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In situ FTIR investigation of the effect of gas-phase reaction on the deposition of $Pb(Zr,Ti)O_3$ films by MOCVD

Gouji Asano [a], Tsukasa Satake [b], Kunio Ohtsuki [b], Hiroshi Funakubo [a,*]

[a] *Department of Innovative and Engineered Materials, Tokyo Institute of Technology, G1-405, 4259 Nagatsuta-cho, Midori-ku, Yokohama 226-8502, Japan*
[b] *Horiba, Ltd. Miyanohigashi, Kisshoin, Minami-ku, Kyoto 601-8510, Japan*

Abstract

The effect of gas-phase reaction on the deposition of $Pb(Zr,Ti)O_3$ films by metal organic chemical vapor deposition (MOCVD) was in situ investigated by Fourier Transform Infrared (FTIR) spectroscopy. $Pb(C_{11}H_{19}O_2)_2$, $Zr(O\cdot t{-}C_4H_9)_4$, and $Ti(O\cdot i{-}C_3H_7)_4$ were used as source gases, which was widely investigated for MOCVD–$Pb(Zr,Ti)O_3$ deposition. We investigated various source-gas combinations and detected a gas-phase reaction in the mixtures containing Zr source gas. Moreover, the deposition rates of the Zr and Ti oxides in the films were found to be determined by the actual source gas concentration after gas-phase reaction and could be controlled by the absorbance spectrum intensities of the Zr and Ti source gases. In contrast, the deposition rate of the Pb oxide was mainly determined by the surface reaction on the substrate for making PZT single phase.

Keywords: In situ observation; MOCVD; FT-IR

1. Introduction

$Pb(Zr,Ti)O_3$ [PZT] has a perovskite type of structure generally described as ABO_3. PZT films have been widely investigated not only for use in ferroelectric random access memory (FeRAM) but also in micro-electro-mechanical system (MEMS) applications [1]. Metal organic chemical vapor deposition (MOCVD) is one of the most promising deposition methods because it has a lot of advantages [2,3]. Film composition must be precisely controlled because it determines the film properties [4–6]. An indirect relationship between the composition of the deposited films and the input source gas concentration was observed in the MOCVD process [7,8]. This suggests the possibility of a gas-phase reaction of the source gases prior to reaching the substrate and/or their selective reaction on the substrate surface. The quantitative evaluation method of gas-phase reaction must be established for the precise control of the film composition. Such a method will also help to understand the surface reaction on the substrate surface. There have been a number of reports of in situ observation of gas-phase reaction [9–17]. One of the widely accepted techniques for this kind of observation is Fourier Transform Infrared (FTIR) spectroscopy having lots of advantages such as a wide dynamic range and the possibility of a detailed analysis of gas-phase reaction.

In the present study, we in situ investigated the dependence of the supply rate and gas-phase reaction of source gases on the composition and the deposition rates of the constituent oxide by using FTIR spectroscopy. On the basis of the obtained data, we examined the effect of gas-phase reaction on the deposition of PZT films.

2. Experimental

PZT films were deposited on a thermally oxidized Si substrates at 510 °C from a $Pb(C_{11}H_{19}O_2)_2$–$Zr(O\cdot t{-}C_4H_9)_4$–$Ti(O\cdot i{-}C_3H_7)_4$–O_2 system which was widely used in MOCVD–PZT [4]. The reactor pressure and the total gas flow rate were 670 Pa and 1000 cm^3/min, respectively. Fig. 1 shows a schematic diagram of the MOCVD apparatus used in the present study. The FTIR equipment (Horiba,

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* Corresponding author. Tel.: +81 45 924 5446; fax: +81 45 924 5446.
E-mail address: funakubo@iem.tittech.ac.jp (H. Funakubo).

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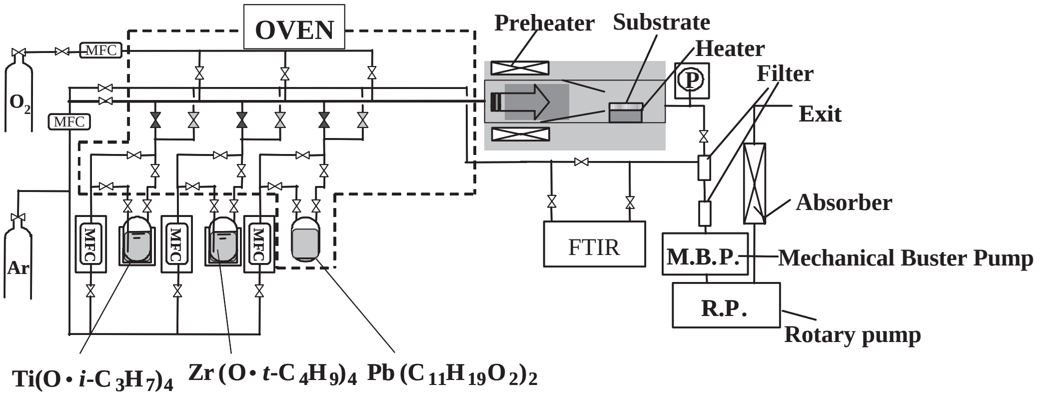

Fig. 1. Schematic diagram of the MOCVD apparatus with an FTIR monitor.

Ltd.) and the high-temperature gas cell with KRS-5 windows kept at 180 °C were set in-line.

The partial pressures of the source gases were controlled through the vapor pressure of the precursor [$P_i(T_v)$], which depends on the temperature of the source (T_v), the pressure of the vessel (P_v), and the carrier gas flow rates (l). These parameters are related to the source gas concentration, R[source] [18].

$$\frac{P_i(T_v)\cdot l}{P_v} = R[\text{source}] \qquad (1)$$

In the present study, the partial pressures of $Pb(C_{11}H_{19}O_2)_2$, $Zr(O\cdot t{-}C_4H_9)_4$, and $Ti(O\cdot i{-}C_3H_7)_4$ during the measurement were 0.4 to 13.3 Pa, 0.3 to 7.5 Pa, and 0.7 to 15.9 Pa, respectively. The film composition was estimated by XRF calibrated using standard samples. The deposition rate of each constituent oxide was measured from the weight gain of the substrate after the deposition and the intensity of the XRF.

3. Results and discussion

3.1. Single-source supply

We measured the FTIR spectrum of each source material in a gas phase. Fig. 2 shows the infrared adsorption spectra of $Pb(C_{11}H_{19}O_2)_2$, $Zr(O\cdot t{-}C_4H_9)_4$, and $Ti(O\cdot i{-}C_3H_7)_4$ in a gas phase, which were introduced individually. A clear spectrum with characteristic peaks was measured for each source gas. Thus, clear spectra with a good signal-to-noise ratio (SNR) can indeed be measured using an actual MOCVD system. The spectrum of $Pb(C_{11}H_{19}O_2)_2$ was in good agreement with that reported previously by Matsuzaki et al. [18].

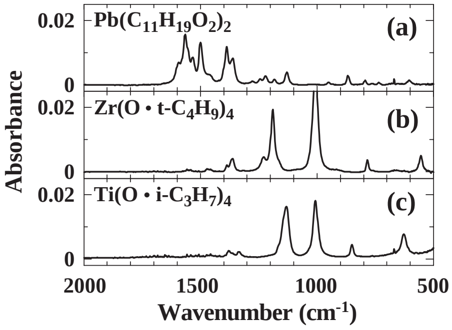

Fig. 2. Infrared absorbance spectra of (a) Pb, (b) Zr and (c) Ti gas-phase material sources.

Fig. 3 shows the absorbance peak intensity of each source gas as a function of the partial pressure of $Pb(C_{11}H_{19}O_2)_2$, $Zr(O\cdot t{-}C_4H_9)_4$, and $Ti(O\cdot i{-}C_3H_7)_4$, which were introduced individually into the gas cell. We selected absorbance peaks at 1500, 555, and 626 cm^{-1} for the Pb, Zr, and Ti sources, which were reported to be assigned to C–O, C–C, and C–H stretching modes [20,21], a Zr–O stretching mode [22], and a Ti–O stretching mode [21,23], respectively. A good linear relationship was observed between the partial pressure of source gas and absorbance peak intensity for all the sources. These results show that the absorbance spectrum intensity of each source depended on the concentration and supply rate of the source gas.

3.2. Multi-source supply

We mixed source gases and observed infrared spectra by supplying multiple sources of gases. Fig. 4(a), (c), and (e) show the mathematical sum of the infrared spectra of $Pb(C_{11}H_{19}O_2)_2$ and $Ti(O\cdot i{-}C_3H_7)_4$, $Pb(C_{11}H_{19}O_2)_2$ and $Zr(O\cdot t{-}C_4H_9)_4$, and $Zr(O\cdot t{-}C_4H_9)_4$ and $Ti(O\cdot i{-}C_3H_7)_4$, respectively. On the other hand, Fig. 4(b), (d), and (f) show the actual measured infrared spectra of the mixed gases. By comparing Fig. 4(a) and (b), we found that the two spectra were practically the same, suggesting that there was no gas-phase reaction by the mixing the gases of $Pb(C_{11}H_{19}O_2)_2$ and $Ti(O\cdot i{-}C_3H_7)_4$. However, as shown in Fig. 4(c)–(f), gas-phase reactions were observed by other mixing source gases combinations because the spectra in Fig. 4(c) and (d) and those in Fig. 4(e) and (f) were different.

In the case of the $Zr(O\cdot t{-}C_4H_9)_4$ and $Ti(O\cdot i{-}C_3H_7)_4$ mixture, peak shifts were observed at 1200–1100 cm^{-1}, 850–750 cm^{-1} and 650–550 cm^{-1}. Fig. 5 shows a typical