

# Guest Forum

Series of Lectures by Screening Committees of the Second Masao Horiba Awards

## Importance of in situ Monitoring in MOCVD Process and Future Prospects



**Hiroshi Funakubo**  
Tokyo Institute of  
Technology  
Graduated School of Science  
and Engineering  
Associate Professor  
Ph. D. in Engineering

There is growing expectation in hopes of finding new or improved substances with excellent properties through further multiply components, in multi-component oxide thin films such as high-temperature superconductors, giant magnetoresistance effect oxides, and ferroelectric oxide. In manufacturing these devices, composition reproducibility that influences properties are important, and MOCVD (Metal Organic Chemical Vapor Deposition) is drawing attention. We will confirm the basic principle of MOCVD such as reaction mechanism in thin film fabrication and the control of compositions, using  $\text{Pb}(\text{Zr,Ti})\text{O}_3$  (PZT) thin film as an examples. We will also explain the effectiveness of Fourier Transform Infrared Spectroscopy (FTIR) as a tool for extracting the optimum conditions for the industrialization process of MOCVD, using hard data. In addition, we will propose a process in which FTIR is installed as an in situ monitor for online feedback controls in the MOCVD process, with excerpts from experiment results. Finally, future prospects will also be discussed.

### Introduction

Recently, there have been notable developments of multi-component oxide thin films such as high-temperature superconductors (Y-Ba-Cu-O, Bi-Sr-Cu-O), giant magnetoresistance effect oxides (La-Ca-Mn-O), and ferroelectric oxides (Pb-Zr-Ti-O, Sr-Bi-Ta-O) in various fields. MOCVD (Metal Organic Chemical Vapor Deposition) has shown excellent aspects (i.e., high step coverage, a high deposition rate, and composition uniformity in a wide range) as a method of device fabrication for multi-component oxide thin film. Properties of multi-component oxide thin film devices depend largely on the composition, in which optimization of composition and securing reproducibility are important. So far, they have been accomplished by optimizing process conditions through trial-and-error. In the future, in order to develop completely new materials, an increase in the number of elements would become inevitable, and this approach requires tremendous amounts of time and money. Figure 1 shows a deposition model of PZT<sup>1</sup> based on MOCVD. It is important to understand gas phase reaction as the material reaches

the substrate, the reaction on the substrate, as well as the material-feeding rate. Development of a system that monitors them in situ, simultaneously, is needed. In this lecture, taking a PZT thin film for example, effectiveness of in situ monitoring in the MOCVD process using FTIR is presented, and future prospects will be discussed.

\*1: Due to its large residual polarization, lead zirconate titanate thin film is applied to ferroelectric memories, and also to actuators and the like due to its excellent piezoelectric property.

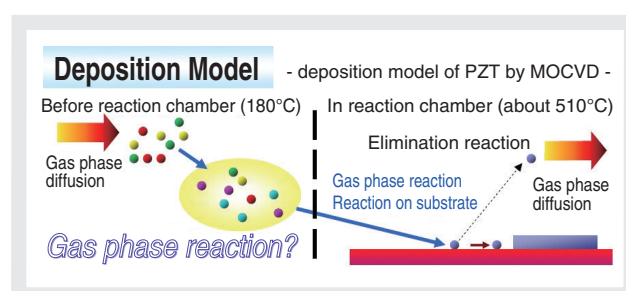


Figure 1 Deposition Model - Deposition Model of PZT by MOCVD -

## Basic Structure and Conditions

Experimental device has an FTIR analyzer installed in the bypass to the reaction chamber as shown in Figure 2. The FTIR analyzer is a commercial FTIR with just a gas cell added. It should be noted that there were doubts concerning whether high S/N analysis data can be obtained (with raw gas temperatures at a high 180°C) along with several unidentified factors such as the measurability at very low concentration levels, the stability of the window material and the lack of actual achievements in multi-component analysis based on FTIR. Table 1 shows the experiment conditions.

Table 1 Conditions

Materials	Pb(C <sub>11</sub> H <sub>19</sub> O <sub>2</sub> ) <sub>2</sub> , Zr(O·t-C <sub>4</sub> H <sub>9</sub> ) <sub>4</sub> , Ti(O·i-C <sub>3</sub> H <sub>7</sub> ) <sub>4</sub>
FTIR Measuring conditions	Wave number resolution: 4cm <sup>-1</sup> , TGS detector, Accumulated number of times: 100
Gas cell	Optical path length: 0.1m, Material: SUS316
Evaporation	Bubbling method (sublimation method)
Partial pressure of measured gas	Pb(C <sub>11</sub> H <sub>19</sub> O <sub>2</sub> ) <sub>2</sub> : 0.003-0.100 Torr
	Zr(O·t-C <sub>4</sub> H <sub>9</sub> ) <sub>4</sub> : 0.002-0.056 Torr
	Ti(O·i-C <sub>3</sub> H <sub>7</sub> ) <sub>4</sub> : 0.005-0.119 Torr
Deposition rate	2 nm/min → 60 minutes detection

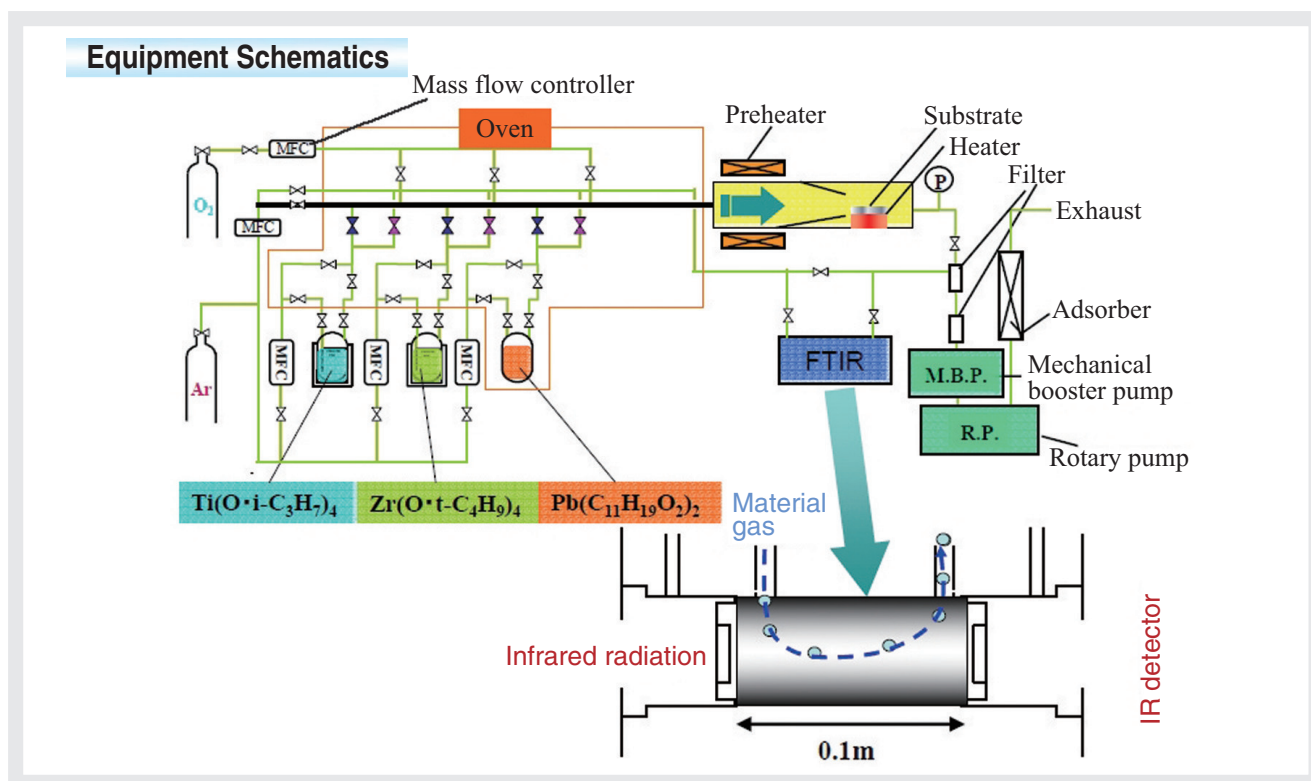


Figure 2 Schematic Diagram of Experiment Equipment

## Confirming FTIR Effectiveness Spectrum and Linearity

Figure 3 shows single gas phase spectrum of each material-gas and the linear relationship between concentration and absorbance with the wave number indicated by arrows. The peak indicated by the arrow in the Zr spectrum represents Zr and O bonding, evidence of Zr existing in the gas that forms a film. Unfortunately, the same could not be observed in Pb and O, but was seen in the bonding of Ti and O.

It has been confirmed that measurement is indeed possible by implementing FTIR in the CVD system, with linearity and dynamic range also secured.

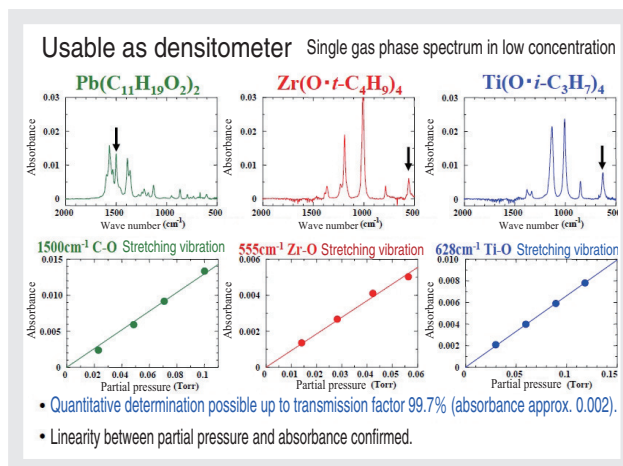


Figure 3 Single Gas Phase Spectrum in Low Concentration and Linearity

## Confirming Gas Phase Reaction

From the mixed spectrum of  $Zr(O \cdot t-C_4H_9)_4$  and  $Ti(O \cdot i-C_3H_7)_4$  (Figure 4), it can be seen that the sum of respective single spectra of Zr and Ti differs from the mixed gas spectrum. The difference indicates that gas phase reaction takes place due to mixing of the gases. Further, data was obtained which indicated that with the altering the ratio of the material-gas feed rates of Zr and Ti at mixing, the Zr-material-derived peak and the Ti-material-derived peak shift cleanly and systematically (Figure 5).

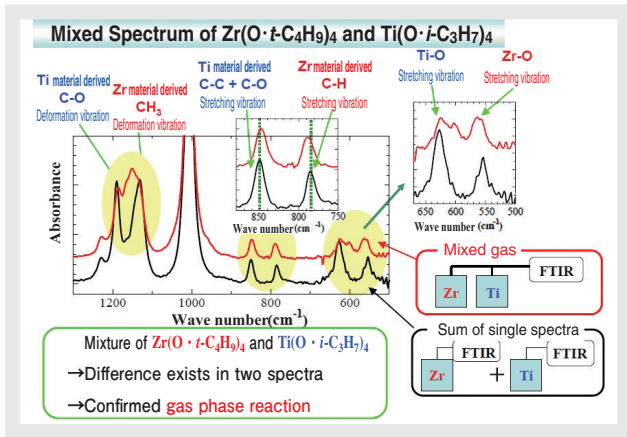


Figure 4 Mixed Spectrum of  $Zr(O \cdot t-C_4H_9)_4$  and  $Ti(O \cdot i-C_3H_7)_4$

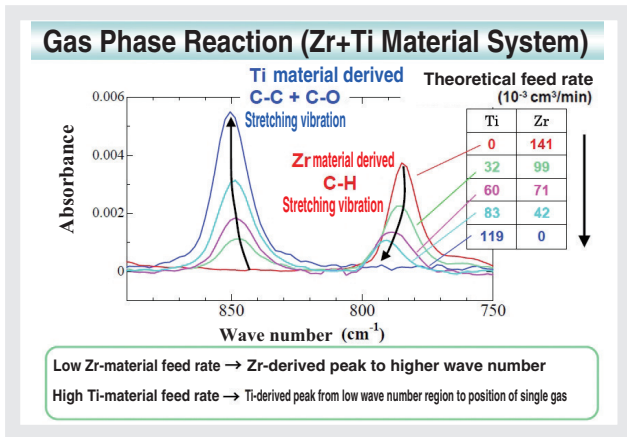


Figure 5 Gas Phase Reaction (Zr+Ti Material System)

## Composition Controllability

It was confirmed that the ratio of Zr-material-derived spectrum intensity to Ti-material-derived spectrum intensity in Figure 5 has a linear relationship with the composition ratio of the actual thin film with a straight line passing through the point of origin (Figure 6). This fact shows that the use of FTIR as an in situ monitor enables control of thin film composition. In other words, film production without waste batches is possible by checking spectra from FTIR.

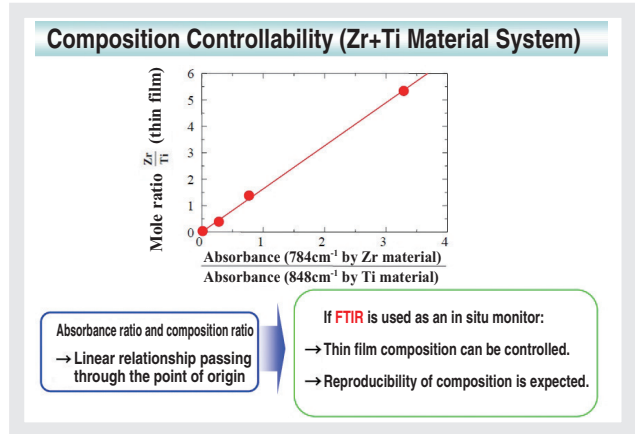


Figure 6 Composition Controllability (Zr+Ti Material System)

## Applying FTIR to Solution Vaporization

Conventional material feed systems such as the bubbling method are insufficient for mass production due to the limitation of the material vapor pressure. Given this factor, the solution vaporization method, where the material is dissolved in a solvent to be pumped to a vaporizer for forced vaporization, is becoming mainstream. When the material is dissolved in the solvent, concentration of the material in the solution is about 1/1000. This increases a degree of difficulty, since spectrum of the solution becomes the background.

The FTIR spectra are stable, and as shown in Figure 7, it was confirmed that subtracting FTIR spectrum of single gas from FTIR spectra of mixed vaporized gas out of lead dipivaloyl-methane ( $Pb(DPM)_2$ ) as Pb-material and tetrahydrofuran (THF) as solution provided the spectrum of the original material. It was also confirmed that the material feed rate has linear relationship with absorbance. Likewise, in the mixed material-gas spectrum of Zr, Ti, and Pb, each mixed gas concentration could also be obtained by subtracting the solution spectrum element.

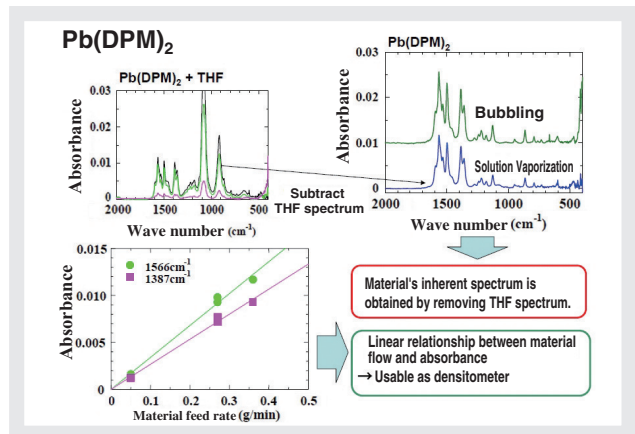


Figure 7 Computing  $Pb(DPM)_2$  Spectrum by Subtracting THF Solution Spectrum

## Application to Industrialization Process

### Application to Process Optimization

Vaporization using a vaporizer has instability factors that affect the vaporized gas concentration, such as thermal transformation of materials, generation of particles, and fluctuation of the gas feed rate caused by residues in the vaporizer. The optimum conditions such as temperature and flow should be determined to feed the material at a steady concentration, but key is determining the conditions. At least one month is needed to optimize conditions for a single material. The following shows how this time was shortened dramatically.

### Optimization of Vaporizer Temperature

The vaporizer should operate at the stabilized feed temperature 1) lower than thermal decomposition and 2) higher than the temperature in which residues are formed in the vaporizer. In addition, 3) it is important to ascertain the stability of gas concentration by measuring it at the vaporizer outlet. Measuring these by FTIR allow for quick determination of the optimum vaporizer temperature.

#### 1) Confirming thermal decomposition temperatures of materials

When measuring the vaporized gas using FTIR by altering the vaporizer temperature, absorbance of the material element spectrum drops at temperatures over 180°C in the case of  $Zr(O \cdot t-C_4H_9)_4$ , and at the same time, the spectrum of the decomposed product isobutene is observed. Likewise, in the case of  $Ti(O \cdot i-C_3H_7)_4$ , the absorbance of the material element spectrum drops at temperatures over 250°C, and at the same time, the spectrum of the decomposed product called propene is observed.

#### 2) Confirming the material's unvaporized temperature

The absorbance of  $Pb(DPM)_2$  increases in the vicinity of 100°C and reaches a plateau from around 180°C to 300°C (Figure 8). The data indicates that the optimum condition of the temperature inside the vaporizer is in the range over 200°C and below 300°C where unvaporized products are no longer created. With the conventional method, where all residues are measured by opening the vaporizer after the material is vaporized (e.g., three hours per condition), it will take several days to confirm the optimum temperature of a material. The effectiveness of FTIR is obvious if one considers the high material cost (several hundreds of thousands of yen) and the costs and time for the confirmation.

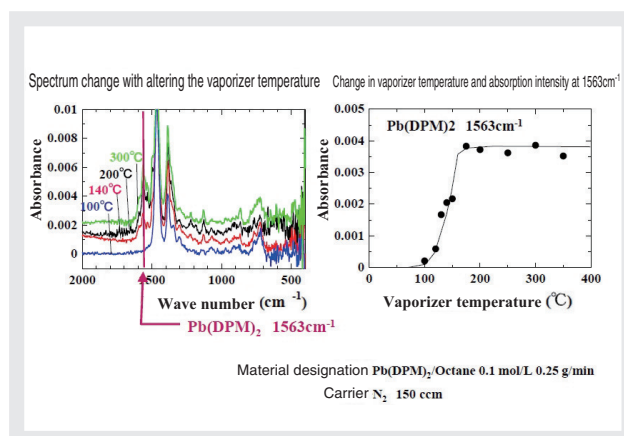


Figure 8 Ascertainment of Non-vaporized Substances in the Vaporizer

#### 3) Measurement of gas concentration at the vaporizer outlet

Monitoring the concentration at the vaporizer outlet is most important for stabilization of the material feed rate. Figure 9 is a graph showing variation of the Pb-material-gas concentration measured by FTIR versus time, where the concentration is instable at 210°C compared to 250°C. The likely cause is the process where the material-gas concentration drops because the solution is first evaporated and the material is condensed at the leading edge of the vaporizer nozzle due to the partial pressure difference between the material and the solution, and the condensed material then vaporized to raise up the concentration. In the previous section, the optimum temperature inside the vaporizer of  $Pb(DPM)_2$  has resulted in the temperature range of 200°C to 300°C, but this is consequent only after stabilization over time. This is an example in which FTIR analysis revealed that the optimization can be attained from the beginning, with the vaporizer set at 250°C.

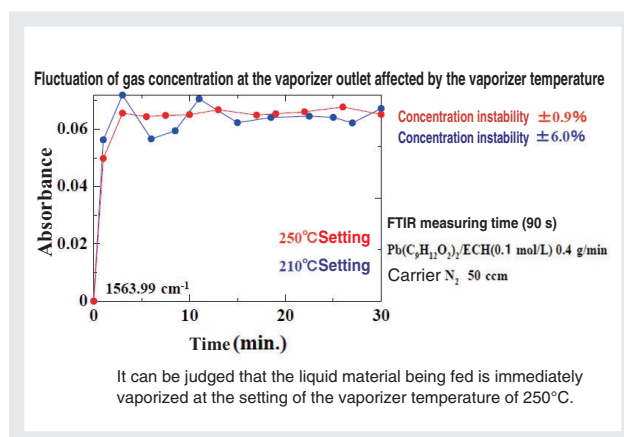


Figure 9 Fluctuation of Gas Concentration at the Vaporizer Outlet



## Optimization of Deposition Process

Figure 10 shows the curves of the film composition rate and the substrate deposition rate versus material feed rate. With an increasing feed of the Pb-material, the deposition speed decreases and in addition, the composition ratio changes even though the feed rate is constant (in the case of Zr and Ti). FTIR measurement revealed that the material-gas concentration of Zr and Ti on the substrate changed to low through the materials' gas phase reaction with each other. Because the material-gas concentration of Zr and Ti observed by FTIR spectrum shows the same trend as the deposition rate does, the deposition rate can be estimated by measuring the FTIR spectrum in front of the reaction chamber. On the other hand, in the case of Pb, it was confirmed that the material-gas concentration observed from the FTIR spectrum increases proportionally with the increasing Pb-material feed rate without having any area where the concentration does not change. For Pb, in the area where the deposition rate does not change, PZT and PbO are deposited on the substrate, but the high deposition temperature re-evaporates PbO selectively due to a high vapor pressure. This is the deposition in the area called a process window in which the PZT single film is formed even though Pb is injected excessively. This is not gas phase reaction, but is considered the reaction on the substrate.

We found that monitoring the gas phase reaction using FTIR is an effective means to control the composition of PZT.

## Outline of Experiment System for Feedback Control Process

The experiment was conducted, in which the spectrum analysis of the PZT mixed gas in the PZT process was performed using FTIR and the results were fed back online to control the material feed, and thus the required material-gas concentration was obtained. In principle, a liquid mass flow meter is not necessary, since the concentration correction of each material element is calculated from spectrum data of the mixed gas in the FTIR analyzer to control the valve in the mass flow controller of the vaporization feeding equipment through a conversion unit. For example, slight deviation of the material concentration in the solution may occur. The idea is to have the process side deal with such cases, and not return the material to the supplier. As a result of the experiment, concentration variation is suppressed within the range of 1 to 2 percent by the FTIR feedback control. The superiority to the method without using FTIR was confirmed. The important point is that only one set of FTIR is needed since the mixed gas is monitored for feedback, instead of each single gas of PZT. Through the feedback experiment using the existing MOCVD, a series of procedures for feedback control of the material system could be established and excellent results were obtained in the course of verification of experiment based on the technique.

Future tasks are to improve sensitivity of FTIR and, in addition, to set up a feedback system that deals with other simple detecting means such as thermal conduction cells.

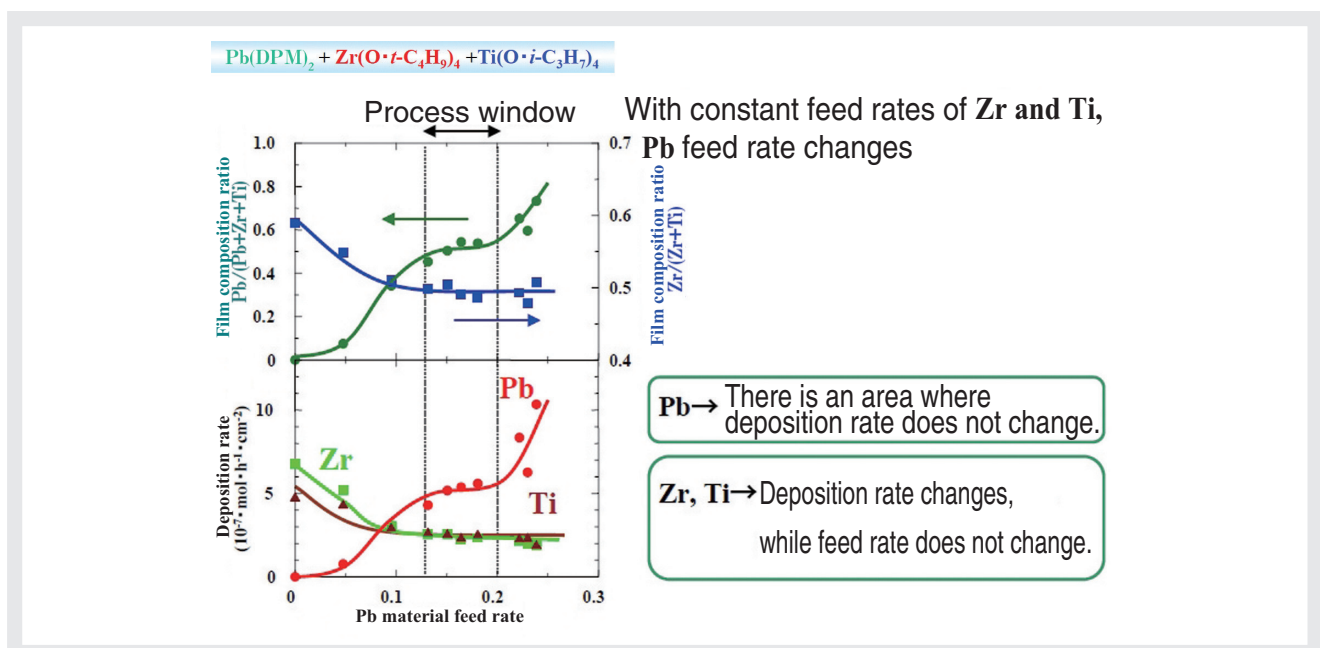


Figure 10 Film Composition Ratio and Substrate Deposition Rate versus Material Feed Rate

## Conclusion

Use of FTIR as an in situ monitor has paved the way for the optimum vaporization conditions and a steady vaporization feed that has been considered difficult to attain via conventional technology, and provides a good prospect for a MOCVD process for PZT thin film fabrication. A use of FTIR demonstrates its strength in the reaction analysis of CVD that has very fast optimization and a difficult deposition mechanism, and to a large extent, is effective at the development phase. In particular, it is considered to help analysis when materials change. Equipment with improved composition controllability using FTIR for gas analysis was developed. Through the Introduction of analytical means alone, we gained considerable knowledge of what was not known, and insight into how to go about implementation. Since in situ analysis of films will become more important, it is imperative that analyzer manufacturers with comprehensive solutions including analyzers other than FTIR become involved in the equipment development for film fabrication of more multiplicated component in the future.

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