STUDY OF DEPOSITION PROCESSES IN PZT FILMS GROWN BY LIQUID DELIVERY MOCVD

Masaki Kurasawa[1)], Masaaki Nakabayashi[2)], Kou Nakamura[2)], Kenji Maruyama[1)], Takashi Eshita[2)], Kazuaki Kurihara[1)]

1) Fujitsu Laboratories LTD. 10-1 Morinosato-Wakamiya, Atsugi 243-0197, Japan
2)Fujitsu LTD. 10-1 Morinosato-Wakamiya, Atsugi 243-0197, Japan

Lead zirconate titanate, $Pb(Zr,Ti)O_3$ (PZT), a ferroelectirc material with perovskte sturcture, is a promising material for application to nonvolatile ferroelectric random access memory. MOCVD is one of the most important techniques for practical applications because of its more conformal coverage, high deposition rate, large area uniformity, and high throughput. Some studies have been widely reported on the structure and properties of the PZT thin films grown by liquid delivery MOCVD. However, there are little reports on the precursor chemistry, and the film-deposition mechanism in PZT films grown by MOCVD. In this paper, we report a deposition process in PZT thin films using several β-diketonate precursors by liquid delivery MOCVD.

Figure 1 shows temperature dependence of incorporation rates for Pb, Zr and Ti elements in PZT films deposited using Pb-bis(tetramethyl-heptanedionate) ($Pb(THD)_2$), Zr-tetrakis(dimethyl-heptandionate) ($Zr(DMHD)_4$), and Ti-di(ipropoxy)bis(tetramehyl-heptanedionate) ($Ti(OiPr)_2(THD)_2$) sources. Decreases of incorporation rates are observed for Pb at temperature above 580 ˚C, for Zr above 500˚C and for Ti above 580˚C.

Figure 2 shows the temperature dependence of incorporation rates for Pb and Ti in $PbTiO_3$ films. Decrease of incorporation rates is not observed at temperature above 580 ˚C even though the same Pb and Ti source materials are used as those in figure 1. This indicates that the decrease of incorporation rate for Pb and Ti with temperature is not due to pyrolysis for PZT film deposition. It is considered to be due to interactions between Pb and Zr sources and between Ti and Zr sources. Furthermore, although a surface reaction kinetics limited deposition is observed in Pb incorporation rate in $PbTiO_3$ films at low temperature below 500 ˚C, it is not found in the case of PZT films deposited using $Zr(DMHD)_4$ sources. Pb incorporation is almost independent on temperature like a mass-transport-limited regime. Ti incorporation rate in PZT films is almost the same with that in $PbTiO_3$ films in low temperature below 550 ˚C. Therefore, an interaction between $Pb(THD)_2$ and $Zr(DMHD)_2$ occurs at temperature as low as 450 ˚C. On the other hand, an interaction between $Ti(OiPr)_2(THD)_2$ and $Zr(DMHD)_4$ occurs at higher temperature above 580˚C.

Figure 3 shows temperature dependence of incorporation rates for Pb, Zr and Ti element in PZT films deposited using $Pb(THD)_2$, Zr-tetrakis(tetramethyl - heptandionate) ($Zr(THD)_4$) and $Ti(OiPr)_2(THD)_2$ as source materials. The decrease of the rate is not observed for all elements above 580 ˚C.

In the case of PZT films grown using all THD-based precursors, the decrease of incorporation rates is not observed at high temperature. In contrast, decrease of incorporation rates is observed in PZT films using $Zr(DMHD)_2$ having different ligands with other sources. We postulated that the deposition rate decrease in the high temperature region was caused by a ligand exchange reaction between THD- and DMHD -based precursors in vapor phase. Generally, DMHD based precursor shows higher vapor pressure and lower decompose temperature rather than those for THD based precursors. Therefore, the incorporation rates for Pb and Ti in PZT deposition using $Zr(DMHD)_4$ decrease due to redesorption or decomposition of ligand exchanged precursors before PZT film deposition.

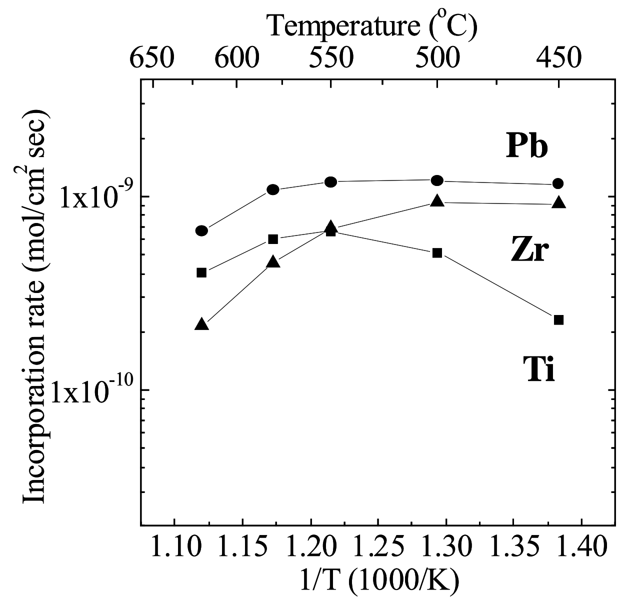

Fig.1 Temperature dependence of incorporation rates for Pb, Zr and Ti in PZT films deposited using $Pb(THD)_2$, $Zr(DMHD)_4$ and $Ti(OiPr)_2(THD)_2$

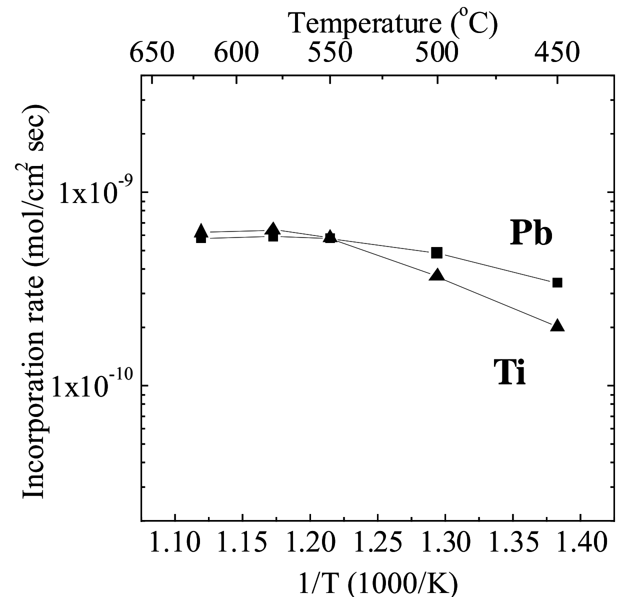

Fig.2 Temperature dependence of incorporation rates for Pb and Ti in $PbTiO_3$ films deposited using $Pb(THD)_2$ and $Ti(OiPr)_2(THD)_2$

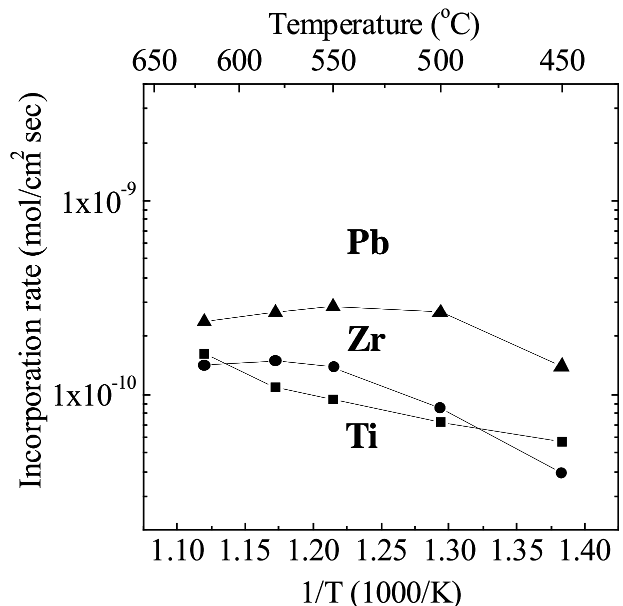

Fig.3 Temperature dependence of incorporation rates for Pb, Zr and Ti in PZT films deposited using all THD-based precursors