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Strain and orientation of $Pb(Zr,Ti)O_3$ and $PbTiO_3$ thin films prepared by MOCVD.

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The mechanism of determining the c-axis orientation of $Pb(Zr,Ti)O_3$ and $PbTiO_3$ films was discussed. The c-axis orientation increased with the increase in deposition temperature and the thermal expansion coefficient of the substrate and with the decrease in Curie temperature. Moreover, it was independent of the cooling rate after the deposition. Compressive strain above Curie temperature resulted in the higher degree of the c-axis orientation, while tensile strain in the lower degree of the c-axis orientation.

1. INTRODUCTION

Properties of $Pb(Zr_xTi_{1-x})O_3$ and $PbTiO_3$ films are known to depend on their orientation. The technology of controlling orientation of the film has been required to be established. Cooling rate[1] and the thermal expansion coefficient of substrate[2] are reported to be the factors that affect the degree of the c-axis orientation. However, the overall mechanism has not yet proposed. The purpose of this study is to establish the mechanism of the degree of the c-axis orientation.

The films of $Pb(Zr_xTi_{1-x})O_3$ and $PbTiO_3$ were prepared by MOCVD because it is characterized by its high controllability of the film composition and lower residual stress owing to the absence of high energy particles during the deposition. Therefore, MOCVD is thought to be the most appropriate process for the understanding of the c-axis orientation mechanism.

2. MODEL

We have already ascertained that $Pb(Zr,Ti)O_3$ and $PbTiO_3$ films transformed from tetragonal to cubic during the cooling process after the deposition[3]. Therefore, the process affecting the c-axis orientation of the film can be classified into following four processes.

(1) the deposition process
(2) the cooling process from deposition temperature to phase transformation temperature
(3) the phase transformation process
(4) the cooling process below the phase transformation temperature

In the process (1), the arrival of high energy particles to the film is considered to affect the c-axis orientation of the required film. In the process (2), strain in the film is caused by the differential thermal expansion between the film and the substrate and is considered to affect the c-axis orientation. The films of $Pb(Zr,Ti)O_3$ and $PbTiO_3$ transform from cubic to tetragonal phase at Curie temperature during cooling. This transformation of grains that are oriented <100> direction along the film thickness is schematically shown in Figure 1. Most of the remnant thermal strain can be supposed to be relieved during transformation by adjusting the volume ratio of c-axis oriented area (I) to a-axis oriented ones (II) and (III) [4] shown in Figure 1. This means that c-axis oriented area (I) increases with the increasing of the compressive strain along film plane and a-axis oriented area (II),(III) increases with the increasing of the tensile strain. Strain during the process (2) is represented by equation (1).

$$\varepsilon = (\alpha[\text{film}] - \alpha[\text{sub}])(T[\text{dep}] - T[\text{Curie point}]) \qquad (1)$$

where ε, α[film], α[sub], T[dep] and T[Curie point] represent thermal strain, thermal expansion coefficient of the film, thermal expansion coefficient of the substrate, deposition temperature and Curie temperature, respectively.

In the process (3), the relief of the strain described above is thought to be related to the state of the microstructure of the film. At this time, the degree of the c-axis orientation changes with microstructure in the process (3). In the process (4), the thermal strain remaining in the film is indicated by equation (2).

$$\varepsilon = (\alpha[\text{film}] - \alpha[\text{sub}])(T[\text{Curie point}] - T[\text{room}]) \qquad (2)$$

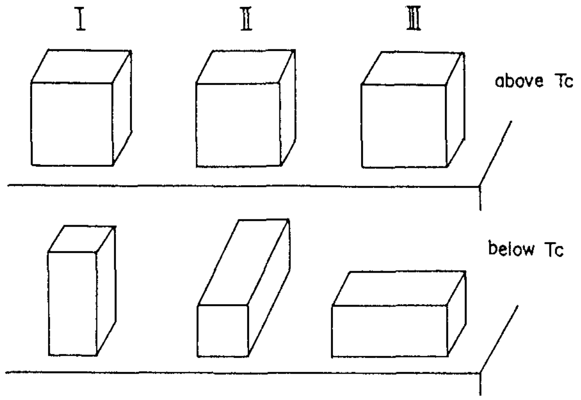

Figure 1. The schematic model of phase transformation of $Pb(Zr,Ti)O_3$ or $PbTiO_3$ from cubic to tetragonal during cooling.

where ε, α[film], α[sub], T[Curie point] and T[room] represent thermal strain, thermal expansion coefficient of the film, thermal expansion coefficient of the substrate, Curie temperature and room temperature, respectively. However, it has already confirmed by high temperature XRD that the degree of the c-axis orientation did not drastically change in the process (4). Therefore, this process (4) can be neglected in the present study. Therefore, the process from (1) to (3) can be thought to play an important role in determining the orientation.

3. EXPERIMENTAL

We investigated the orientation of tetragonal $Pb(Zr,Ti)O_3$ and $PbTiO_3$ films as parameters of cooling rate, compositions of the films, deposition temperature and thermal expansion of the substrates. The films of $Pb(Zr,Ti)O_3$ and $PbTiO_3$ were prepared by MOCVD from $Pb(DPM)_2$ - $Ti(O \cdot i\text{-}Pr)_4$ - $Zr(O \cdot t\text{-}Bu)_4$ -O_2 using a horizontal cold wall type apparatus. X-ray diffraction (XRD) was used for phase identification and estimation of the degree of the c-axis orientation. Degree of the c-axis orientation was defined as

$$I(001)/[I(100)+I(001)] \qquad (3)$$

where I(100) and I(001) represent the XRD intensity of (100) and (001) reflections, respectively. The composition of the films was measured by EDS analysis attached to SEM.

The deposition condition is summarized in Table 1. A single crystal of (100)MgO, (111)Pt(1000A)/SiO_2(1000A)/Si and fused silica were used as substrates and their thermal expansion coefficients were $13.8x10^{-6}$, $4.2x10^{-6}$ and $0.55x10^{-6}$, respectively[5]. The thermal expansion coefficient of the substrate of (111)Pt/SiO_2/Si is considered to be nearly equal to that of Si. The films of $Pb(Zr,Ti)O_3$ and $PbTiO_3$ on (100)MgO substrate were ascertained to be epitaxially grown and those on (111)Pt/SiO_2/Si substrates to have <100> and <001> orientation by pole figure measurement. On the other hand, those on fused silica substrates were nearly polycrystals.

4. RESULTS

Figure 2 shows the dependence of the degree of the c-axis orientation of $PbTiO_3$ films deposited on (111)Pt/SiO_2/Si and (100)MgO substrates on cooling rate after the deposition from 1 to 30°C/min. Matsubara et al.[1] reported that the orientation strongly depended on cooling rate in the case of epitaxially grown $PbTiO_3$ films on $MgAl_2O_4$/Si substrates prepared by RF magnetron sputtering. The cooling rate of 30°C/min and 1°C/min led to c-axis orientation and a-axis orientation, respectively. However, as shown in Figure 2 the degree of the c-axis orientation was independent of the cooling rate within the range from 1 to 30 °C/min irrespective of the substrate. Moreover, the degree of the c-axis orientation of film on (100)MgO substrate was larger than that on (111)Pt/SiO_2/Si substrate.

Figure 3 shows the degree of the c-axis orientation as a function of deposition temperature for $PbTiO_3$ film formed on (100)MgO substrate. The degree of the c-axis orientation increased linearly with the increase in the deposition temperature.

Figure 4 shows x in $Pb(Zr_xTi_{1-x})O_3$ dependence of the degree of the c-axis orientation of the films deposited

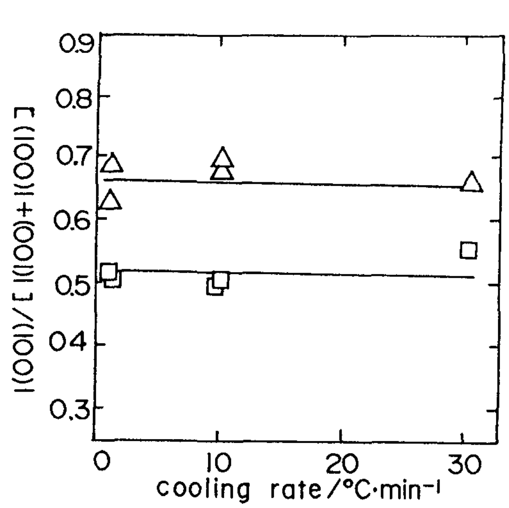

Figure 2. Degree of the c-axis orientation of $PbTiO_3$ films prepared at 570°C as a function of cooling rate. Substrate ; △: (100)MgO □: (111)Pt/SiO_2/Si

Table 1
Deposition conditions

Depositiontemperature	520-670°C
Substrate (100)MgO, (111)$Pt/O_2/Si$, fused silica	
Total presure	5 Torr
Totalgasflow rate	1000 SCCM
Flow rate of O_2	500 SCCM

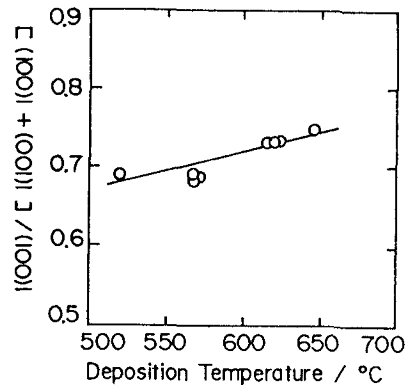

Figure 3. Degree of the c-axis orientation of $PbTiO_3$ films prepared on (100)MgO substrate as a function of deposition temperature.

on various substrates. The degree of the c-axis orientation of $Pb(Zr,Ti)O_3$ films on (100)MgO substrates increased with x in $Pb(Zr_xTi_{1-x})O_3$. On the other hand, those on (111)$Pt/SiO_2/Si$ substrates and fused silica substrates were independent of the composition x except the film with x=0 on fused silica substrate. Moreover, the degree of the c-axis orientation increased with the increase in the thermal expansion coefficient, that is, (100)MgO>(111)$Pt/SiO_2/Si$>fused silica.

5. DISCUSSION

5.1. Process (1)

Matsubara et al. [1] pointed out that the plasma field gave a serious effect on the orientation. The result of Matsubara et al. is considered to be affected by the factors that were peculiar to sputtering, such as the plasma field, the attack of accelerated high energy ions on the surface in the process (1) and so on. However, dependence of the cooling rate was not observed within the limit of the present study as shown in Figure 2. Therefore, the effect of the process (1) on the orientation is thought to be small. It can be concluded that the phenomena in the process (1) do not mainly determine the degree of the c-axis orientation of the film. This is attributed to the fact that MOCVD does not contain the high energy particles during the deposition, so that the strain in the film is lower than the other deposition methods from the vapor.

5.2. Process (2)

If the strain of the process (2) is most effective on the degree of the c-axis orientation, it is strongly influenced by equation (1). Equation (1) shows that the increase in the deposition temperature, the difference of the thermal expansion between the film and the substrate and the decrease in Curie temperature increase the strain in the film. In such a case, the c-axis orientation increased with the compressive strain and it decreased with the tensile strain. As shown in Figure 3, the degree of the c-axis orientation is linearly increased with the increase in the deposition temperature for $PbTiO_3$ films on (100)MgO substrate. Taking account of the fact that the thermal expansion of (100)MgO is larger than that of $PbTiO_3$ so that the compressive strain is applied to the film along the film plain, this result well agreed with the expectation from equation (1). Moreover, the degree of the c-axis orientation also increased with the increase in the thermal expansion coefficient of the substrate as shown in Figure 4. This result also well agrees with that from equation (1).

It is well known from $PbTiO_3$-$PbZrO_3$ phase diagram that the Curie temperature decreases with the increase in x in $Pb(Zr_xTi_{1-x})O_3$. Therefore, with the increase in x in $Pb(Zr_xTi_{1-x})O_3$, the strain in the film at Curie temperature is considered to increase according to equation (1). The strain for Figure 4 is calculated from equation (1) in order to investigate the effect of x and the thermal expansion of the film and shown in Figure 5. Tensile strain is expressed by positive value and compressive strain by negative value. Figure 5 shows that, overall composition range, the tensile and compressive strain in the process (2) result in the lower and higher degree of the c-axis orientation, respectively. The compressive strain of $Pb(Zr,Ti)O_3$ film prepared on (100)MgO substrate in the process (2) increased with the composition x in $Pb(Zr_xTi_{1-x})O_3$. It is clear that the increase in compressive strain in Figure 5 corresponded to the increase in the degree of the c-axis orientation of $Pb(Zr,Ti)O_3$ film on (100)MgO substrate in Figure 4. On the other hand, tensile strains of those on (111)$Pt/SiO_2/Si$ substrate and on fused silica substrate are nearly constant over the composition x in Figure 5. Therefore, the degrees of the c-axis orientation of those on (111)$Pt/SiO_2/Si$ substrate and on fused silica substrate do not change so much in Figure 4.

It is concluded that the degree of the c-axis

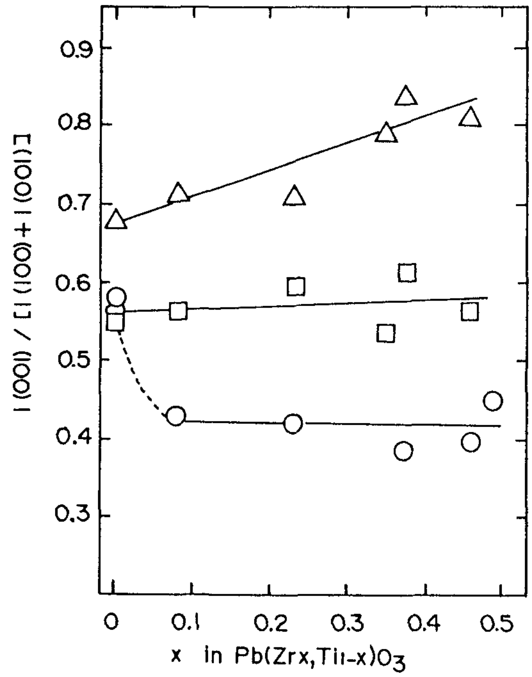

Figure 4. Degree of the c-axis orientation as a function of x in $Pb(Zr_xTi_{1-x})O_3$ films prepared at 570°C.
Substrate ; △: (100)MgO □: (111)$Pt/SiO_2/Si$
○ : fused silica

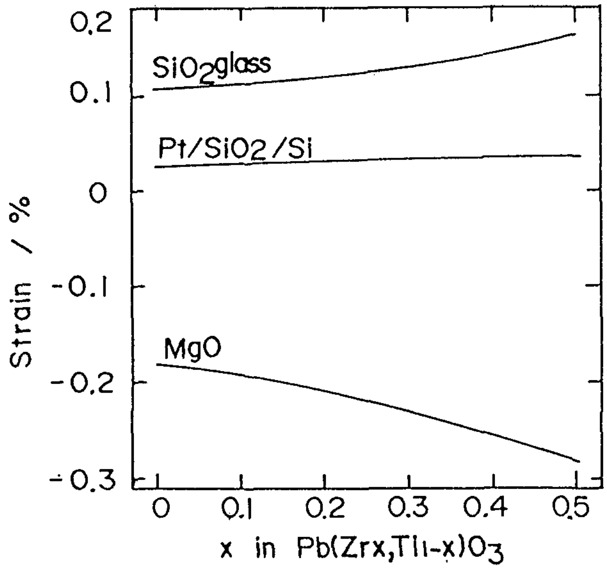

Figure 5. Calculated value of strain generated by cooling $Pb(Zr_xTi_{1-x})O_3$ films on (100)MgO, (111)$Pt/SiO_2/Si$ and fused silica substrates from 620°C of substrate temperature to Curie temperature.

orientation of $PbTiO_3$ and $Pb(Zr,Ti)O_3$ films by MOCVD must be mainly decided by the amount of thermal strain in the process (2). Based on the result of the present study, highly c-axis oriented $Pb(Zr,Ti)O_3$ and $PbTiO_3$ films could be prepared under more compressive strain in the process (2). Therefore, the degree of the c-axis orientation of $Pb(Zr,Ti)O_3$ and $PbTiO_3$ films can be increased by high deposition temperature, large thermal expansion coefficient of the substrate and low Curie temperature from equation (1).

5.3. Process (3)

As shown in Figure 2, the degree of the c-axis orientation was independent of the cooling rate after the deposition. It is revealed that the thermal strain in the process(2) is rapidly relieved by the phase transformation during the process(3). Under the thermal equilibrium condition, the total amount of thermal strain is apparently independent of cooling rate. Therefore, the effect of the process (3) on the degree of the c-axis orientation can be concluded to be smaller than that of the process (2).

6. CONCLUSION

We investigated the effect of the deposition parameters on the c-axis orientation and elucidated the c-axis orientation mechanism. The degree of the c-axis orientation increased with the increase in the deposition temperature and the thermal expansion coefficient of the substrate and with the decrease in Curie temperature. Moreover, it was independent of the cooling rate after the deposition. The model of classifying the cooling process into four parts was established. On the basis of this model and simple calculations, it was revealed that thermal strain from the deposition temperature and Curie temperature mainly determined orientation of $Pb(Zr,Ti)O_3$ and $PbTiO_3$ films.

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