3.0 $\times 10^{-4}$ Torr |
| Ion beam voltage | 1100V |
| current | Pb: 8.0-12 mA<br>La: 4.0 mA<br>Zr,Ti: 12-15 mA |
| Deposition rate | 7.5 Å/min. |
| Film thickness | 600 - 1850 Å |

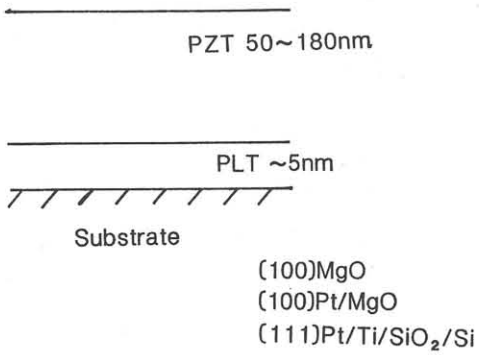


Fig.2. Cross-sectional view of the deposited film.

typically 50/50, were successively deposited by sputtering Pb, Ti and Zr targets. The deposition rate of the PZT film was about 7.5Å /min. and very thin films from 600 to 1850Å in thickness including 50Å -thick PLT layer were prepared.

The composition of the resulting films was estimated by energy dispersive x-ray microanalyzer (EDX), and the crystalline structure of the films was examined by x-ray diffraction (XRD). Film thickness was measured using a stylus profilometer.

The electrical properties of the PZT films were examined with gold top electrodes of 0.5 or 0.3 mm in diameter. The dielectric properties were measured by LCR meter and the D-E hysteresis curves were measured using a Sawyer-Tower circuit.

## RESULTS AND DISCUSSION

Figure 3 shows the XRD patterns of PZT films with PLT buffer layer deposited on (100)MgO, (100)Pt/MgO and (111)Pt/Ti/$SiO_2$/Si substrates. Note that for the (100)MgO and (100)Pt/MgO substrates, the PZT films were preferentially oriented along c-axis and no other orientations were observed. While for the (111)Pt/Ti/$SiO_2$/Si substrate the PZT film was mainly oriented along <111>-axis and small reflections of <001>- and <101>-axes could be found. On the other hand when the deposition of PZT films were performed without the buffer layer, zirconium oxide or pyrochlore phase was formed and perovskite phase was hardly observed. It should be emphasized that the crystalline structure of the PZT films is remarkably improved by inserting a PLT buffer layer between a substrate and a

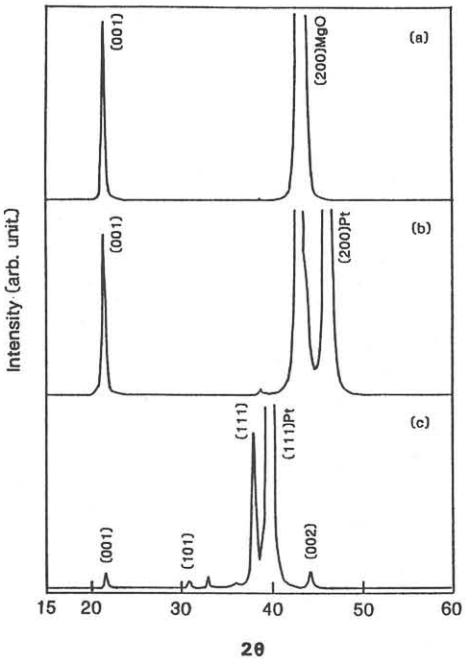


Fig.3. X-ray diffraction patterns of PZT films with PLT buffer layer. The films were deposited on (a) (100)MgO, (b) (100)Pt/MgO and (c) (111)Pt/Ti/$SiO_2$/Si substrates.

PZT film. Same effects was also confirmed for the$PbTiO_3$ buffer layer. These phenomena sugest that without PLT layer, the zirconium oxide or pyrochlore adheres to the surface of the substrate at the initial stage of the PZT deposition and disturbs the growth of perovskite phase, whereas the PZT films can be successively and epitaxially grown on the PLT layer which can be easily formed on the substrates because of the absence of Zr. The modification of the film growth with PLT buffer layer was also reported on the lead-lanthanum-zirconate-titanate (PLZT) film deposited on a sapphire substrate by multi-target dc-sputtering at the substrate temperature of 700 °C [3]. In the present study PZT thin films could be fabricated at a lower substrate temperature due to the advantages of ion beam sputtering such as the deposition with energetic species suitable for the film growth in high vacuum. As

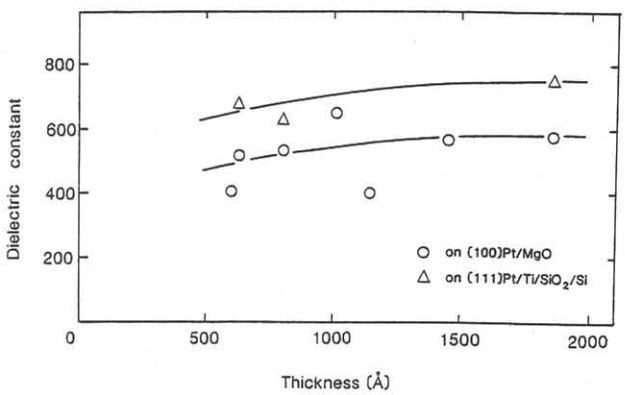


Fig.4. The dielectric constant of the PZT films as a function of the film thickness.

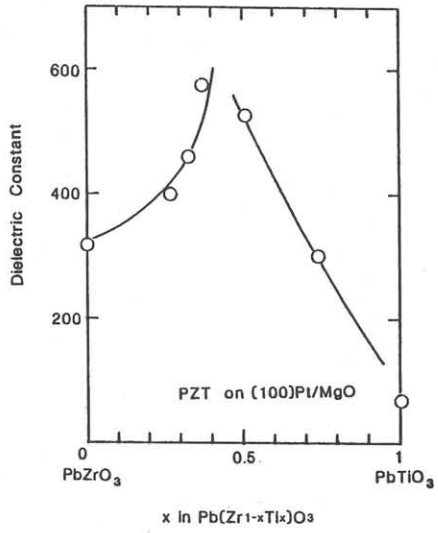


Fig.5. The dielectric constant of c-axis oriented PZT films as a function of Zr/Ti ratio.

for the thickness of the PLT buffer layer, it was found that 10Å is enough to form the epitaxial PZT films.

Figure 4 shows the relative dielectric constant ($\varepsilon_r$) of the PZT films with Zr/Ti ratio of 50/50 as a function of film thickness. The measurement was performed at a frequency of 1 kHz. In spite of very thin film thickness, PZT films deposited on both substrates maintain high $\varepsilon_r$ in thickness down to 600Å and the 630 Å-thick PZT film on the Pt/Ti/$SiO_2$/Si has high $\varepsilon_r$ of 615. The abrupt reduction of the dielectric constant which was reported before [4] is hardly observed. The PZT films deposited on (111)Pt/Ti/$SiO_2$/Si substrates show higher dielectric constant than those on (100)Pt/MgO. This is attributed to the different crystal orientations of the PZT films as shown in Fig. 3.

The variation of $\varepsilon_r$ as a function of the film composition of Zr/Ti ratio was measured and the results were shown in Fig. 5. The c-axis oriented PZT films of 800Å in thickness were prepared on (100)Pt/MgO. Figure 5 indicates that the dielectric constant is strongly dependent on the film composition of Zr/Ti ratio and when the Zr/Ti ratio is near 55/45, the dielectric constant shows the highest value, that is approximately consistent with the tendency of the bulk PZT.

The ferroelectric properties were investigated by observing the hysteresis loops using triangular signals at 1 kHz for PZT films. Figure 6 shows the ferroelectric hysteresis loops for PZT films of 630Å in thickness deposited on the substrates. The films have good ferroelectric properties even in very thin thickness with a remanent polarization of 23 $\mu C/cm^2$ for (100)Pt/MgO, and 18 $\mu C/cm^2$ for (111)Pt/Ti/$SiO_2$/Si, respectively. As for the dependence of a remanent polarization (Pr) and coercive field (Ec) on the film thickness ranging from 600 to 1850Å , the values of Pr were nearly constant for both substrates, while the values of Ec increase with decreasing the film thickness. Little dependence of Pr as well as dielectric constant on film thickness may suggest that the degraded layer near the interface of the electrodes scarcely exists in the resulting film and whole film maintains excellent crystallinity.

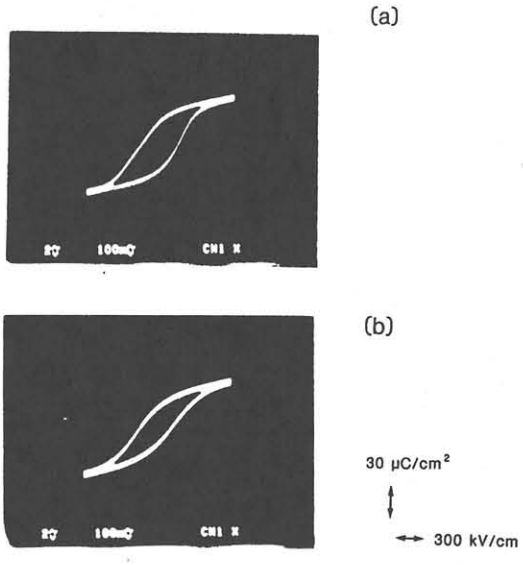


Fig.6. Hysteresis loops of the PZT films 630Å in thickness on (a) Pt/MgO and (b) Pt/Ti/$SiO_2$/Si substrates. Pr and Ec are 23 $\mu C/cm^2$, 240 kV/cm for Pt/MgO, and 18 $\mu C/cm^2$, 200 kV/cm for Pt/Ti/$SiO_2$/Si respectively.

## CONCLUSIONS

Very thin PZT films, from 600 to 1850Å in thickness, were successfully fabricated using multi-ion-beam sputtering deposition at a low substrate temperature of 415 °C. The growth of PZT film could be remarkably modified by insertion of a PLT buffer layer between a substrate and a PZT film, and the films show the excellent crystallinity. The PZT films on the (100)MgO and (100)Pt/MgO substrates are preferentially oriented along <001>-axis, while the PZT films on the (111)Pt/Ti/$SiO_2$/Si substrate are mainly oriented along <111>-axis. These films have good dielectric and ferroelectric properties, such as $\varepsilon$ of 700, Pr= 20 $\mu C/cm^2$ and Ec= 200 kV/cm, even in thickness as thin as 600Å.

## ACKNOWLEDGEMENT

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