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Preparation of Nb-doped $PbTiO_3$ Thin Films by Metalorganic Chemical Vapor Deposition

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Nb-doped $PbTiO_3[Pb(Nb,Ti)O_3]$ thin films were deposited by metalorganic chemical vapor deposition from $Pb(C_{11}H_{19}O_2)_2$ - $Nb(O\cdot C_2H_5)_5$ - $Ti(O\cdot i\text{-}C_3H_7)_4$ - O_2 system. The lattice parameters of c-axis and a-axis of the film decreased and increased, respectively, and the tetragonallity of the film decreased with increasing Nb content. Pyrochlore phase was codeposited with pervskite phase when the Nb content increased for the film deposited on (111)Pt/Ti/SiO_2/Si substrate. This pyrochlore phase was disappeared when the 60 nm-thick $PbTiO_3$ buffer film was firstly deposited on (111)Pt/Ti/SiO_2/Si substrate. The remanent polarization and coercive field of 400 nm thick $Pb(Nb,Ti)O_3$ film were 20.0 μC/cm^2 and 145 kV/cm, respectively.

Key words: $Pb(Nb,Ti)O_3$, MOCVD, ferroelectric property

1. INTRODUCTION

Lead titanate ($PbTiO_3$) type ferroelectric thin film has been demanded for the application to ferroelectric random access memories. Especially, Zr modified $PbTiO_3$, $Pb(Zr_xTi_{1-x})O_3$, film has been studied because of its high saturation polarization and Curie temperature[1]. However, Zr ion is greater than Ti ion, so that the temperature to get crystalline $Pb(Zr_xTi_{1-x})O_3$ film was about 100°C higher than that of $PbTiO_3$ film. Therefore, the investigation of another modified elements of $PbTiO_3$ is desirable. Some of elements , such as La and Ca, modified $PbTiO_3$ films were studied for the application to a infrared(IR) detector[2-3].

In the present study, we tried to prepared Nb-doped $PbTiO_3$, $Pb(Nb,Ti)O_3$, film. Nb ion substituting Ti site act as a donor and is expected to compensate the electron carrier originated from lead or oxygen vacancy, so that the leakage of the film decreased. Moreover, the size of Nb ion is almost the same as Ti ion, so that the crystalline temperature is expected to be almost equal to that of $PbTiO_3$ film. Nb-doped $PbTiO_3$ films have been prepared by sputtering [4,5] and sol-gel method[6,7]. In the present study, we firstly prepared Nb-doped $PbTiO_3$ film by metalorganic chemical vapor deposition(MOCVD) and investigated the constituent phase and the ferroelectric properties of these films. As a result, the film with high remanent polarization almost equal to $Pb(Zr_xTi_{1-x})O_3$ film was obtained.

2.EXPERIMENTAL

$Pb(Nb,Ti)O_3$ films were prepared by MOCVD

Table I Detailed deposition conditions

Source materials:	Temperature	Pressure	Ar carrier gas flow rate
$Pb(C_{11}H_{19}O_{11})_2$	140 °C	26.6 – 66.5 kPa	100-200 cm^3/min
$Nb(O\cdot C_2H_5)_5$	120 °C	26.6 – 66.5 kPa	12 - 100 cm^3/min
$Ti(O\cdot i\text{-}C_3H_7)_4$	41 °C	26.6 – 66.5 kPa	25 - 100 cm^3/min

Deposition temperature : 620 °C
Total gas flow rate : 1000 cm^3/min
(O_2 gas : 500 cm^3/min)
Chamber pressure : 665Pa

Substrate : (111)Pt/Ti/SiO_2/Si, (100)MgO single crystal
$PbTiO_3$/(111)Pt/Ti/SiO_2/Si

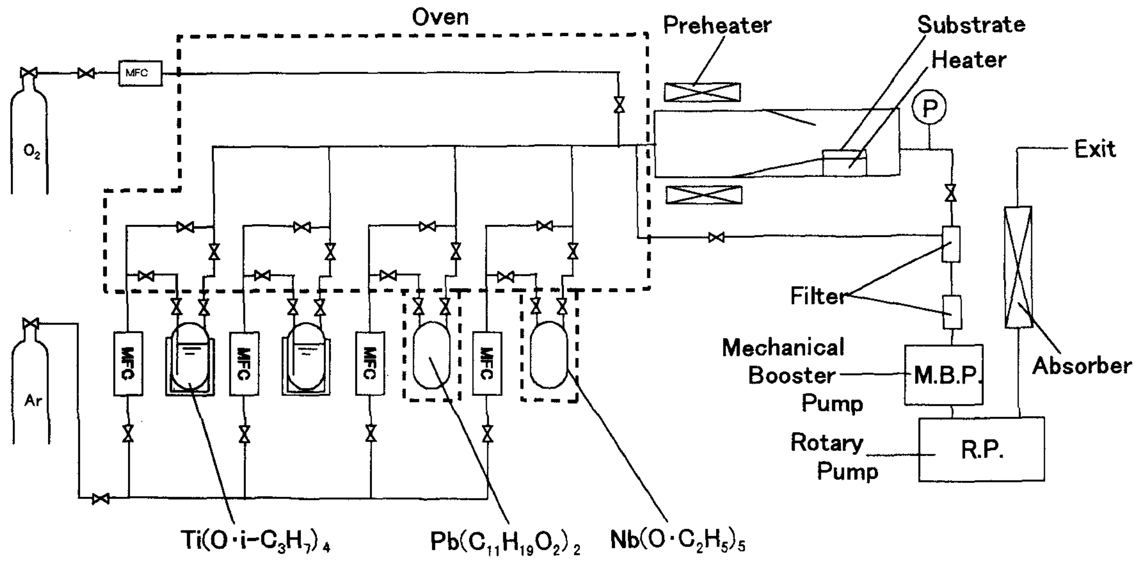

Figure1 Schematic diagram of the MOCVD apparatus used for $Pb(Nb,Ti)O_3$ film preparation.

using $Pb(C_{11}H_{19}O_2)_2$, $Nb(O\cdot C_2H_5)_5$, $Ti(O\cdot i\text{-}C_3H_7)_4$ and O_2 as source materials. Figure 1 shows the schematic diagram of the MOCVD apparatus used in the present study. Horizontal cold-wall type rector was used for the film deposition. This apparatus was almost the same for $Pb(Zr,Ti)O_3$ film preparation[8]. The vapor of $Pb(C_{11}H_{19}O_2)_2$ was generated by passing N_2 gas over a heated solid source. On the other hand, the vapors of $Ti(O\cdot i\text{-}C_3H_7)_4$ and $Nb(O\cdot C_2H_5)_5$ were generated by bubbling N_2 gases through heated liquid sources. Theoretical input gas concentration was defined as R[source][9]. $(111)Pt/Ti/SiO_2/Si$, (100)MgO single crystal and $PbTiO_3/(111)Pt/Ti/SiO_2/Si$ were used as substrates. The detailed deposition conditions are summarized in Table.I.

The constituent phase of the film was characterized by X-ray diffraction (XRD). The deposition amounts of each constituent elements and the composition of the films were measured by X-ray fluorescent (XRF). P-E hysteresis loops were measured using Sawyer-Tower circuit.

3. RESULTS AND DISCUSSION

Figure 2 shows the changes of the deposition rates of Pb, Nb and Ti elements in $Pb(Nb, Ti)O_3$ film as a function o f the input gas concentration of $Nb(O\cdot C_2H_5)_5$, $R[Nb(O\cdot C_2H_5)_5]$, under the fixed gas concentrations of $Pb(C_{11}H_{19}O_2)_2$ and $Ti(O\cdot i\text{-}C_3H_7)_4$. Deposition amount of Nb element increased with increasing $R[Nb(O\cdot C_2H_5)_5]$. However, the deposition amounts of Pb and Ti elements decreased and increased, respectively with increasing $R[Nb(O\cdot C_2H_5)_5]$ even though the gas concentrations of $Pb(C_{11}H_{19}O_2)_2$ and $Ti(O\cdot i\text{-}C_3H_7)_4$ were kept constant.

Figure 3 shows the XRD patterns of the same films shown in Fig.2 on $(111)Pt/Ti/SiO_2/Si$ substrates. The composition of the film was also shown in Fig.3. The perovskyte single phase changed to the mixed phases of perovskyte and pyrochlore with increaseing Nb content in the film. Pb/Ti ratio of pyrochlore phase is considered to be smaller than that of perovskite phase[10], so that the codeposition of pyrochlore phase at higher Nb content is considered to be originated to the decrease of Pb/Ti ratio in the film as shown in Fig.3. Therefore, Pb/Ti ratio was increased by changing the input gas concentration ratio of $Pb(C_{11}H_{19}O_2)_2$ to $Ti(O\cdot i\text{-}C_3H_7)_4$. However, pyrochlore phase was not disappeared, even though the Pb/Ti ratio was above unity. Therefore, the codeposition of the pyrochrore phase with perovskite phase was considered to be due to the incorporation of excess amount of Nb atom into the film as Iijima et al pointed out[5, 6].

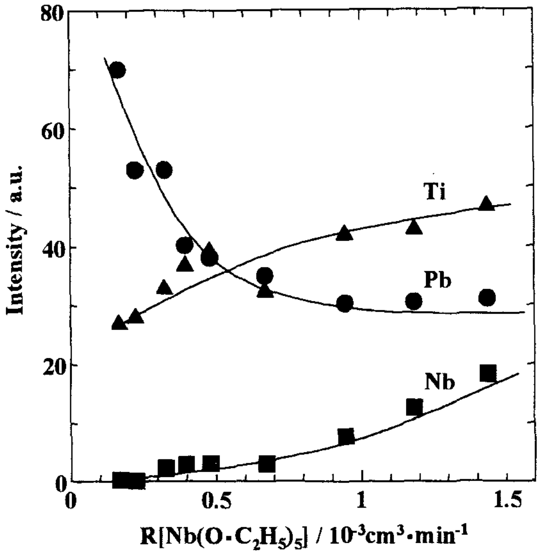

Figure2 Deposition amounts of Pb, Nb and Ti elements in $Pb(Nb,Ti)O_3$ film as a function of $R[Nb(O\cdot C_3H_5)_6]$. $\{R[Pb(C_{11}H_{19}O_2)_2=0.118cm^3/min$, $R[Ti(O\cdot i\text{-}C_3H_7)_4]=0.115cm^3/min\}$

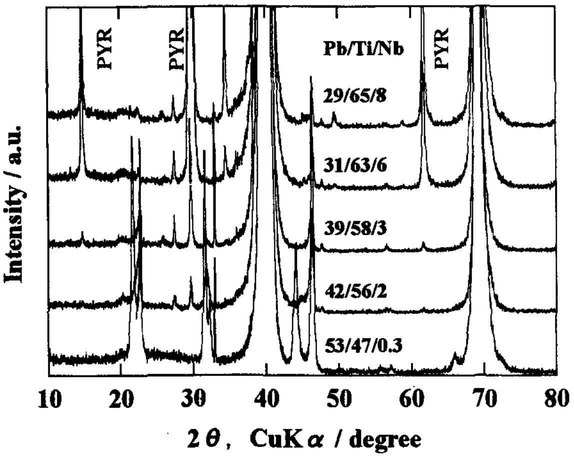

Figure3 Change of the XRD patterns with the film composition for the same films shown in Fig.2. Pb/Ti/Nb shows the atomic % of these elements. PRY: Pyrochlore phase

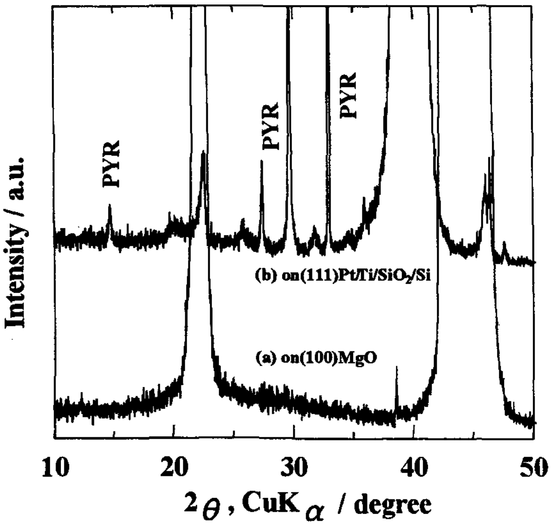

Figure4 XRD patterns of Pb (Nb, Ti)O_3 film on (a)(100)MgO (b)(111)Pt/SiO_2/ Si and (b)(111)Pt/SiO_2/Si substrate. Pb/Ti/Nb=39/58/3(at%)

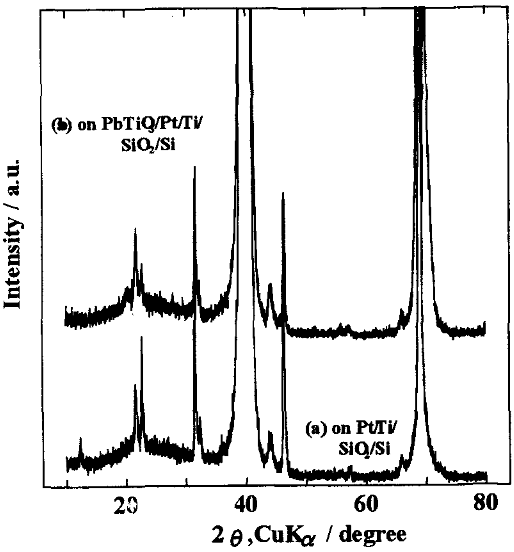

Figure5 XRD patterns of (a) $PbTiO_3$ buffer layer(60nm) on (111)Pt/Ti/SiO_2/Si substrate and (b)Pb(Nb,Ti)O_3 film deposition on it.

Figure 4 shows the XRD patterns of the film with Nb content of 3 at % on (111)Pt/SiO_2/Si and (100)MgO substrates. Pyrochlore phase was codeposited with perovskite phase on (111)Pt/Ti/SiO_2/Si substrate as shown in Fig.4(b). On the other hand, the perovskite single phase was deposited on (100)MgO substrate. Moreover, this film was ascertained to be epitaxially grown, (100)Pb(Nb,Ti)O_3//(100)MgO, by the X-ray pole figure measurement. This suggests that not only the composition of the film but also the kinds of the substrate affected the deposition of pyrochrore phase. Therefore, we tried to deposited buffer layer for the film preparation on (111)Pt/SiO_2/Si substrate. We selected $PbTiO_3$ as a buffer layer because this buffer layer is known to be effective to diminish pyrochlore phase in the case of Pb(Zr,Ti)O_3 film prepared by sol-gel method[11]. Figure 5 shows the XRD patterns of the 60 nm thick $PbTiO_3$ buffer layer on (111)Pt/Ti/SiO_2/Si substrate and Pb(Nb,Ti)O_3 film deposited on it. Nb content of this film was almost the same as that in Fig.4. Pyrochlore phase was not appeared by using $PbTiO_3$ buffer layer as shown in Fig.5. As a result, the $PbTiO_3$ buffer layer was also effective for the diminish of the pyrochlore phase in the case of Pb(Nb,Ti)O_3 film.

Figure 6 shows the change of the lattice parameters of Pb(Nb,Ti)O_3 film with Nb content in the film. The lattice parameters of c-axis and a-axis decreased and increased, respectively with increasing Nb content in the film. This tendency agreed with the previous Iijima's reports for the film deposited by sol-gel method[6,7]. This shows the lattice parameter ratio of c-axis to a-axis(c/a), tetragonallity, decreased with increasing Nb content. This result also suggested that Nb atom substituted to the $PbTiO_3$ lattice.

Figure 7 shows the P-E hysteresis curve of 400 nm-thick Pb(Nb,Ti)O_3 films deposited on 60 nm-thick $PbTiO_3$ buffered (111)Pt/SiO_2/Si substrate. Nb content of this film was about 5 at%. P-E hysteresis in Fig.7 showed the ferroelectric property of this film. The remanent polarization(P_r) and coercive field(E_c) of this film were 20.0 $\mu C/cm^2$ and 145 kV/cm, respectively. This E_c value was higher than the previous data for Pb(Nb,Ti)O_3 film and was almost equal to that of $Pb(Zr_{0.45}Ti_{0.55})O_3$ film[11]. However the leakage was relative high as shown in Fig.7, so that the depositions condition to get the lower leakage film is under optimization.

4.CONCLUSION

Nb-doped $PbTiO_3$[Pb(Nb,Ti)O_3] thin films were deposited by metalorganic chemical vapor deposition. $Pb(C_{11}H_{19}O_2)_2$, $Nb(O\cdot C_2H_5)_5$, Ti(O i-$C_3H_7)_4$ and O_2 were used as source materials. The lattice parameters of c-axis and a-axis of the film

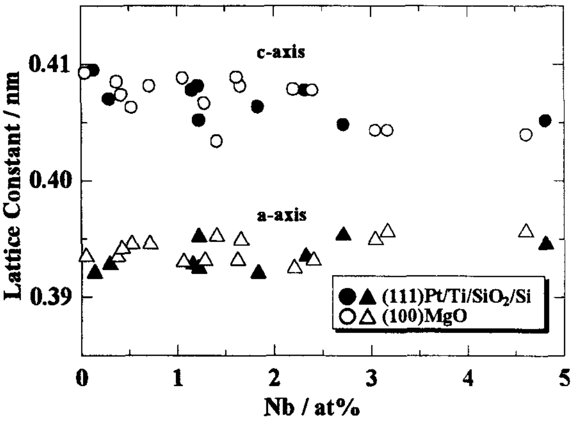

Figure6 Lattice parameters change of $Pb(Nb,Ti)O_3$ film with Nb content in the film.

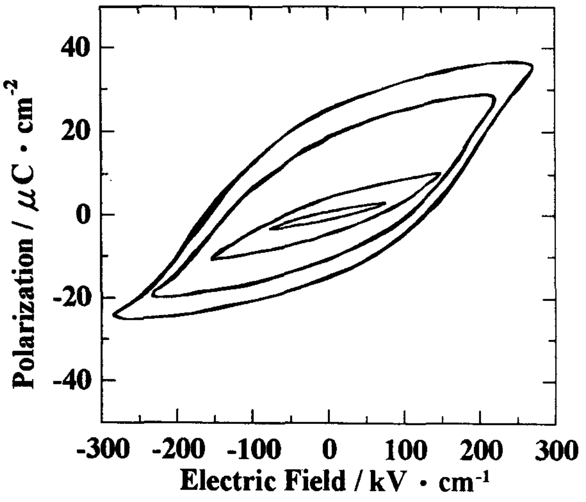

Figure7 P-E hysteresis loops of as-deposited $Pb(Nb,Ti)O_3$ film on $PbTiO_3$ buffered $(111)Pt/Ti/SiO_2/Si$ substrate.

were decreased and increased, respectively, and the tetragonallity of the film decreased with increasing Nb content. Pyrochlore phase was deposited when the Nb content in the film increased for the film deposited on $(111)Pt/Ti/SiO_2/Si$ substrate. This pyrochlore phase was disappeared when the 60 nm-thick $PbTiO_3$ buffer film was firstly deposited on $(111)Pt/Ti/SiO_2/Si$ substrate. The remanent polarization and coercive field of 400 nm thick $Pb(Nb,Ti)O_3$ films were 20.0 μC/cm^2 and 145 kV/cm, respectively.

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