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Gas Phase Analysis of MOCVD Source Materials by FTIR

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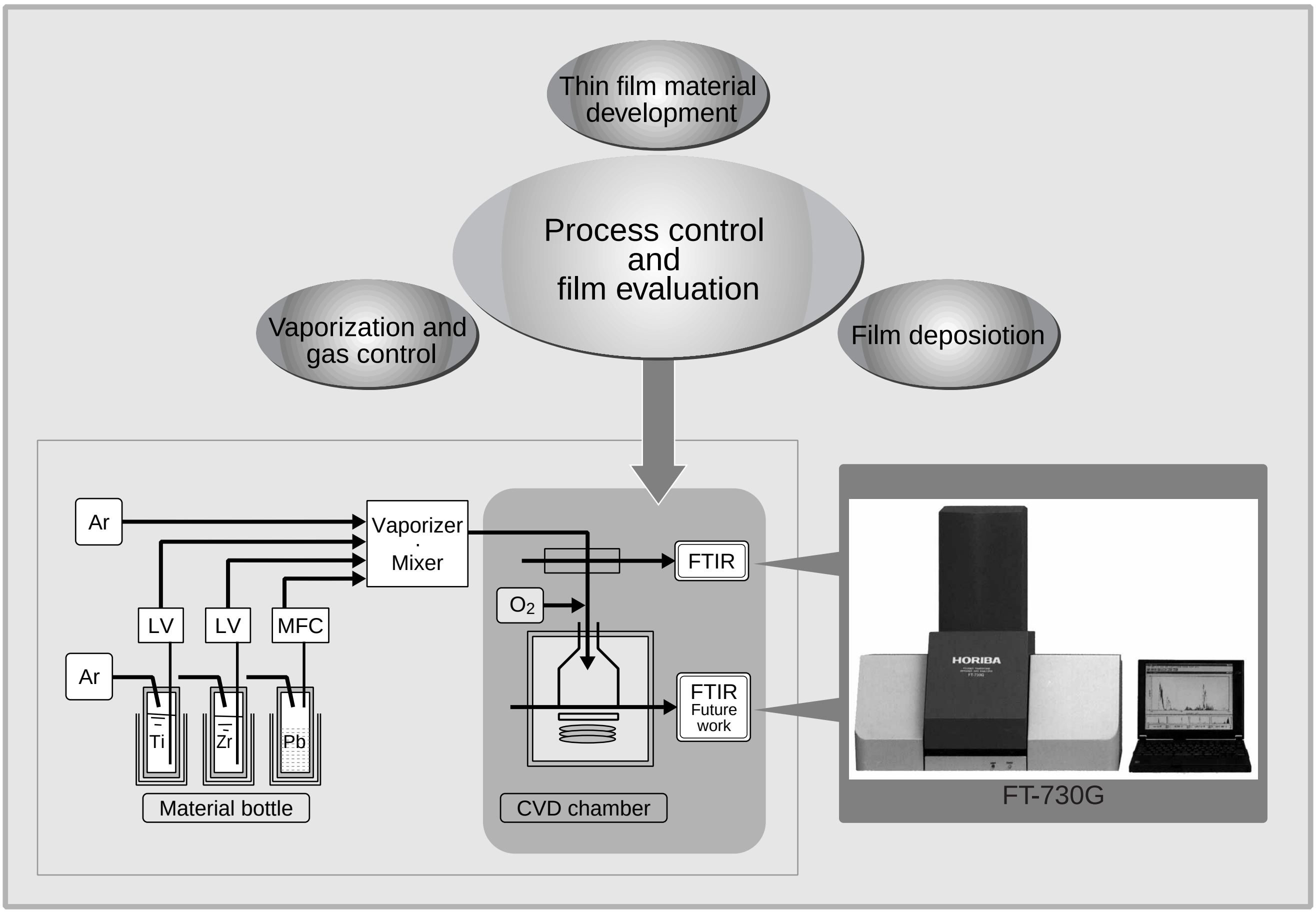


Abstract

A new type of semiconductor memory, called Ferro-electric Random Access Memory (FeRAM) because it is manufactured using thin film Ferro-electric materials, is now under development for practical use. Several kinds of source materials and manufacturing methods have been suggested, but an MOCVD process is attracting the most attention at present. By investigating the source materials for $Pb(Zr,Ti)O_3$,[PZT] thin film at the gas phase of the MOCVD process by taking measurements using Horiba's FT-IR gas spectrometer (model FT-730), we have confirmed the fact that the three source materials combine to form an intermediate material as they are vaporized/mixed. Based on our results, we expect that the FTIR will have an important role to play in both the development of the sources and the manufacturing process of FeRAM products.

1 Introduction

The idea that Fourier spectroscopy analysis was in principle superior to other methods was first put forward sometime around 1950 (1). Since then, with the development of some key technologies such as gas lasers and FFT (fast Fourier transform) algorithms, we have evolved to a stage where we now have FTIR (Fourier transform Infrared) spectroscopy. It is no exaggeration to claim that the types of FTIR spectrometer widely spread for general purpose in the 1980s - thanks to the semiconductor industry which was producing ever more powerful and ever more low cost microcomputers—are now commonplace.

Development work on FeRAM (Ferro-electric Random Access Memory) devices is ongoing. FeRAM will allow future semiconductor systems to be faster, and able to process greater amounts of data, than the current generation of semiconductor devices. FeRAM development has now reached a stage where the technologies and methods necessary for commercial production of FeRAM devices are being debated.

For the method of the thin Ferro-electric film deposition, sol-gel and sputtering methods have been suggested, but our research has shown that an MOCVD (metal organic chemical vapor deposition) process could be the best choice, especially in terms of high deposition rate and good step coverage. We have already reported on our experiments using the FITR spectrometer for vapor phase monitoring in the MOCVD process (2).

The source materials for the MOCVD process are normally either liquid or solid in their natural state, but they are used after first being vaporized in a CVD (chemical vapor deposition) chamber. For MOCVD, FTIR spectroscopy could be employed to monitor the condition of the source material vapor, allowing feedback to be given to the system that controls the supply of the source material into the process. Thereby, our method should help to further the development of deposition technologies and also contribute to the creation of more reliable semiconductor manufacturing processes.

2 Subjects of the Measurements

Fig.1 shows the thin film deposition equipment and the source material supply system used in the MOCVD process. In this case a Pb(Zr,Ti)O_3, [PZT] thin film is used. The three source materials are first put into bottles where a constant temperature is maintained in order to ensure the optimal vapor pressure for the experiment. A carrier gas, such as Argon, is then used to transfer the source materials to the mixture chamber ready for vaporization and mixing, after the vaporization and mixing is completed, oxygen is added and the resulting mixture is transferred to the CVD chamber. As Fig.1 shows, measurements using the FTIR spectrometer is obtained in the mixture chamber, during the vaporization and mixing stage.

Examples of source materials for FeRAM are given in Table 1. Just as film deposition technologies are being further developed, source materials are also being improved and developed.

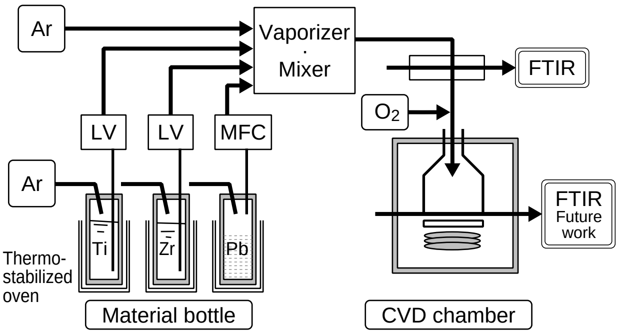


Fig.1 Thin film deposition system for MOCVD

	Chemical Formula	Melting point°C	Properties
For PZT	Pb ($C_{11}H_{19}O_2$)$_2$	130	white/solid
	Zr (O·t-C_4H_9)$_4$	3	light brown/liquid
	Ti (O·i-C_3H_7)$_4$	20	colorless/liquid
	Ti (O·i-C_4H_9)$_4$	4	lightbrown /liquid
	Ti(O·i-C_3H_7)$_4$($C_{11}H_{19}O_2$)$_2$	160	light yellow/solid
For SBT	Sr ($C_{11}H_{19}O_2$)$_2$	210	white/solid
SBTN	Bi (O·t-C_4H_9)$_3$	150	white/solid
	Bi (O·t-C_5H_{11})$_3$	90	white/solid
	Bi (C_6H_5)$_3$	80	white/solid
	Ta (OC_2H_5)$_5$	21	colorless/solid · liquid
	Ta (O·i-C_3H_7)$_5$	107	white/solid
	Nb (OC_2H_5)$_5$	6	amber/liquid
	Nb (O·i-C_3H_7)$_5$	5	white/solid
	Sr[Ta(OC_2H_5)$_6$]$_2$	130	white/solid
	Sr[Ta(O·i-C_3H_7)$_6$]$_2$	256	white/solid
	Sr[Nb(OC_2H_5)$_6$]$_2$	120	white/solid
	Sr[Nb(O·i-C_3H_7)$_6$]$_2$	250	white/solid

Table 1 Source materials for MOCVD

3 Experiment to Measure the Vapor Phase

To assess the condition of the PZT thin film, measurements were carried out using Horiba's FTIR spectrometer (model FT-730) and a special gas cell.

Fig.2 shows the chemical structure of the source materials, Fig.3 shows the setting for the measurements, and Table 2 shows the measurement conditions.

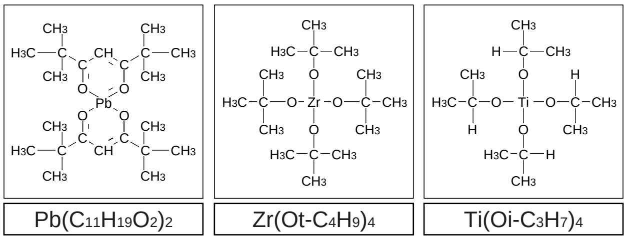


Fig.2 Source materials and their molecular structures

Fig.3 Horiba's FTIR spectrometer and its gas cell

FTIR measurement condition	Resolution	4cm^{-1}
	Measurement time	90s
	Detector	TGS
Gas cell condition	Optical path length	0.1m
	Body material	SUS316
	Window material	KRS-5
	Temperature	25～140°C
Vaporization	Directly vaporized in gas cell	

Table 2 Measurement conditions

4 Results of the Experiment

4.1 Absorption spectra for each of the source material components.

Fig.4 shows the results obtained when each of the three source materials is vaporized separately. Peaks can be seen, especially in the low wavenumber region, caused by the bonding between metal and oxygen.

By studying the characteristic peaks of each of the three source materials, it is possible for us to identify the components.

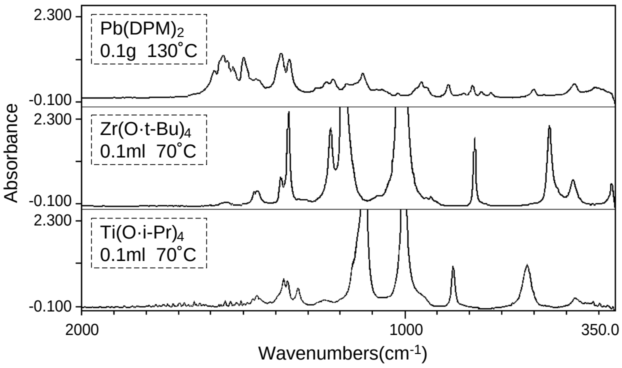


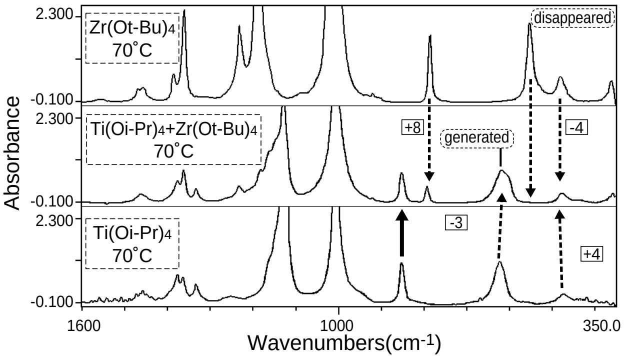
Fig.4 Infrared absorption spectra for each of the source materials

4.2 Spectra of source mixtures

For the MOCVD process, the gaseous mixture sent to the CVD chamber is a combination of all the three source materials.

Therefore, we studied the spectra of mixtures of the components to ascertain what properties they have.

Fig.5 shows the spectra for the zirconium and titanium source materials. The second spectrum shows the two materials combined in a vapor mixture. Compared with the spectra for the individual materials, that for the mixture shows that some peaks have disappeared and others have shifted position. This suggests that in the mixture the source materials do not maintain their own existence, but that the way their molecules bond with each other is actually altered.



Wavenumber shift value

Fig.5 Infrared spectrum for Zr-Ti sources vapor and the mixture

The result of infrared spectroscopy carried out on the zirconium and titanium materials with the lead (Pb) source material also added is shown in Fig.6. It shows that with all three materials used in the vapor mixture, the resultant spectrum differs greatly from the individual spectra of the three components. This means that by mixing the three materials they already form an intermediate before they move to the CVD chamber.

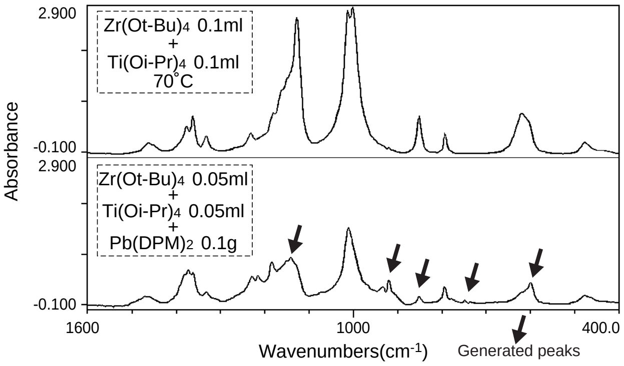


Fig.6 Infrared spectrum for Pb-Zr-Ti sources vapor and the mixture

5 The Future

Regarding possible commercial production of FeRAM semiconductors, in the short term it appears that PZT thin films are more advantageous, in terms of the temperature used for their deposition process, than those created with the $SrBi_2Ta_2O_9$, [SBT] thin film.

On the other hand, SBT thin films will likely gain favor in the long run by their superior characteristics.

Taking technological trends into account, the following points are those that makers of measuring instruments will need to find solutions to:

1) To create gas cells that can withstand higher temperatures, so that the source materials used in the SBT deposition process can be monitored.
2) To be able to respond rapidly whenever new source materials appear.
3) To design and build more compact and more robust FTIR spectrometer equipment that can be incorporated into the MOCVD chamber.
4) To develop better calibration systems (3).

6 Conclusions

We used an FTIR spectrometer to monitor the mixture of vaporized source materials used to create a PZT Ferro-electric thin film in the MOCVD process. Our data leads us to believe that upon vaporization in the mixing chamber, the intermediate is formed.

This is a new parameter to be taken into consideration for better controlling by the intermediate which itself is the most important stage in the whole thin film deposition process (4).

Also, because of the FTIR spectrometer's high performance, we have confidence that it could be incorporated into the semiconductor manufacturing process as a control sensor.

References

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