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In situ gas-phase FTIR monitoring of liquid delivery MOCVD process for PZT film preparation

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Abstract

Fourier transform infrared (FTIR) monitoring of the $Pb(C_{11}H_{19}O_2)_2$–$Zr(C_9H_{15}O_2)_4$–$i(Oi\text{-}C_3H_7)_2(C_{11}H_{19}O_2)_2$–$O_2$ system diluted in C_8H_{18} solvent and used to fabricate MOCVD-$Pb(Zr,Ti)O_3$ films was investigated. No obvious gas-phase reactions between the sources and the C_8H_{18} were detected. Analysis of the FTIR spectra of single source supply and of mixtures after removing the C_8H_{18} spectrum showed that FTIR concentration monitoring was able to measure the concentration of source gases in a mixture by identifying the characteristic FTIR peaks.

Keywords: MOCVD; $Pb(Zr,Ti)O_3$; FTIR; In situ monitoring

1. Introduction

Thin films of multi-component oxides with perovskite structures, such as $Pb(Zr,Ti)O_3$ [PZT] and $(La,Sr)MnO_3$, have a variety of functions [1]. The properties that make these oxides so useful depend on the composition of the films, so controlling the composition of the films is key to controlling the properties of the obtained films.

Metal organic chemical vapor deposition (MOCVD) is one of the most important methods of preparing these films because of the large area uniformity of film thickness and the compositions of the films it can create [2]. Indirect relationships between the input source gas ratio and the composition of the deposited film have been reported for MOCVD-PZT films, and the gas-phase reaction was found to be one of the origins of this indirect relationship [3,4]. Therefore, precisely controlling the concentration of each source material supplied to the substrate and controlling the gas-phase reaction are critical issues in fabricating films with the desired composition.

We proposed in situ gas-phase monitoring using Fourier transform infrared (FTIR) for the MOCVD-PZT process to detect the gas-phase reaction and determine the concentration of each source gas [5]. Recently, source materials with lower vapor pressure were vaporized using the so-called liquid delivery method, in which source materials are dissolved into the solvent and are vaporized with a vaporizer [4,6,7]. This liquid delivery MOCVD has the advantage of being able to increase the deposition rate by increasing the input gas flow rates of the source, even if the vapor pressure of the source is low. However, this process introduces additional solvent into the source gas system, makes in situ monitoring by FTIR difficult, and increases the likelihood of an additional gas-phase reaction [7].

In the present study, the application of in situ FTIR monitoring of a source gas system using MOCVD-PZT film deposition was investigated.

2. Experimental

The source gas system for $Pb(C_{11}H_{19}O_2)_2$–$Zr(C_9H_{15}O_2)_4$–$Ti(Oi\text{-}C_3H_7)_2(C_{11}H_{19}O_2)_2$–$O_2$ for MOCVD-PZT film deposition was investigated [6]. These source materials were dissolved into C_8H_{18} and vaporized in individual vaporizers [7]. Vaporizer

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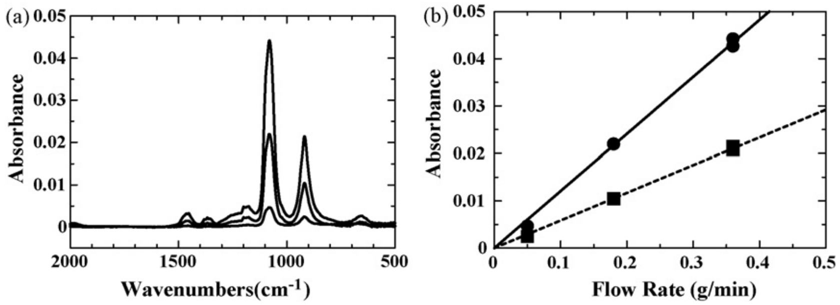

Fig. 1. (a) FTIR spectra of C_8H_{18} at different flow rates and (b) absorbance peak intensity at 1080 cm^{-1} (closed square) and 918 cm^{-1} (closed square) as a function of flow rate of C_8H_{18}.

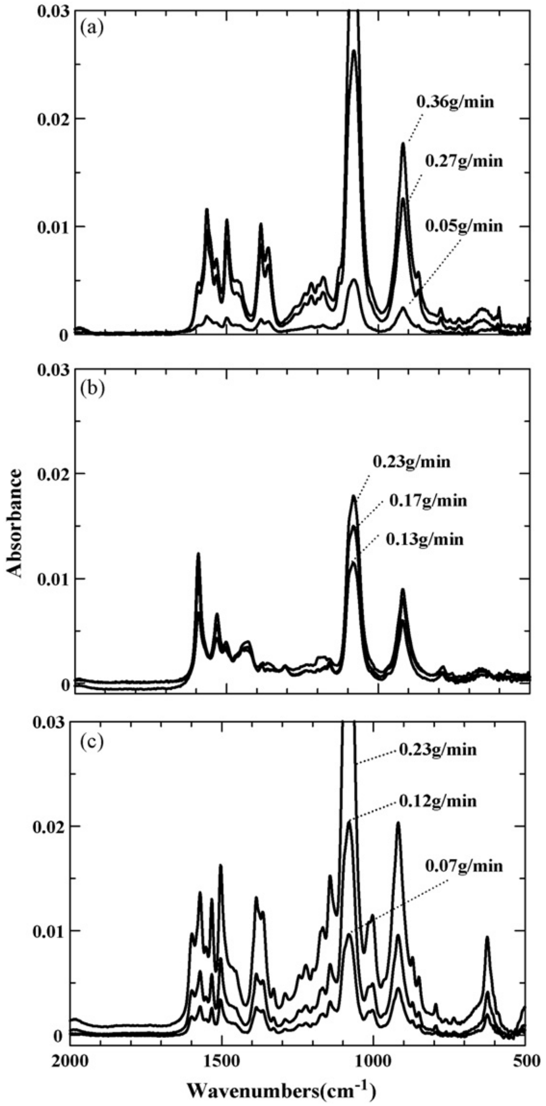

Fig. 2. FTIR spectra of (a) Pb, (b) Zr and (c) Ti sources dissolved in C_8H_{18} at various flow rates.

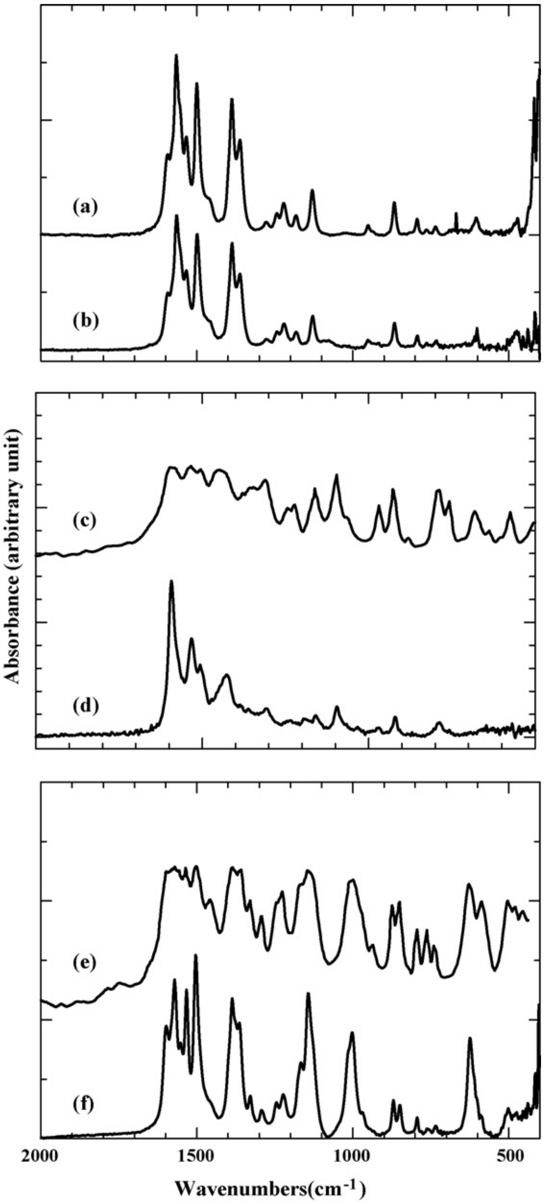

Fig. 3. Flow rate dependence of FTIR spectra for (b) Pb, (d) Zr and (f) Ti sources after removal of C_8H_{18} spectrum. Reference data for (a) Pb source vaporized by sublimation method, and (c) Zr and (e) Ti sources obtained by KBr method are also shown. Some peaks in (c) and (e) are saturated.

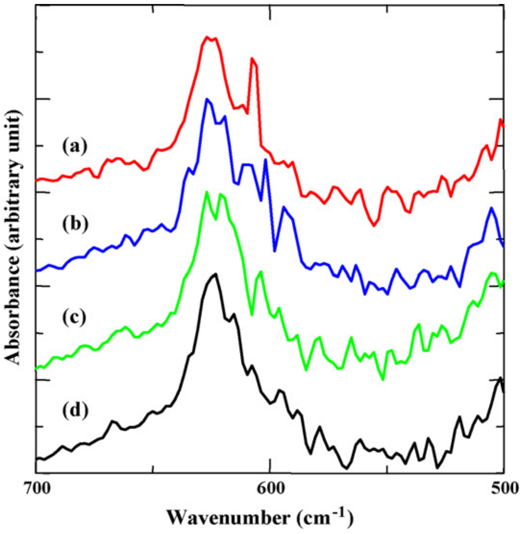

Fig. 4. Vaporizer temperature dependency of FTIR spectra of Ti after removal of C_8H_{18} using C_8H_{18} spectrum shown in Fig. 1. Vaporizer temperature: (a) 170 °C, (b) 190 °C, (c) 210 °C and (d) 2301 °C.

temperatures for Pb, Zr and Ti sources were, respectively, optimized at 210, 250 and 230 °C. Vaporized sources were mixed and introduced to the chamber of the FTIR equipment (Horiba Ltd.) and the high-temperature gas cell with KRS-5 windows under the all line while the vaporizer was kept at 230 °C. Pure $Pb(C_{11}H_{19}O_2)_2$ vapor obtained by sublimation was also introduced to the FTIR as a reference. Also, pure FTIR spectra for $Zr(C_9H_{15}O_2)_4$ and $Ti(Oi\text{-}C_3H_7)_2(C_{11}H_{19}O_2)_2$ were obtained at room temperature with the KBr method using powdered forms of these sources.

3. Results and discussion

3.1. Single source supply

Fig. 1(a) shows the FTIR spectrum of pure C_8H_{18}, which responds to the concentration of C_8H_{18} vapor, supplied at different flow rates. Absorbance peak intensities were found to increase as the flow rate of C_8H_{18} increased. Fig. 1(b) shows absorbance peak intensities at 1080 and 918 cm^{-1} in Fig. 1(a) as a function of the flow rate of C_8H_{18}. Good linearity was observed between absorbance peak intensities and flow rate.

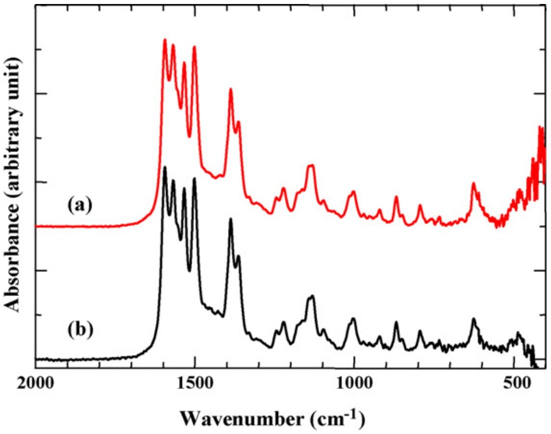

Fig. 6. Comparison of FTIR spectra for (a) mixture of Pb, Zr and Ti sources after removal of C_8H_{18} and (b) mathematical summation of FTIR spectra of each source gas shown in Fig. 3(b, d and f).

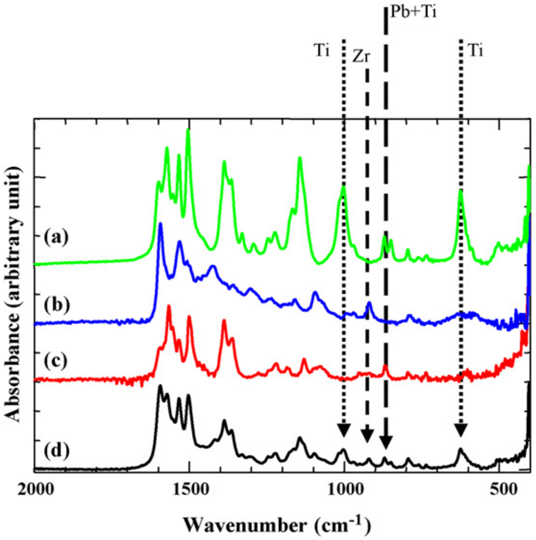

Fig. 7. FTIR spectra of single source supplies of (a) Pb, (b) Zr, (c) Ti and (d) their mixtures after removal of C_8H_{18}.

Fig. 2 shows the flow rate dependence of the FTIR spectrum of the gas phase of each source dissolved into C_8H_{18}. Absorbance was found to increase as the flow rate of each source increased, but almost all spectrum peaks are due to the C_8H_{18}.

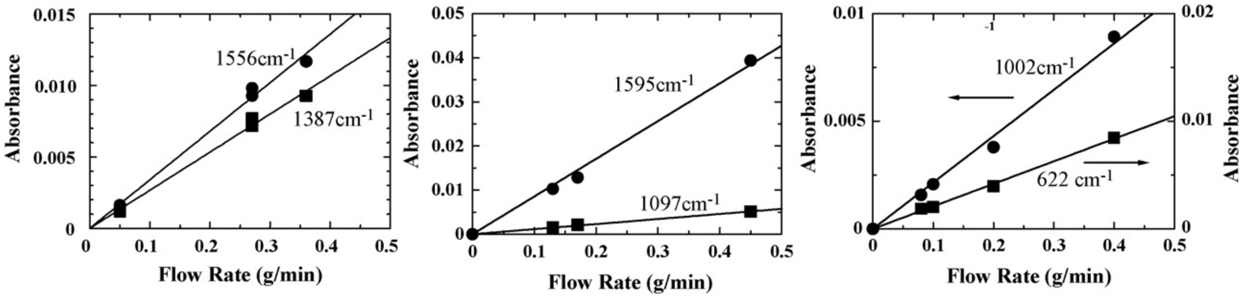

Fig. 5. Flow rate dependence of absorbance peak intensity for (a) Pb, (b) Zr and (c) Ti sources obtained from FTIR spectra after removal of C_8H_{18}, shown in Fig. 1. Flow rate response to concentration.

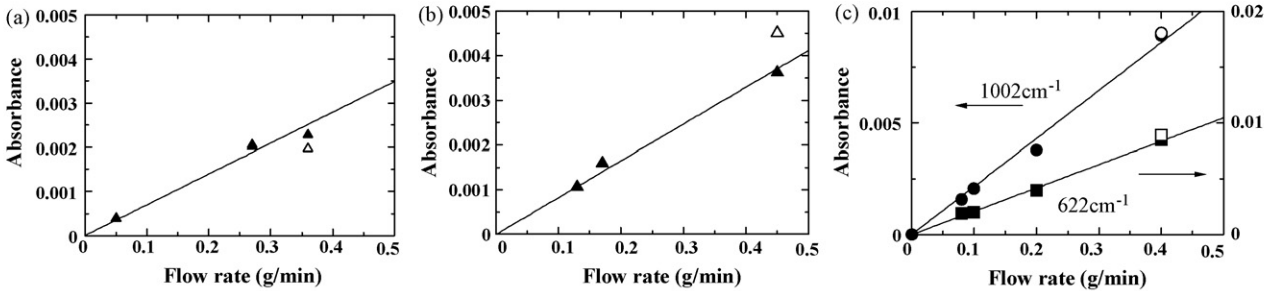

Fig. 8. Absorbance intensity of typical FTIR spectrum of: (a) Pb peak (867 cm^{-1} after removal of Ti source), (b) Zr peak (919 cm^{-1}) and (c) Ti peak (1002 and 622 cm^{-1}) as a function of flow rate for single source supplies of Pb, Zr and Ti (closed symbols) and their mixture (open symbol). Flow rate response to concentration.

Fig. 3(b, d and f) show the spectra after removal of the C_8H_{18} spectrum shown in Fig. 1. As a reference, measured data without C_8H_{18} are also shown in Fig. 3(a, c and e). It should be noted that the absolute values of the absorbance for the present and reference data measured by the KBr method, as shown in Fig. 3(c and e), are not the same. In addition, some peaks in Fig. 3(c and e) were saturated due to high vapor concentrations. The spectra shown in Fig. 3(b, d and f) were almost identical to the reference ones for the points of the peak numbers and their positions as well as the peak intensity of the unsaturated peaks. This shows that the spectra of the source gas were obtained even when the sources were diluted in C_8H_{18}.

However, a more careful comparison at around 600 cm^{-1} found that the spectra of the Ti source shown in Fig. 3(e and f) were not identical because of the Ti–O stretch bond [8,9]. Two peaks observed in the spectrum measured by the KBr method (Fig. 3(e)) merged into one in a direct observation of the gas phase by diminishing the peak located at 590 cm^{-1} (Fig. 3(f)). The same result was reported by Nakamura et al. [9]. They thought this was due to distortion and/or decomposition in isopropoxy moieties. To check the stability of the present Ti source, the vaporizer temperature dependency of the FTIR spectrum was measured and is shown in Fig. 4. The obvious peak at 590 cm^{-1} observed using the KBr method and shown in Fig. 3(e) was not detected down to 170 °C. This shows that the present change observed in the FTIR spectrum occurred below 170 °C. Detailed analysis is under way.

Fig. 5 shows the typical absorbance peak intensities for each source as a function of its flow rate and response to concentration. These increased linearly as flow rates of each source increased. This indicates that FTIR is applicable to the estimation of concentration of source materials by removing C_8H_{18}.

3.2. Multi-source supply

Fig. 6 compares the FTIR spectra for the mixture of Pb, Zr and Ti after removal of C_8H_{18} and the mathematical summation of the FTIR spectrum of each source gas shown in Fig. 3(b, d and f). It was found that these two are basically the same. This indicates that there is no obvious gas-phase reaction between the source materials and C_8H_{18}.

Fig. 7 compares the FTIR spectra of single phase Pb, Zr and Ti and their mixtures after removal of the C_8H_{18} spectrum. Individual peaks originating only from Zr and Ti sources were detected at 919 and 622 cm^{-1}, respectively. No peak originating from a Pb source alone was detected, except the one that originated from the summation of Pb and Ti sources at 867 cm^{-1}. Peak intensity of a Pb source at this wavelength can be estimated by comparing the peak intensity ratio from Pb sources alone to combined Pb and Ti sources.

Fig. 8 plots the peak intensity absorbance of the Pb, Zr and Ti gases as a function of flow rate and response to concentration, for single source supplies of Pb, Zr and Ti and their mixtures. Intensity of the Pb source at 867 cm^{-1} was obtained after removing the intensity of the Ti source. Almost perfect matching can be observed, suggesting that the concentration of each source material was detected even in the mixture when C_8H_{18} was present.

This shows that FTIR can be used to monitor the concentration of each source gas in a mixture of gases when C_8H_{18} is present. This demonstrates that FTIR is a promising method of monitoring the supply rate of each source vapor, even though the vaporizer tended to stack and can feed back to the source supply system, such as a liquid mass flow controller, to keep a constant source concentration just in front of the reaction chamber. It was also useful in determining the maintenance period of the source supply system, due to the stack of the vaporizer.

4. Conclusions

$Pb(C_{11}H_{19}O_2)_2$–$Zr(C_9H_{15}O_2)_4$–$Ti(O\textit{i}\text{-}C_3H_7)_2(C_{11}H_{19}O_2)_2$–$O_2$ source gas system diluted in C_8H_{18} for MOCVD-Pb(Zr,Ti)O_3 films was investigated by FTIR. No obvious gas-phase reactions between the source and C_8H_{18} were detected. The analysis of the spectra of single source supplies and their mixtures showed that FTIR concentration can be used to monitor the mixture of source gases by identifying the characteristic FTIR absorbance peaks of each source material.

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