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The perovskite phase formation of $0.4Pb(Yb_{1/2}Nb_{1/2})O_3$–$0.6PbTiO_3$ thin films prepared on Pt/Ti electrode by reactive magnetron sputtering

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Abstract

Ferroelectric $0.4Pb(Yb_{1/2}Nb_{1/2})O_3$–$0.6PbTiO_3$ (PYNT) thin film was prepared on $Pt/Ti/SiO_2/Si(100)$ substrates by multi-target rf magnetron sputtering deposition at substrate temperature of 550°C. The $YbNbO_4$ oxide target was used as Yb and Nb sources. The effect of composition and substrate was investigated by X-ray diffraction analysis. Although the formation of perovskite phase mainly depends on the Pb sputtering power, the processing window is very narrow on $Pt/Ti/SiO_2/Si$ substrate. The substrates with the thick Pt electrodes tend to reduce the perovskite phase. Meanwhile, the TiO_2 buffer layer deposited on the Pt surface is observed to enhance the formation of the perovskite phase. © 2001 Published by Elsevier Science Ltd.

Keywords: Ferroelectric properties; Films; $(1-x)Pb(Yb_{1/2}Nb_{1/2})O_3$–$xPbTiO_3$; Perovskites

1. Introduction

Ferroelectric thin films have been widely investigated for application as sensor, memory and actor elements. The potential for future applications includes micro electromechanical systems like pumps or valves[1] as well as the piezoelectric motors of very small size.[2] In the piezoelectric thin film application areas, lead-base relaxor-$PbTiO_3$(PT) solid solutions such as $Pb(Mg_{1/3}Nb_{2/3})O_3$–PT and $Pb(Sc_{1/2}Nb_{1/2})O_3$–PT are very attractive ferroelectric materials because they show large piezoelectric response and low thermal expansion. In particular, the recently synthesized relaxor ferroelectric single crystals yield superior electromechanical properties compared to the conventionally prepared polycrystalline ceramics.[3]

The relaxor-PT material, however, has been shown to exhibit low transition temperature like pumps or valves[1] as well as the piezoelectric motors of very small size.[2] In the piezoelectric thin film application areas, lead-base relaxor-$PbTiO_3$(PT) solid solutions such as $Pb(Mg_{1/3}Nb_{2/3})O_3$–PT and $Pb(Sc_{1/2}Nb_{1/2})O_3$–PT are very attractive ferroelectric materials because they show large piezoelectric response and low thermal expansion. In particular, the recently synthesized relaxor ferroelectric single crystals yield superior electromechanical properties compared to the conventionally prepared polycrystalline ceramics.[3]

The relaxor-PT material, however, has been shown to exhibit low transition temperature (typically less than 200°C). For the desired temperature stability in the piezoelectric application, the phase transition temperature of the relaxor-PT materials ought to preferably increase. Among the relaxor-PT solid solution systems, the $(1-x)Pb(Yb_{1/2}Nb_{1/2})O_3$–$x$PT (PYNT) system has been shown to posses the highest transition temperature (~360°C) near the morphotropic phase boundary (MPB) between the pseudocubic and tetragonal phases (x~0.5).[4,5] Although pure $Pb(Yb_{1/2}Nb_{1/2})O_3$(PYN) is a B-site ordered antiferroelectric, the substitution of Ti at B-sites induces sequential phase change from the orthorhombic antiferroelectic to relaxor ferroelectric and finally into the tetragonal ferroelectrics. Optimized electromechanical properties are observed at compositions just near the MPB.

In this work, the preparation of perovskite 0.4PYN–0.6PT thin film by rf magnetron sputtering will be reported with particular attention paid to the effects

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attributed to the various growth conditions and substrates on the formation of the perovskite phase.

2. Experimental

0.4PYN–0.6PT (PYNT (40/60)) films were deposited on the Pt(100nm)/Ti(20nm)/SiO_2/Si(100) wafer by rf sputtering method using multiple targets of oxide and metal. As Yb and Nb sources, a 2 inch oxide target having the composition of $YbNbO_4$ was prepared from the Yb_2O_3 and Nb_2O_5 powder mixture. The mixture was pressed into a 6 cm pellet, and then the pellet was sintered at 1300°C for 3 h. The Pb and Ti metal targets of 3 inch diameter were also used. Each target is individually supplied with RF power. After the vacuum pressure reached 5×10^{-6} Torr, an O_2/Ar mixture gas was admitted to maintain the working pressure of 10 mTorr. The oxygen flow ratio (O_2/Ar + O_2) was 10% and the substrate temperature was 550~600°C. The overall sputtering conditions are listed in Table 1. X-ray diffraction technique was used to characterize the deposited film. The chemical composition of PYNT films was measured by electromicro probe analysis (EPMA).

3. Results

For multi-target sputtering deposition of PYNT films, their composition control is important. The formation of perovskite phase is critically affected by the stoichiometry of sputtered films. Careful attention needs to be paid to obtain the stoichiometric Yb/Nb ratio. As the Yb and Nb ions located at the B-site have different charge state (Yb^{3+} and Nb^{4+}), the compositional deviation from the stoichiometry breaks charge valence at the B-sites and inhibits formation of perovskite phase. In the case using separate metal targets of Yb and Nb, composition control was very difficult because total target was so many. To reduce the processing factor, the compound target of Yb and Nb was considered. Ceramic oxide compound of Yb and Nb could be easily synthesized by conventional solid solution reaction. We tried rf sputtering of the compound oxide target of $YbNbO_4$ (YN). Fig. 1 shows the Nb/(Yb + Nb) ratio obtained from EPMA results of the as-deposited PYNT film. The power density of Pb and Ti targets was fixed respectively at 2.2 and 1.8 W/cm^2. Although the measured ratio of Nb/(Yb + Nb) is dependent on the oxygen flow rate and the sputtering power, it was found that the sputtering conditions only marginally affected the film composition: the Yb/Nb ratios of the PYNT films broadly agreed with target composition.

PYNT films were prepared at 550°C with various sputtering power of Ti target to investigate the Ti composition effect on the perovskite phase formation. The powers of Pb and YN targets were fixed. The XRD profiles of PYNT film deposited indicate that the formation of the perovskite phase is very difficult below the critical sputtering power of Ti target (Fig. 2). Below 110 W of the Ti target power, the diffraction lines of pyrochlore phase becomes very large. Generally, the appearance of pyrochlore phase is believed to result from the Pb deficiency. In order to examine the Pb deficiency of thin films deposited at low Ti power, the film deposition was repeated at various sputtering powers applied to the Pb target.

Fig. 3 shows the XRD profiles of PYNT films deposited at 550°C as function of the Pb power (YN and Ti target powers are 130 and 105 W respectively). From compositional analysis, it has been found that that the ratios of Ti/(Yb + Nb + Ti) and Nb/(Yb + Nb) are about 0.6 and 0.5 respectively. Pb composition linearly increases and is finally saturated on further increasing

Table 1
Sputtering conditions of PYNT thin film

Base pressure (Torr)		$<5\times10^{-6}$
Working pressure (mTorr)		10
Ar:O_2		10:0~5:5
Substrate		PT/Ti/SiO_2/Si(100)
Substrate temperature (°C)		550–600
Substrate-target distance (cm)		10
Deposition rate		~5 nm/min
Power density (W/cm^2)	Pb (RF)	1.6–2.5
	Ti (RF)	1.6–2.5
	$YbNbO_4$(RF)	4.1–7.5

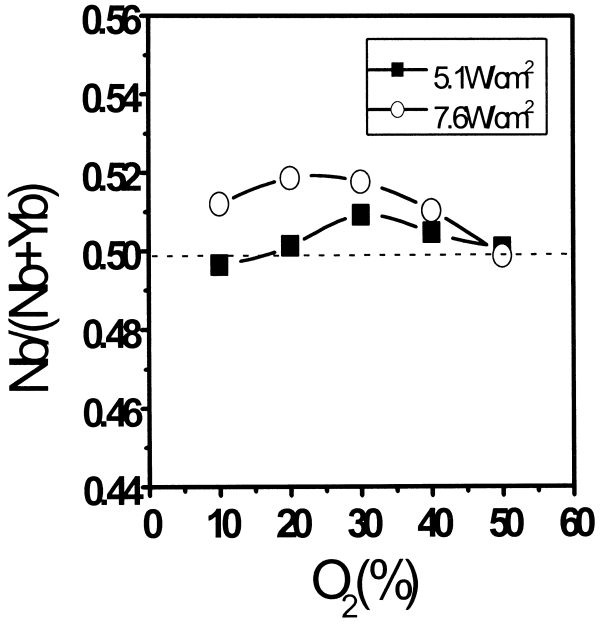

Fig. 1. Nb concentration of the deposited films analyzed by EPMA on the ration of O_2 flow rate (O_2/(Ar + O_2)). The sputtering power densities of $YbNbO_4$ target are 5.1 W/cm^2 (■) and 7.6W/cm^2 (○). Pb and Ti are fixed for the 2.2 and 18 W/cm^2.

Pb target power. The influence of Pb composition on formation of the perovskite phase is clearly observed in XRD results. With increase in the Pb power, the relative amount of pyrochlore phase is notably reduced. However, the pyroelectric phase is not completely removed by only control of Pb composition and its remnant becomes minimum at 100 W of the Pb target power. Beyond 100 W, a large amount of pyrochlore phase is observed again. This result indicates that Pb deficiency as well as its excess suppresses the formation of perovskite PYNT. Therefore, the processing window for deposition of perovskite PYNT thin films is very narrow. Among the many processing factors, the Pt substrate effect ought to be firstly considered. Difficulty in growing the perovskite phase of relaxor-PT on Pt substrate was previous reported in deposition of $Pb(Mg_{1/3}Nb_{2/3})O_3$-PT.[6] On conventional $Pt/Ti/SiO_2/Si$ substrates, thin films of pyrochlore phase were always formed in that experiment. The Pt layer is considered to play very crucial role in formation of the perovskite PYNT film.

The effect of Pt layer thickness of $Pt/Ti/SiO_2/Si$ substrate on the formation of perovskite phase was investigated. PYNT films were deposited on the substrates having the different thickness of Pt layer of 500, 2700 and 100 nm at 550°C. Before the deposition, each substrates were preheated at 550°C in 30 min. Although pyroclore phase is predominant on the 500 and 270 nm thick Pt layer, perovskite phase formed on the 100 nm Pt layer (Fig. 4). The formation and growth of perovskite phase can be affected by condition of the surface of Pt layer. For the $Pb(Zr,Ti)O_3$ (PZT) thin film, it was reported that intermetallic compound of Pt_3Pb have a influence on the perovskite orientation.[7] In the early study for the RF

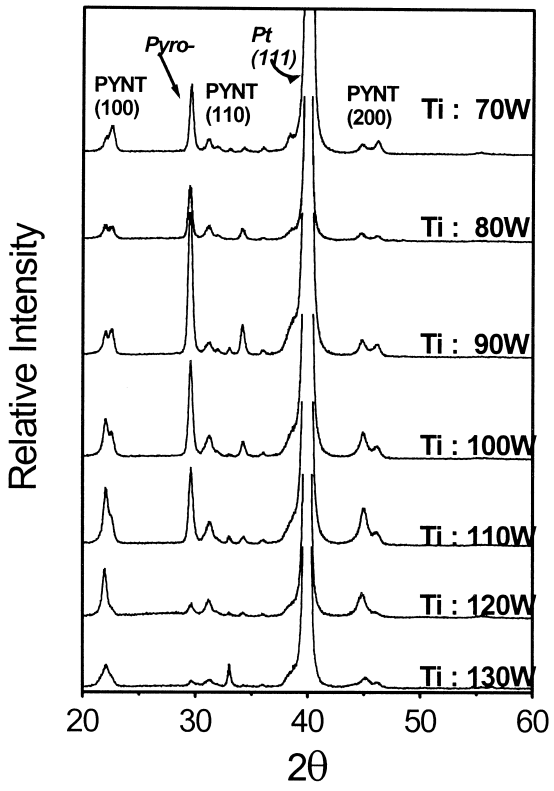

Fig. 2. XRD patterns of the PYNT films grown at 550°C in various Ti target powers. Sputtering powers of $YbNbO_3$ and Pb are fixed.

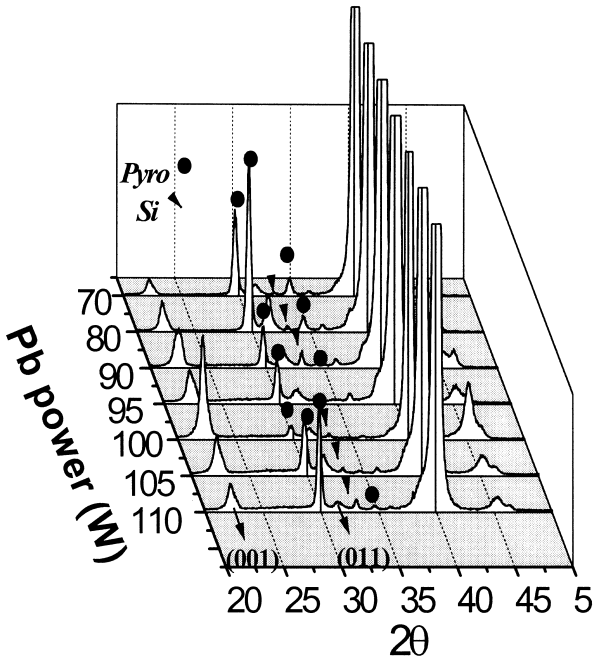

Fig. 3. XRD profiles of PYNT thin film with the Pb target power at 550°C.

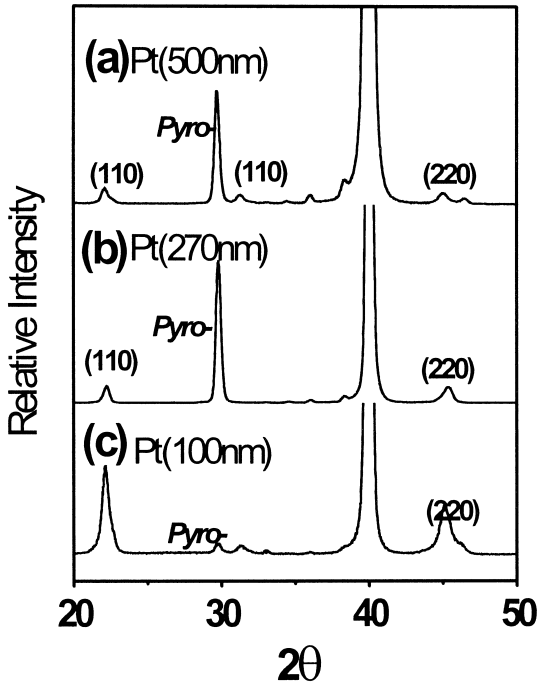

Fig. 4. X-ray diffraction patterns of thin film grown at 550°C with the same condition (Pb 100 W, YN 130 W, Ti 100 W) on the various substrate. (a) Pt(500 nm)/Ti(50 nm)/SiO_2/Si,(b) Pt(270 nm)/Ti (20 nm)/SiO_2/Si and (c) Pt(100 nm)/Ti(20 nm)/SiO_2/Si.

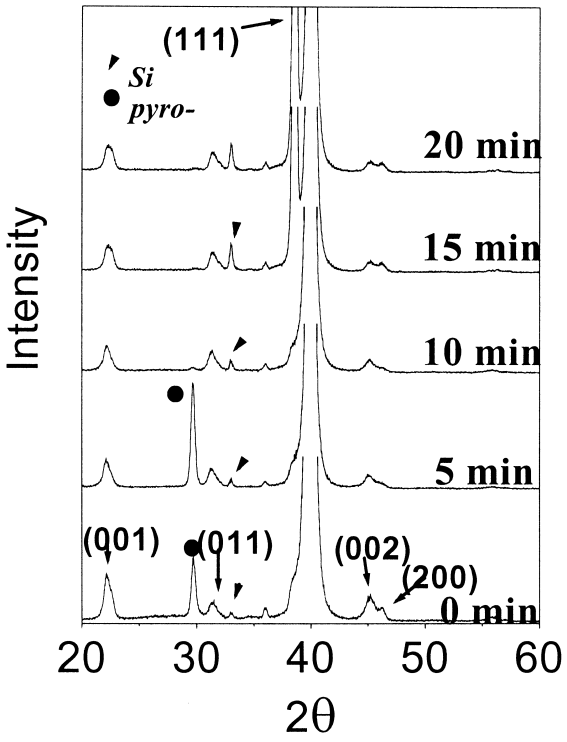

Fig. 5. XDR patterns of PYNT(40/60) thin film grown after deposition of TiO_2 on time of (a) 0 min, (b) 5 min, (c) 10 min, (d) 15 min and (e) 20 min.

sputtered PZT film, perovskite phase could be obtained only on the Pt/Ti/SiO_2/Si substrate.[8] On the pure Pt/SiO_2/Si, prochlore phase was observed. Ti moved toward surface of Pt layer by thermal diffusion was proposed to enhance the formation of perovskite. In the case of rather thin 100 nm Pt layer, Ti induced by thermal diffusion seems to assist the growth of perovskite PYNT phase by supplying nucleation sites. In the case using 500 and 270 nm Pt substrate, preheating time required for the diffusion of Ti atom may be insufficient because diffusion pass is relatively long.

Seed effect of Ti could be more clearly shown by using the substrate of Ti buffer layer on Pt. When PYNT was deposited on the substrates having Ti buffer layer, random orientated perovskite thin film was obtained. In order to control the orientation of PYNT film, it was also grown on the TiO_2 buffer layer. Fig. 5 shows the XRD patterns of the PYNT thin film on the TiO_2 buffer layer. Before deposition of the PYNT film, a TiO_2 layer was predeposited by the same condition of sputtering PYNT. At the power density of 2.27 W/cm^2, the growth rate of TiO_2 buffer layer was roughly about 1.2 nm/min. According to the change of deposition time of buffer TO_2 layer, the relative amounts of perovskite phase abruptly changed. While the perovskite and pyroclore phases coexist below 5 min of the time of TiO_2 deposition, the PYNT films on TiO_2 deposited longer than 10 min consist only of perovskite phase. The orientation of PYNT film is also affected by the TiO_2 buffer layer. Above 15 min of TiO_2 deposition time, strong perovskite 111 peak appears. Preferential (111) orientation of film on TiO_2 seed layer was also observed in the sol-gel coated $Pb(Mg_{1/3}Nb_{2/3})O_3$[9] and sputtering deposited PZT film.[10] The TiO_2 seed layer on top of Pt facilitates the perovskite nucleation and allows the growth of highly (111) oriented PYNT layer.

4. Conclusion

Rf magnetron sputtering was used to prepare ferroelectric PYNT films on the Pt/Ti/SiO_2/Si substrate. For control of composition, three targets of Pb, Ti and $YbNbO_4$ were used. The formation of perovskite phase was strongly affected by the Pt/Ti substrate. Thick Pt layers restrain the formation of perovskite grain, whereas pure perovskite phase is grown when TiO_2 buffer layer are used between PYNT and Pt.

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