

INVESTIGATION OF GAS-PHASE REACTION EFFECTIVE ON DEPOSITION BEHAVIOR IN MOCVD-Pb(Zr,Ti)O₃ FILM USING *IN-SITU*-MONITORED BY FOURIER TRANSFORM INFRARED SPECTROSCOPY

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Introduction

Pb(Zr,Ti)O₃ (PZT) films has been widely investigated not only for ferroelectric random access memory (FeRAM) but also MEMS applications. MOCVD is one of the most promising deposition methods because of its high conformability, high deposition rate, and large area uniformity of the film quality (1). However, indirect response between the deposited film composition and that of the starting source gases were ascertained for the film preparation from Pb(C₁₁H₁₉O₂)₂, Zr(O·*t*-C₄H₉)₄, Ti(O·*i*-C₃H₇)₄ and O₂ system (2). This suggests the possibility of the pre reaction of the sources prior to reaching the substrate and/or the selective reaction on the surface. In the present study, the gas phase reaction of source gases was *in-situ* observed using Fourier Transform Infrared Spectroscopy (FT-IR). On the basis of these data, the effect of the gas-phase reaction on the deposition behavior was investigated.

Experimental

PZT film were deposited on thermally oxidized Si substrate at 510 °C from Pb(C₁₁H₁₉O₂)₂-Zr(O·*t*-C₄H₉)₄-Ti(O·*i*-C₃H₇)₄-O₂ system, using horizontal cold-wall type reactor. FT-IR equipment (Horiba, Ltd.) and high temperature gas cell were set in-line where the temperature was kept at 180 °C.

Theoretical gas concentration of each gas was defined as $R[\text{source}]$ (3), and only $R[\text{Pb}(\text{C}_{11}\text{H}_{19}\text{O}_2)_2]$ was changed under constant $R[\text{Zr}(\text{O}\cdot t\text{-C}_4\text{H}_9)_4]$ and $R[\text{Ti}(\text{O}\cdot i\text{-C}_3\text{H}_7)_4]$. Deposition rates of the constituent element were estimated by XRF using standard samples.

Results and Discussions

Figures 1 (a) and (b) show the summation of IR spectra separately measured for each source gas and that of mixture of above sources, respectively. By comparing these two spectra, the gas phase reaction was confirmed by mixing, e.g. peak shift around 1200-1100 cm⁻¹ and the increase and the decrease of the peak intensity around 1000cm⁻¹ and 900-700 cm⁻¹, respectively. Therefore, the gas phase reaction was occurred before these gases reached to the reaction chamber. Figure 1 (c) shows the spectrum in which O₂ gas was added into the source system as shown in Fig. 1 (b), suggesting that O₂ gas did not react at gas phase at this temperature.

Figure 2 shows $R[\text{Pb}(\text{C}_{11}\text{H}_{19}\text{O}_2)_2]$ dependence of the deposition rate of the constituent elements of the film and the absorbance of the characteristic peak of the corresponding source element under the fixed $R[\text{Zr}(\text{O}\cdot t\text{-C}_4\text{H}_9)_4]$

and $R[\text{Ti}(\text{O}\cdot i\text{-C}_3\text{H}_7)_4]$. Deposition rate and the absorbance show almost same tendency against $R[\text{Pb}(\text{C}_{11}\text{H}_{19}\text{O}_2)_2]$. This suggests that the deposition rates of Zr and Ti elements were determined by gas-phase reaction and can be controlled by their absorbances of Zr and Ti. On the other hand, the absorbance related to the Pb source linearly increased with $R[\text{Pb}(\text{C}_{11}\text{H}_{19}\text{O}_2)_2]$, but did not respond to the deposition rate of Pb element, as shown in Fig. 2 (a). Especially, the deposition rate of Pb became constant in the rang of $R[\text{Pb}(\text{C}_{11}\text{H}_{19}\text{O}_2)_2]$ from 0.15-0.22 cm³/min. This deposition rate corresponds to the summation of those of Zr and Ti elements, suggesting to maintain the stoichiometric PZT. This denotes that the deposition rate of Pb element mainly determined by surface reaction on substrates.

References

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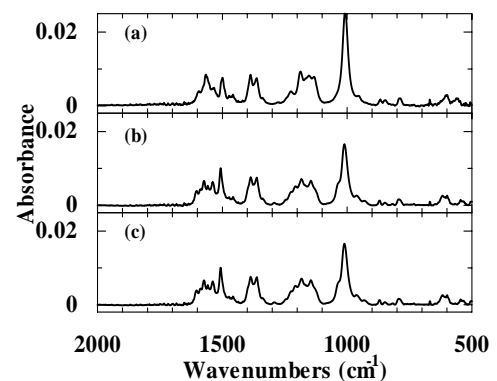


Fig. 1. Infrared spectra of (a) summation of individually measured each source, (b) mixture of Pb, Zr and Ti sources, and (c) mixture of Pb, Zr and Ti sources with O₂.

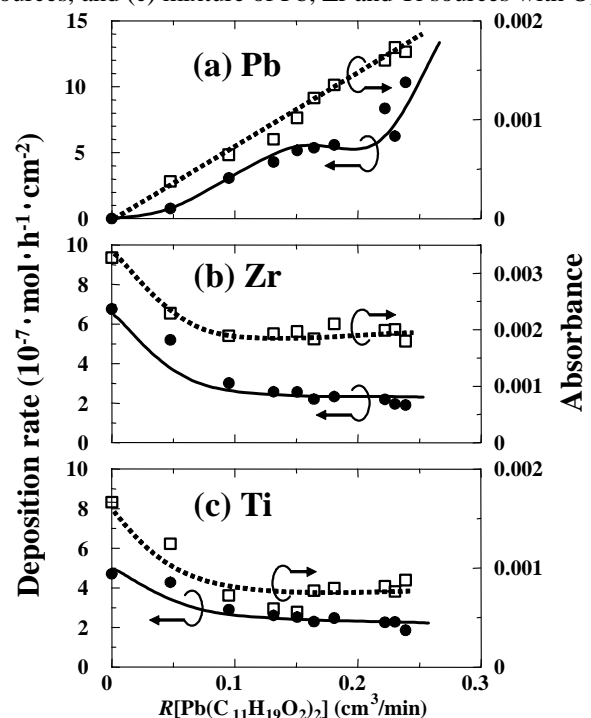


Fig. 2. $R[\text{Pb}(\text{C}_{11}\text{H}_{19}\text{O}_2)_2]$ dependence of the deposition rate of the constituent elements (○) and the absorbance of the characteristic peak of the each corresponding elements (□).