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Bias Effects on Epitaxial PZT Films in Reactive Sputtering

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Epitaxial PZT thin films on MgO(001) substrates were successfully prepared by means of a reactive sputtering using a composite ceramic target. A DC bias voltages from –200V to +100V were applied to substrates during the deposition in order to suppress resputtering by energetic negative oxygen ions. XRD intensities of 001 and 002 diffraction peaks of PZT showed maxima at the bias voltage of -100V. The rocking curve full width at half-maximum (FWHM) for (001) plane of PZT film deposited without the bias voltage is about 1.9 degree, but it is markedly improved to 0.8 degree by the application of -100V bias. From the analyses of the film composition, the Ti/Zr ratio was increased by applying both negative and positive bias voltages. The film thickness decreased with decreasing the negative bias voltage and showed a minimum at 0V, which indicated application of negative bias voltage suppressed resputtering. Surface of the films deposited with –100V bias was very clean and smooth in comparison with those deposited without application of the bias voltage. As a result, applying DC negative bias voltage to substrates could suppress resputtering by energetic negative oxygen ions and then enhance the surface morphology and crystalline quality of PZT films.

Key words: epitaxial PZT thin films, reactive sputtering, substrate bias voltage, resputtering, energetic negative oxygen ions, composite ceramic target

1. INTRODUCTION

$Pb(Zr_xTi_{1-x})O_3$(PZT) thin films is one of the most promising materials to be applied to ferroelectric non-volatile memories. PZT films have been prepared by sputtering, MOCVD, MOD and sol-gel methods. Sputtering method has some advantages over the other methods from the view point of industrialization. But there still remain problems, such as rough surface morphology and composition control. These problems are attributable to the effect of resputtering by energetic negative oxygen ions. It has been reported in the sputtering of oxides such as ZnO and $BaTiO_3$ that the bombardment of energetic oxygen atoms and/or ions reduced the quality of growing films [1-5]. In order to minimize the damage by the ion bombardments, the application of bias voltage to the substrates seems to be effective. There are some reports on bias sputtering for the deposition of metal films [6][7] but the those on oxide film are extremely limited [8]. In this study, PZT films were deposited using RF-magnetron sputtering system with applying negative or positive bias voltages to substrates, and the bias effects on PZT films was investigated. It was suggested that the negative bias voltage to substrates suppressed the collisions of energetic oxygen ions to growing films in reactive sputtering.

2. EXPERIMENTAL PROCEDURE

Epitaxial PZT thin films were grown using an RF-magnetron sputtering system (Seed Lab. Co.) with applying bias voltages to substrates. As shown in Fig.1, this deposition apparatus has DC power supply (Kikusui Electronics Co.) to be able to apply both negative and positive bias to substrates.

MgO(001) single crystals ($10 \times 10 \times 0.5mm^3$, Shinkosha Ltd.) were used as substrates which have a good lattice match with PZT. They were cleaned using ethanol and acetone with an ultrasonic cleaner in order to remove organic contamination on the surface of substrates. As sputtering targets, PZT ceramic targets with 50mm in diameter and 4mm thick were prepared by sintering PbO, ZrO_2 and TiO_2 powders (99.9% purity). The molar ratio of Zr and Ti in the targets was 0.4 and 0.6, respectively, and excess PbO was added by 10mol% or 20mol%. And a composite ceramic target, where a PbO pellet of 25mm in diameter and 2mm thick was placed at the center of the PZT target with 20mol% excess PbO, was also prepared.

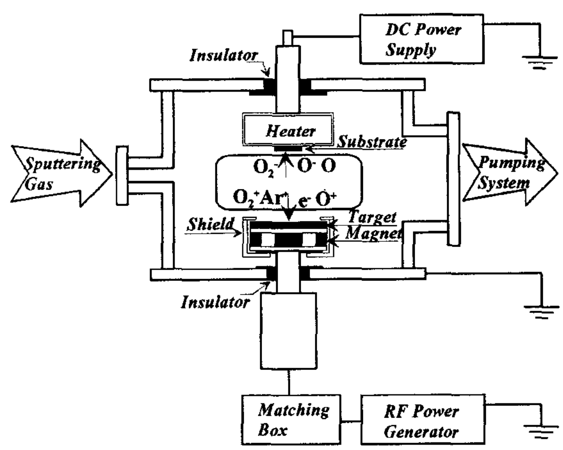

Fig. 1. Schematic diagram illustrating RF-magnetron sputtering system combined with DC power supply to substrates.

The deposition chamber was evacuated to 2×10^{-6} Torr by a diffusion pumping system before the deposition. Substrates were heated at 620°C using a halogen lamp. The deposition of films was carried out at 20mTorr for 30min using $Ar/O_2(8/2)$ as a sputtering gas. The RF power was 200W and the DC bias voltages to the substrate were changed from –200V to +100V. Table I shows the deposition conditions for PZT films.

Phase identification of the deposited films was performed by X-ray diffractometer (XRD). The crystallinity and the epitaxy were analyzed from rocking curves and pole figures, respectively. The film thickness was measured using a stylus method (DEKTAK). The chemical composition of the films was analyzed by inductively coupled plasma atomic emission spectrometry (ICP-AES) and X-ray fluorescence spectroscopy (XRF), and the surface morphology of the films was observed by field emission scanning electron microscope (FE-SEM).

Table I. Deposition conditions for PZT film growth.

Substrate	MgO(001)
Substrate Temperature	620 °C
Target	$Pb_{1.1}(Zr_{0.4}Ti_{0.6})O_3$, $Pb_{1.2}(Zr_{0.4}Ti_{0.6})O_3$ $Pb_{1.2}(Zr_{0.4}Ti_{0.6})O_3$+PbO
Substrate-Target Distance	3 cm
Base Pressure	2×10^{-6} Torr
Working Pressure	20 mTorr
Ar/O_2	8/2
RF Power	200 W (10.19 W/cm^2)
Bias to Substrate	-200V, -100V, -50V, 0V, 50V, 100V
Deposition Time	30min

3. RESULTS AND DISCUSSION

3.1. Bias Effects on Crystallographic Properties and Surface Morphology of PZT films

Thin films of PZT single phase were not obtained when the PZT ceramic targets were used. As shown in Fig. 2, $(Zr,Ti)O_2$ and $Pb(Zr,Ti)_3O_7$ phases were formed from the 10mol% excess PbO target and pyrochlore phase was formed from the 20mol% excess PbO target in the deposition conditions used in this study. Thin films of PZT single phase were obtained when the composite target was used, therefore the bias effects were studied for these films.

Fig. 3 shows XRD profiles of PZT films with a variation of DC bias voltages. Except the case of +200V, single phase PZT films was grown on MgO(001) substrates. The intensity of PZT phase is strongest at –100V bias.

A x-ray pole figure of the film grown at -100V is shown in Fig. 4. The pole figure was taken by ϕ scanning technique, where ϕ is the rotational angle around the surface normal to [101] axis. The intensity peaks with the four-fold symmetry indicates that the film is not only a c-axis oriented but was epitaxially grown on MgO(001) substrates.

X-ray rocking-curves of the films deposited at -100V and at 0V were compared in Fig. 5. The full width at half maximum (FWHM) of the film deposited without the bias voltage is about 1.9 degree, but it is markedly improved to 0.8 degree by the application of -100V bias. As a reference, the FWHM of MgO(001) single crystal was 0.210. These results indicated that the bias voltage was effective to obtain PZT films with good crystallinity.

Fig. 6 is surface morphology of the films deposited at 0V and -100V observed by FE-SEM. It is seen that the surface of films deposited at -100V is very clean and smooth in comparison with the film deposited without bias voltage.

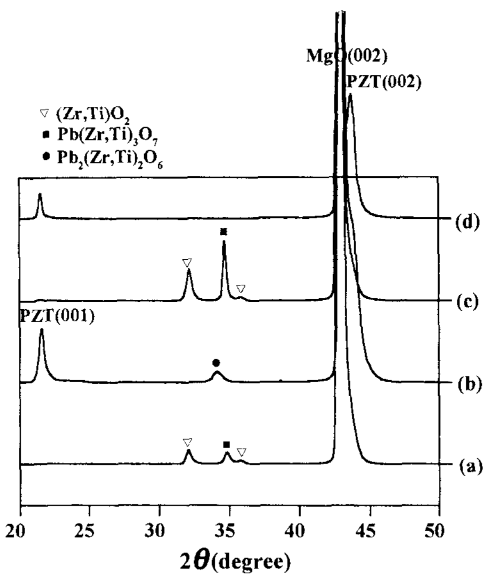

Fig. 2. XRD patterns of films on MgO(001) deposited using (a) $Pb_{1.1}(Zr_{0.4}Ti_{0.6})O_3$ target, (b) $Pb_{1.2}(Zr_{0.4}Ti_{0.6})O_3$ target (first time), (c) $Pb_{1.2}(Zr_{0.4}Ti_{0.6})O_3$ target (second time), and (d) $Pb_{1.2}(Zr_{0.4}Ti_{0.6})O_3$+PbO composite target.

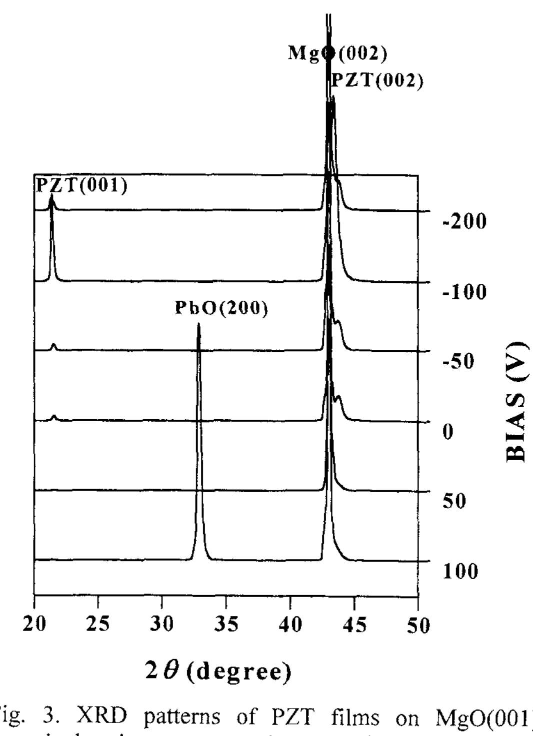

Fig. 3. XRD patterns of PZT films on MgO(001) deposited using a composite ceramic target with a variation of DC bias voltages to substrates.

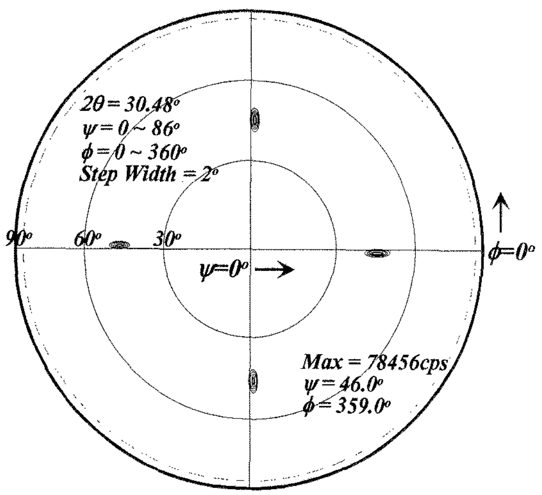

Fig. 4. X-ray (101) pole figure of epitaxial PZT(001) film on MgO(001).

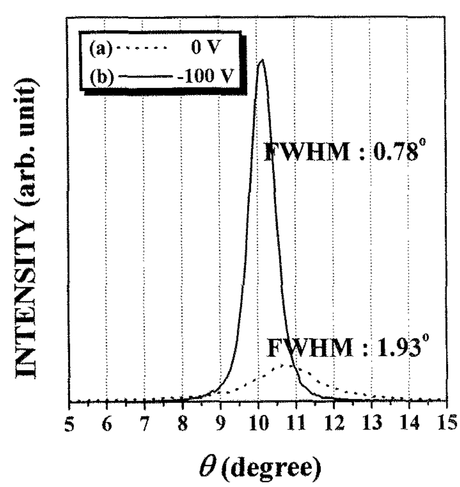

Fig. 5. Rocking Curves of PZT(001) peaks for the films deposited (a) at OV bias and (b) at -100V bias.

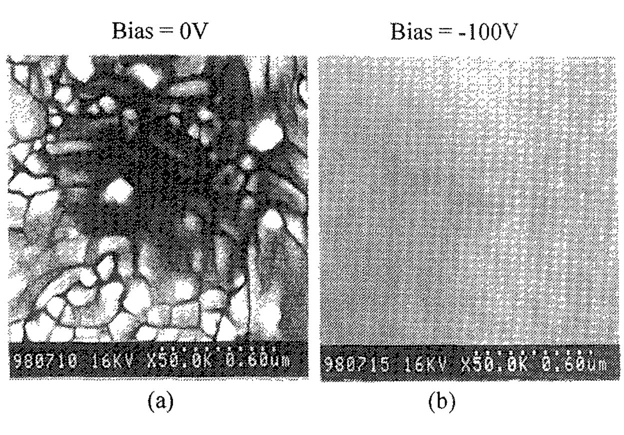

Fig. 6. FE-SEM micrographs showing surface morphology of PZT films deposited on MgO(001) at (a) 0V bias and (b) -100V bias.

3.2 Bias Effects on Thickness and Composition of PZT Films

The thickness of films also depended on the bias voltage. Fig. 7 shows bias dependence of PZT film thickness. The thickness decreases with decreasing negative bias voltage, shows a minimum at 0V and increases steeply at +100V.

The results of the chemical composition analyses of PZT films showed that the PbO content in the films was almost stoichiometry or little excess and was independent of the DC bias. Therefore, we focused on the change in the Ti/Zr ratio which is important for the properties of PZT. The Ti and Zr contents were changed by the bias voltage as shown in Fig. 8, and it was found that the contents in the films became near the target composition (Ti:Zr=0.6:0.4) when the films were deposited under negative bias voltages.

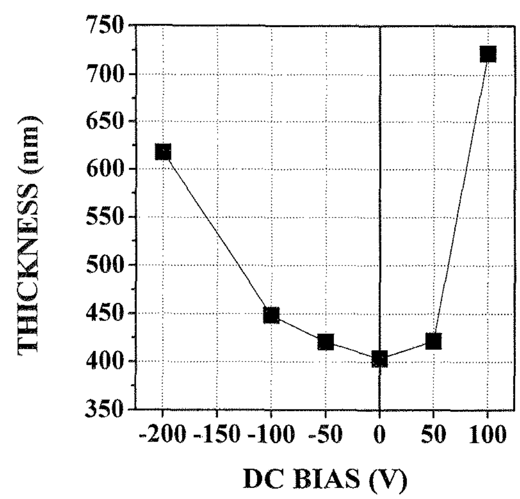

Fig. 7. Dependence of thickness with a variation of DC bias voltages to substrates.

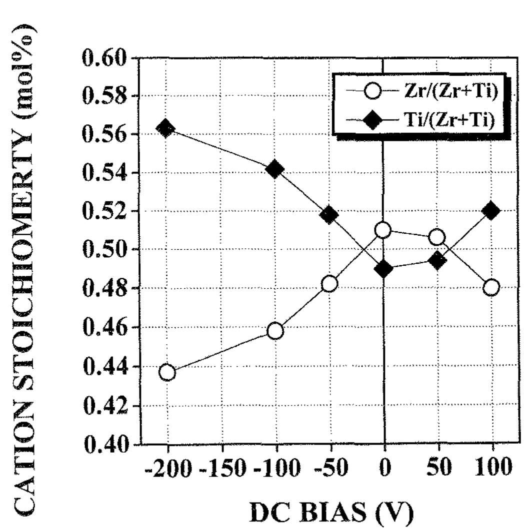

Fig. 8. Dependence of cation stoichiomerty with a variation of DC bias voltages to substrates.

3.3 Discussion

As shown above, the application of negative bias voltage around -100V markedly improved the crystallinity and the surface morphology of PZT films, and epitaxial PZT films were obtained. And the film thickness decreased with decreasing negative bias voltage and showed a minimum at 0V. The effects of the bias voltages are attributable to the suppression of the oxygen ion bombardment to the growing films.

Fig. 9 shows the relation between the bias voltage and currents flowing between substrate holder and ground level. The current values when applying positive bias voltages were much higher than those when applying negative bias voltages. Furthermore, the sputtering system became much more unstable as increasing positive bias voltages. Because of the unstable system, PbO phase existed in the PZT film and its Pb composition was extraordinarily higher than others. The mechanism is not yet understood. As a result, negative bias voltages were effective to growing good quality PZT films. And it was found that there was the optimum negative bias voltage to improve film quality. It can be thought that applying negative bias voltages to substrates slowed down energetic negative oxygen ions but higher value of negative bias than critical voltage could cause for positive ions to be accelerated so that film quality could be deteriorated.

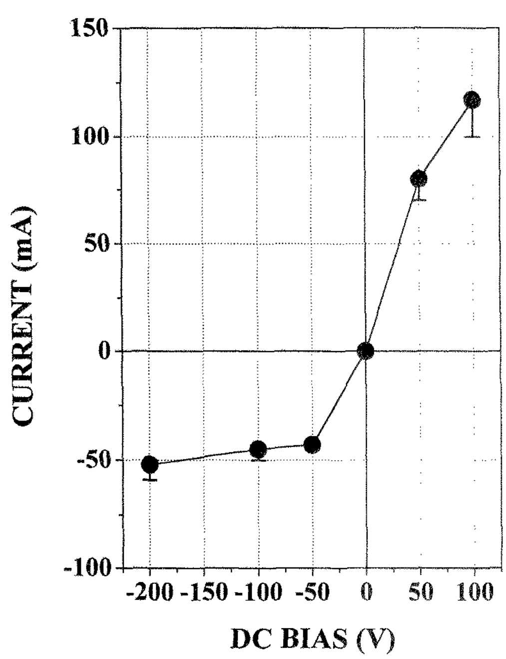

Fig. 9. Current flows through DC power supply with a variation of DC bias voltages to substrates.

4. CONCLUSION

In this study, epitaxial PZT films with a good quality were successfully grown on MgO(001) substrates at 620°C by reactive sputtering with applying negative bias voltages to substrates.

When using one target for reactive sputtering with high RF power, a composite ceramic target of PZT and PbO was suitable for growing epitaxial PZT films due to constant supplement of Pb source. And Ti/Zr ratio and thickness of PZT films were increased as increasing both negative an positive bias voltages to substrates in comparison without bias voltages, but negative bias voltages were more effective than positive bias voltages.

Applying −100V bias to substrates remarkably enhanced the crystalline quality and surface morphology of the epitaxial PZT films. The reason can be thought as follows. The optimum negative bias voltage suppressed collisions of the energetic negative oxygen ions to growing films by slowing down them. But, when applying over the critical negative bias voltage, the films were degraded because positive ions were accelerated as much as deteriorating growing films.

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