Self-organized one-axis-oriented PZT films with nano-domain structure

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Abstract

{100} One-axis-oriented PZT films with a thickness of 2 μm were obtained on (111)Pt/TiO2/SiO2/(100)Si substrates by metal organic chemical vapor deposition (MOCVD). These were obtained irrespective of the film thickness up to 2 μm and with a Zr/(Zr + Ti) ratio from 0.20 to 0.75. This was found to be due to the higher growth rate of these orientation grains than {110} and {111)} orientation grains. These films had columnar grains 50–100 nm in width. Moreover, they were found to include 90° nano-domains 10–20 nm in width. Dielectric constant, 1 and the field induced-strain were maximum around a Zr/(Zr + Ti) ratio of 0.5, which was in good agreement with previous reports on sintered bodies with 100 times larger domains. This means that the domain size had any effect on 1 or field-induced strain.

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1. Introduction

Pb(Zr,Ti)O3 (PZT) has been widely used as an actuator and resonator due to its good piezoelectric and ferroelectric properties. Ways to control the crystal orientation of PZT films have been widely investigated so that they can be used in high performance devices. This is because these properties are known to strongly depend on crystal orientation [1]. In addition, the domain structure is also important in obtaining good piezoelectric and ferroelectric properties. Domain diameters have been observed to be less than 100 nm in films with thicknesses down to 10 μm, which is quite different from the widely used PZT sintered body where it has been above 1 μm [2]. An understanding of the formation mechanism behind nano-size domains and its contribution is essential to obtaining good film properties. The effect on the size of these domains on these properties is especially important because it is widely known to affect dielectric and ferroelectric characteristics [3].

In the present paper, we summarize the growth mechanism and the properties of self-organized one-axis-oriented PZT films deposited on an Si substrate covered with (111) preferred oriented Pt layers.

2. Experimental

PZT films were prepared at 600 °C by metal organic chemical vapor deposition (MOCVD) using apparatus with a vertical cold-wall-type reactor. Details on the preparation methods have already been reported elsewhere [4–6]. We selected MOCVD as the preparation method because of its high deposition rate and the high crystal quality of deposited films. (111)Pt/TiO2/SiO2/Si was used as the substrate, which is widely used in PZT-film preparation, especially non-volatile memory applications. (100), (110), and (111) orientated SrRuO3/SrTiO3 was also used as substrates to create epitaxial PZT films with {100}, {110} and {111} orientations [7].

The crystal structure and orientation of the films were measured by XRD and their microstructure was observed by transmission electron microscopy (TEM). The composition of the films was measured by wave length dispersive X-ray fluorescence. Electric-field-induced displacement and ferroelectric properties were measured simultaneously through a scanning probe microscope connected to a ferroelectric test system with a 100 μm-diameter Pt top electrode. Details on the measurement have already been reported elsewhere [8]. The dielectric constant was measured with an impedance analyzer with an oscillation voltage of 10 mV.
3. Results and discussions

3.1. Self-organized growth

Fig. 1 shows the thickness dependence of the XRD patterns for the PZT film thicknesses with a Zr/(Zr + Ti) ratio of 0.35. Film thicknesses were controlled by changing the deposition time. Only PZT 100 and PZT 001 peaks with tetragonal symmetry were observed together with those from substrates irrespective of the film thickness. This suggests that film was oriented to (100) and (001) irrespective of film thickness. Fig. 2 plots XRD patterns for 2 μm-thick PZT films with various Zr/(Zr + Ti) ratios from 0.20 to 0.75. The preferred orientation of (100) and/or (001) was ascertained irrespective of the Zr/(Zr + Ti) ratio of the films.

Taking into account the fact that the deposited films had a cubic symmetry when deposited at 600 °C and transformed from cubic to tetragonal and/or rhombohedral during cooling, the orientation in Fig. 2 originates from the same (100) orientation of the cubic PZT phase at a deposition temperature of 600 °C [9]. The results in Figs. 1 and 2 suggest that the PZT films are oriented to (100) of cubic PZT at the same deposition temperature, regardless of the film thickness or the Zr/(Zr + Ti) ratio in the film.

To understand the origin of the [100] orientation in Figs. 1 and 2, epitaxially grown films with [100], [110] and [111] orientations were grown on (100), (110) and (111) SrRuO3//SrTiO3 substrates. The films were ascertained to be epitaxially grown with in-plane alignment. Fig. 3 plots the thickness of these films as a function of the deposition time together with deposited on (111)Pt/TiO2/SiO2/Si substrates. The deposition rate of [100]-oriented epitaxial films was almost equal to that of [100]-oriented ones and was more than 1.5 times that of [110] and [111] substrates. These data clearly indicate that the [100] preferred orientations of PZT films on (111) Pt-coated Si substrates...
are due to their higher deposition rate than other orientations, i.e. self-organized {100} orientations.

When the deposition rate was 0.12 μm/h, 10 times lower than in the present study, the PZT films tended to have a (111) orientation because their grains were locally epitaxially grown on (111)Pt grains, (111)PZT//(111)Pt, due to its similar lattice parameters [10]. However, this local epitaxial growth was difficult to achieve when the deposition rate increased. Taking into account of the fact that film orientation changed from {111} to {100}, when the deposition temperature decreased [11], the relatively low deposition temperature and higher deposition rates are considered to be the key experimental parameters to {100} self-organized orientation.

Fig. 4 has TEM images of the interface between a PZT film with a Zr/(Zr + Ti) ratio of 0.33 prepared on (111)Pt/TiO2/SiO2/Si substrates. Polycrystalline {100}-preferred oriented PZT film with in-plane random orientation was ascertained to be directly prepared on (111)-oriented Pt layers without any noticeable interfacial layers. The films consisted of columnar grains that were 50–100 nm in width. In addition, clear 90° nano-domains 10–20 nm in thickness were clearly observed. This was about one-hundredth the thickness the sintered body.

4. Electrical properties

Fig. 5 plots the dielectric constant, $\varepsilon_r$, measured at 1 kHz as a function of the Zr/(Zr + Ti) ratio of the film. $\varepsilon_r$ had a maximum value of around 0.5, which was in good agreement with the reported data for a sintered body [11] and for PZT thin films [12,13].

Fig. 6 plots polarization–electric field ($P$–$E$) hysteresis loops and the saturation properties of remanent polarization ($P_r$) and coercive field ($E_c$) against the maximum applied electric field for {100}-oriented PZT films with different Zr/(Zr + Ti) ratios. Good saturation properties were obtained for all films. The $P_r$ value was almost constant above 30 μC/cm², but the $E_c$ value continued to decrease when the Zr/(Zr + Ti) ratio was increased.

Fig. 7(a) plots field-induced strain as a function of the Zr/(Zr + Ti) ratio. This was estimated from a unipolar-derived electric field between 0 and 100 kV/cm. It almost had a maximum around a Zr/(Zr + Ti) ratio of 0.5, which was also in good agreement with the reported data for a sintered body [11]. The field-induced strain from the electric field, from 0 to maximum ($E_{max}$), was proportional to $(P_{max}^2 - P_r^2)$, where $P_{max}$ was the polarization at $E_{max}$ [5]. $(P_{max}^2 - P_r^2)$ is also plotted in Fig. 7(b) as a function of the Zr/(Zr + Ti) ratio, where $P_{max}$ and $P_r$ were calculated from $P$–$E$ hysteresis under a unipolar-derived electric field. The Zr/(Zr + Ti) ratio dependency of the $(P_{max}^2 - P_r^2)$ is in good agreement with that of field-induced strain as we can seen in Fig. 7(a) and (b). These data indicate that field-induced strain can be estimated from $P$–$E$ hysteresis loops.

These data indicate that the change in $\varepsilon_r$ and field-induced strain based on the Zr/(Zr + Ti) ratio are in good agreement with the reported data on a PZT sintered body despite the fact that the domain size of the present films...
was about one hundredth the thickness of the sintered body. These data show that the effect domain size, the decrease of the $\varepsilon_r$ and $P_r$ with decreasing the domain size, had on the $\varepsilon_r$ and the field-induced strain were hardly noticeable down to 10 nm in the PZT.

5. Conclusions

Two micrometer thick PZT films were deposited on (111)Pt/TiO$_2$/SiO$_2$/(100)Si substrates by MOCVD. $\{100\}$ One-axis-oriented films were obtained, irrespective of film thickness up to 2 $\mu$m and with a Zr/(Zr + Ti) ratio from 0.20 to 0.75. $\{100\}$ orientation was due to the higher growth rate of their oriented grains than $\{110\}$ and $\{111\}$ oriented grains. These films consisted of columnar grains 50–100 nm in width, which included 90° nano-domains 10–20 nm in width. The $\varepsilon_r$ and field-induced strain were maximum around 0.5, which was in good agreement with previous reports on a sintered body with 100-times-larger domains. These data show that the effect domain size, decrease of the $\varepsilon_r$ and $P_r$ with decreasing the domain size, had on the $\varepsilon_r$ and the field-induced strain were hardly noticeable down to 10 nm in the PZT.

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