A study on the real-time decomposition monitoring of a metal organic precursor for metal organic chemical vapor deposition processes

To cite this article: Ju-Young Yun *et al* 2009 *Meas. Sci. Technol.* **20** 025701

View the article online for updates and enhancements.

Related content

- Effect of Post-Treatments on Atomic Layer Deposition of TiN Thin Films Using Tetrakis(dimethylamido)titanium and Ammonia
  Jong-Ho Yun, Eun-Seok Choi, Choel-Min Jang et al.
- Real-Time Diagnosis of Nano-Sized Contaminant Particles Generated in TiN Metal Organic Chemical Vapor Deposition
  Jeonggil Na, Taesung Kim, Jae-Boong Choi et al.
- Atomic layer deposition: an enabling technology for the growth of functional nanoscale semiconductors
  Necmi Biyikli and Ali Haider

Recent citations

- Rutile-structured TiO2 deposited by plasma enhanced atomic layer deposition using tetrakis(dimethylamino)titanium precursor on in-situ oxidized Ru electrode
  John Pointet *et al*
- Effects of catalyst material and atomic layer deposited TiO2 oxide thickness on the water oxidation performance of metal–insulator–silicon anodes
  Andrew G. Scheuermann *et al*
- Real-Time Diagnosis of Nano-Sized Contaminant Particles Generated in TiN Metal Organic Chemical Vapor Deposition
  Jeonggil Na *et al*

IOP ebooks™

Bringing you innovative digital publishing with leading voices to create your essential collection of books in STEM research.

Start exploring the collection - download the first chapter of every title for free.

This content was downloaded from IP address 203.252.134.41 on 04/12/2018 at 09:32

Meas. Sci. Technol. **20** (2009) 025701 (6pp) doi:10.1088/0957-0233/20/2/025701

A study on the real-time decomposition monitoring of a metal organic precursor for metal organic chemical vapor deposition processes

Ju-Young Yun[1], Soo-Won Heo[2], Sang-Woo Kang[1], Jeong-Gil Na[3], Young-Jae Park[1], Yong-Hyeon Shin[1], Ji-Hoon Lee[2], Tae-Sung Kim[3] and Doo-Kyung Moon[2]

[1] Vacuum Center, Korea Research Institute of Standards and Science, Doryong-dong, Yuseong, Daejeon 305-600, Korea
[2] Department of Materials Chemistry, Konkuk University, Hwayang-dong, Kwangjin, Seoul 143-701, Korea
[3] Department of Mechanical Engineering, Sungkyunkwan University, Suwon, 440-746, Korea

E-mail: dkmoon@konkuk.ac.kr

Received 15 May 2008, in final form 13 November 2008
Published 17 December 2008
Online at stacks.iop.org/MST/20/025701

Abstract
This study proposes a method for monitoring the decomposition state of a metal organic precursor which is used for the metal organic chemical vapor deposition (MOCVD) system. As many kinds of precursors for MOCVD such as tetrakis(dimethylamido)titanium (TDMAT) are highly likely to decompose due to the instability of their chemical structure during processing, critical problems are generated for thin film formation and its yield in this case. Although real-time monitoring technology on the decomposition degree of these precursors is essential for metallization, metal gate or electrode processes for memory devices, both commercialized technology and fundamental research have scarcely been accomplished. Therefore, this study endeavors for acknowledgment by the semiconductor industry with a proposal for a real-time monitoring method on the decomposition degree of the precursor through an ultrasonic diagnosis method. However, it is difficult to perform a degradation mechanism analysis since measuring the viscosity and physical properties of TDMAT is complicated due to its sensitivity to air. Therefore, viscosity was measured using a Pd compound (tetrakis(triphenylphosphine)palladium(0), $Pd(PPh_3)_4$) which is stable in air and has a similar chemical structure to TDMAT.

Keywords: MOCVD, metal organic chemical vapor deposition

(Some figures in this article are in colour only in the electronic version)

1. Introduction

The importance of the MOCVD process, through which the deep contact characteristics can be met, is on the increase as the dimensions of semiconductor devices shrink to nanometer sizes [1–3]. MOCVD is a chemical vapor deposition method of epitaxial growth of materials from the surface reaction of organic compounds or metal organics and metal hydrides containing the required chemical elements [2, 3].

Although the trend of a sharp increase is apparent in the consumption quantity of metal organic precursors due to the increase in the usage of the MOCVD process, research on the monitoring of this precursor is scarce. Specifically, in the case of TDMAT, which is used for the TiN MOCVD process,

 © 2009 IOP Publishing Ltd Printed in the UK

the decomposition of TDMAT occurs easily because the binding energy between the organic ligand that combines with the metallic ion is weak; problems of overall yield reduction and production cost increases are created because of the generation of particles and the decrease of the reproducibility of thin film formation due to the deterioration of the precursor used in the process [4]. However, precursor development companies and semiconductor device companies have had difficulties as there is no real-time method for measuring the decomposition of TDMAT as yet. This study has performed a test related to a system which is to enable the real-time monitoring of the decomposition degree of the precursor by utilizing ultrasonic wave technology [5]. The possibility of real-time monitoring technology for the decomposition of TDMAT has been confirmed through a change in ultrasonic echo strength and time of flight (TOF).

2. Experiment

Pure tetrakis(dimethylamido)titanium (TDMAT) was used as a precursor [4, 6]. To verify indirectly the properties of TDMAT, for which the measurement of viscosity is difficult due to its sensitivity to air, a Pd compound (tetrakis(triphenylphosphine)palladium(0)) having a similar chemical structure has been used. The 5 wt% $Pd(PPh_3)_4$ compound (dissolved in chloroform ($CHCl_3$)) was decomposed at a temperature of 100 °C.

As the precursor was decomposed by heat in a reservoir, the changing ultrasonic wave signal was collected by utilizing an ultrasonic wave sensor (diameter = 6.35 mm, Technisonic Co., for high temperatures). The experimental setup to measure the decomposition state of the precursor is shown in figure 1. The combined transmitting/receiving sensor (diameter = 6.35 mm, Technisonic Co.) was installed at the side of the reservoir. After a pulse (2.5 MHz) was discharged from the transmitter installed at the side of the container, it passed the precursor and was reflected by the surface on the opposite side. The pulse was monitored by a receiver (Model PMS-1000, Polynano tech.). Subsequently, the waveform was displayed on an oscilloscope and the strength of the waveform was examined. The interval between the transmission and the reception of the ultrasonic pulse was also used to determine the round trip time of the precursor [7].

Also, an analysis of the heat characteristics and chemical structure was performed by utilizing thermogravimetry (TGA 2050, TA instrument) and ^{1}H-nuclear magnetic resonance (^{1}H-NMR, Bruker DRX300, 300 MHz) in order to observe the change of the precursor inside during the change of the ultrasonic signal. *In situ* monitoring of the decomposition was performed with a Fourier transform infrared spectrometer (AVATAR 360, Thermo Fisher scientific). Once the precursor decomposed, viscosity increase was expected due to the byproduct. The Cannon viscometer (E 71 200 model) was introduced to measure the viscosity change.

3. Results and discussion

Generally, in the case of TDMAT, as the binding energy between the metallic atom and the organic ligand is the weakest, it is easy to break the combination and initiate decomposition so that the liquid property is changed due to the creation of the new material [8, 9]. Particularly, as it is assumed that the echo velocity and strength of an ultrasonic wave are affected in accordance with the change of the material property in the course of the decomposition of the precursor, the state of decomposition of the precursor can be observed in real time by utilizing an ultrasonic wave based on the above characteristics [7].

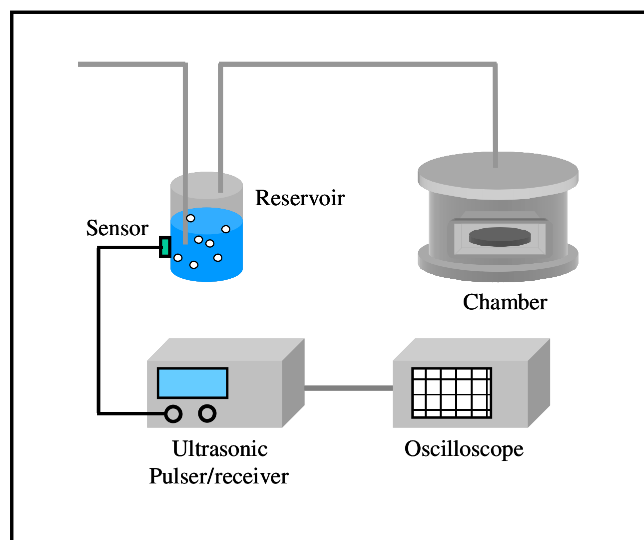

Figure 1. Precursor decomposition monitoring equipment setup using ultrasonic pulse.

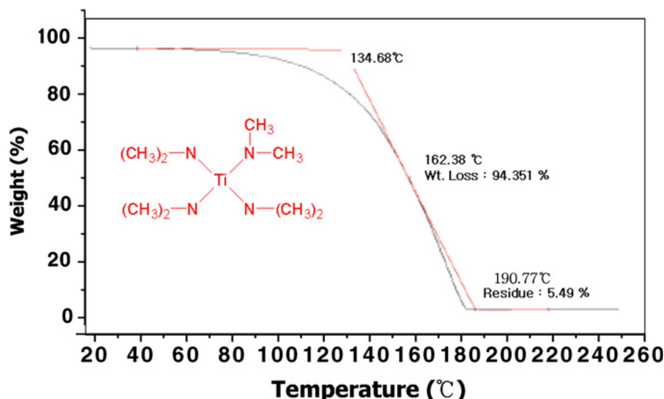

Figure 2. TGA data of TDMAT.

In order to measure the change of the ultrasonic characteristics during heat decomposition, the decomposition state, under a constant temperature, is observed in real time through the use of TDMAT, which is used, as in the TiN MOCVD process, etc, as a precursor [8, 9]. First of all, it is measured with TGA in order to have an overall observation of the decomposition temperature of TDMAT figure 2. Although it is not possible to observe the aging effect as related to time in the case of TGA measurement, it is possible to have a look at the overall decomposition temperature characteristic [10]. According to the TGA result, it is confirmed that heat decomposition begins at about 130 °C.

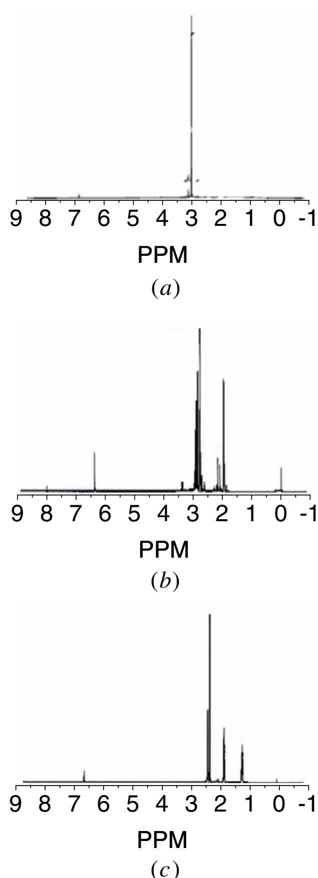

Figure 3. ^{1}H-NMR data: (*a*) 0 h (reference), (*b*) 12 h and (*c*) 36 h.

The degree of decomposition of TDMAT in accordance with time has been monitored through ^{1}H-NMR and ultrasonic diagnosis by fixing the temperature at 130 °C, at which temperature the most active decomposition begins to take place according to the TGA result. In the case of ultrasonic diagnosis, measurement was performed in real time under the same conditions as the system of figure 1. It was confirmed that the peak begins to be observed around a peak of 3.1 ppm due to the dimethyl base. The methyl peak shifted over 12 h at 130 °C. Therefore, substantial degradation was observed. After 36 h, the methyl peak at 3.1 ppm disappears completely due to the final, complete decomposition at 130 °C, 36 h as shown in figure 3.

Therefore, as can be estimated from the TGA data, decomposition takes place in a temperature range of 130–190 °C; decomposition becomes active at over 130 °C. In order to compare the ultrasonic wave change in accordance with this heat decomposition based on this result, an ultrasonic measurement of the precursor (TDMAT) was performed at 130 °C. The result was that the round trip time (velocity) of the ultrasonic wave increases considerably from 22.3 μs (1120 m s^{-1}) before decomposition to 31 μs (806 m s^{-1}) at 130 °C, 36 h through 26.2 μs (950 m s^{-1}) at 130 °C, 12 h (figure 4).

The ultrasound method is available in stainless steel as well as glass flask. If an ultrasonic wave is applied after attaching an ultrasonic wave sensor to stainless steel, a noise peak can occur due to stainless steel anti-glare.

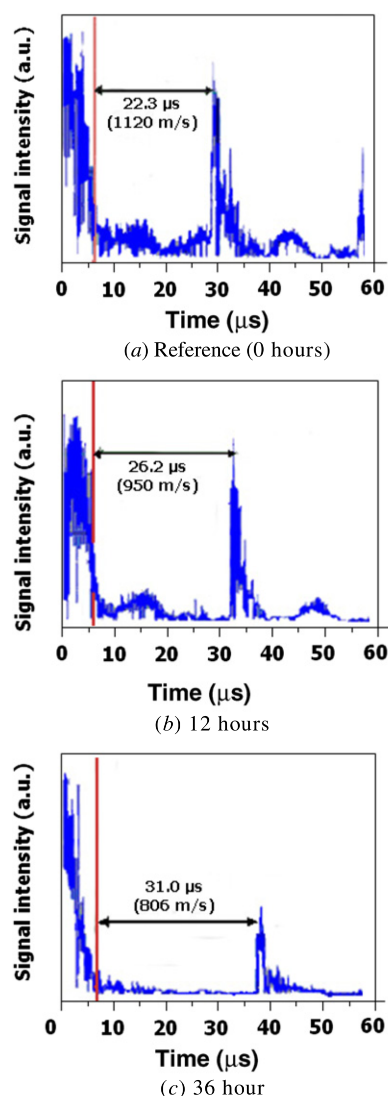

Figure 4. Ultrasonic sonography of TDMAT at different elapsed times.

First of all, the time between the first echo and the second echo peaks after the ultrasonic sensor is attached to the container and reflected.

Once the ultrasonic wave is applied, however, it comes and goes a number of times in the stainless steel wall, which causes severe noise. Then, the echo peak is overlapped.

Therefore, it is hard to have the first echo separated from noise automatically. Therefore, it should be programmed for exclusion time conditions to be set. If the value is set at the end of the first peak, then the noise peak by stainless steel does not change. Therefore, it could be eliminated. In other words, the peaks before the exclusion time are eliminated. The measurement is carried out from the second peak.

For quantitative data on the correlation between the change in the ultrasonic wave and the amount of degraded precursor, the change in the precursor was quantitatively observed using FT-IR. The degradation of the precursor was observed on a real-time basis using FT-IR while maintaining

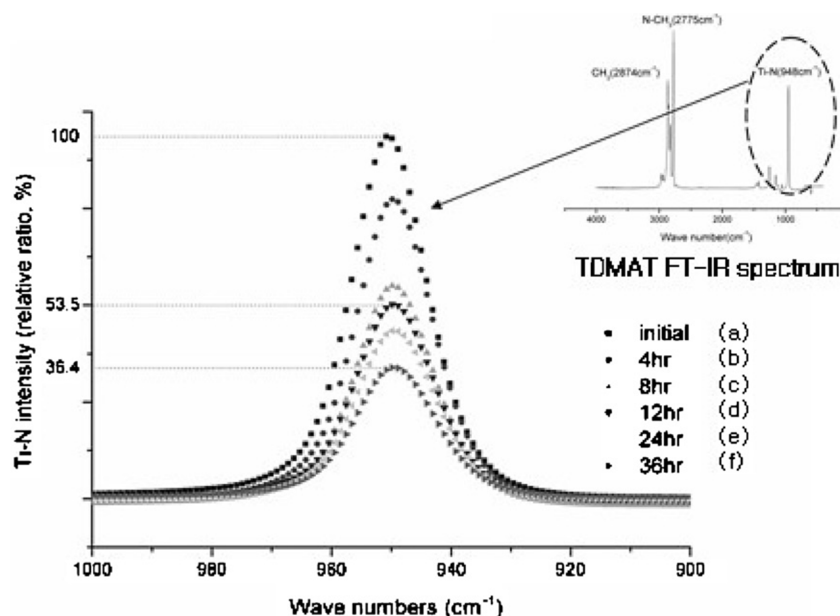

Figure 5. The intensity change of the Ti–N peak in TDMAT with the degree of decomposition.

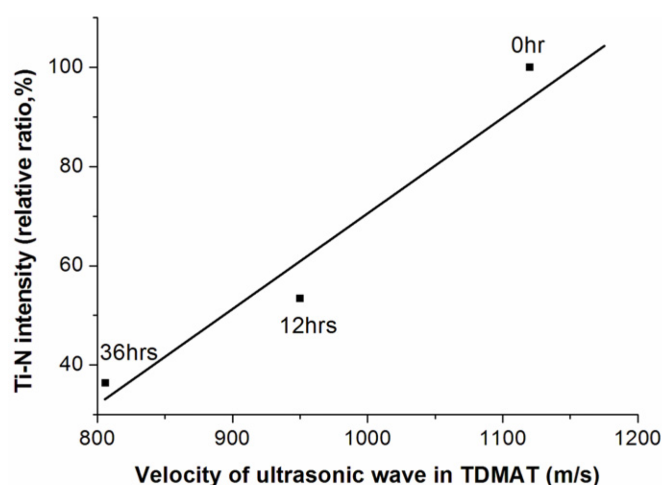

Figure 6. Correlation between the change in the velocity of the ultrasonic wave and the change in the Ti–N peak of FT-IR.

the temperature at 130 °C for 0–36 h. As shown in figure 5, the gradual weakening of the Ti–N peak in the TDMAT spectra was verified.

In TDMAT, dissociation first occurs if heat is applied due to the weak Ti–N bond. The degree of decomposition can be quantitatively measured by observing the change in the strength of the Ti–N peak. Figure 5(*a*) shows the Ti–N peak at the pure state of TDMAT while (*b*)–(*f*) demonstrate that the peak weakens over time due to the peak change spectrum. Particularly, (*f*) shows about 63.6% degradation. Based on the above result, figure 6 shows a quantitative description of the correlation between the change in the velocity of the ultrasonic wave and the change in the Ti–N peak of FT-IR. As shown in figure 6, the quantitative measurement of precursor degradation on a real-time basis was verified by using the velocity of ultrasonic wave.

If the ultrasonic wave is continuously used for measurement, however, it could be possible that this could also cause precursor degradation [11]. An ultrasonic wave was applied to TDMAT for 10 days, and an NMR analysis was performed both before and after the application of the ultrasonic wave. As shown in figure 7, no degradation was observed despite the continuous application of ultrasonic wave over 10 days. Therefore, it was verified that the ultrasonic wave creates no issues in the performance of a TDMAT analysis.

To determine why the ultrasonic wave data change because of the TDMAT decomposition, a measurement of the change in viscosity of TDMAT after degradation was initially planned. However, this measurement was not performed due to the air-sensitive nature of TDMAT.

A $Pd(PPh_3)_4$ compound was therefore used in this study. This compound is stable in air and has metal–organic bonding with properties very similar to TDMAT. The decomposition characteristic of TDMAT can therefore be indirectly anticipated by using a $Pd(PPh_3)_4$ compound, which is inexpensive and very easy to use. The status of the $Pd(PPh_3)_4$ compound both before and after degradation was compared using ^{1}H-NMR and ultrasonic waves, and the change in viscosity was observed.

Before the decomposition of the $Pd(PPh_3)_4$ compound, the protons of the phenyl group were approximately 7.5 ppm. As decomposition continued, the protons that were detached from the Pd and the phenyl group were approximately 1 ppm (figure 8).

According to the ultrasonic wave measurement of TDMAT both before and after degradation, in 5 days the ultrasonic peak intensity had decreased and the round trip time had increased. The velocity change of the ultrasonic wave and the drastic reduction of the peak strength can be seen from the oscilloscope image (figure 9). This shows that the

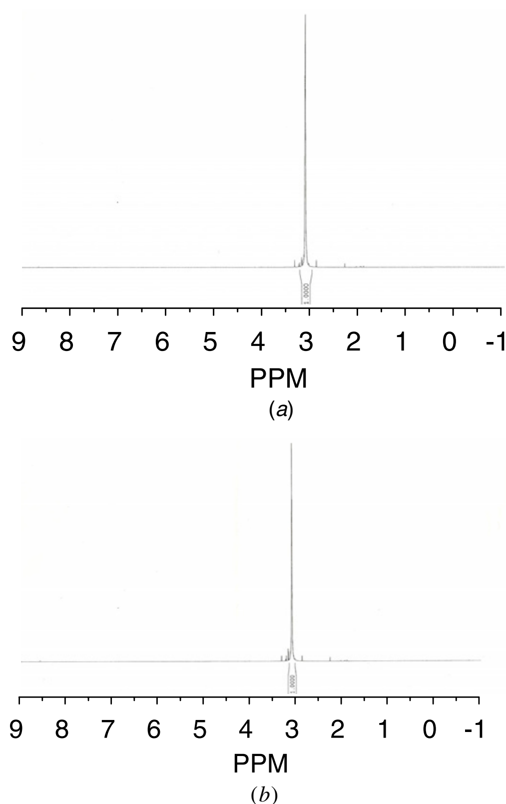

Figure 7. ^{1}H-NMR data for observing the degradation effect of ultrasonic wave on TDMAT: (*a*) reference (0 h), (*b*) 10 days.

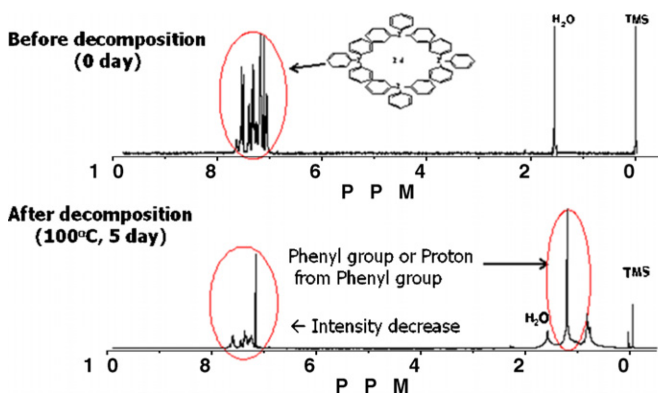

Figure 8. ^{1}H-NMR spectra of the 1wt% $Pd(PPh_3)_4$ compound at different elapsed times (fixed at 100 °C).

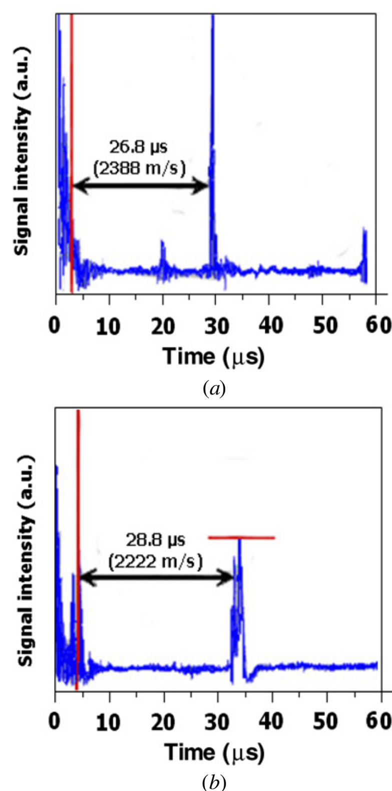

Figure 9. Time of flight (TOF) measurement of the $Pd(PPh_3)_4$ compound at different elapsed times: (*a*) reference (0 day), 100 °C; (*b*) 5 day, 100 °C.

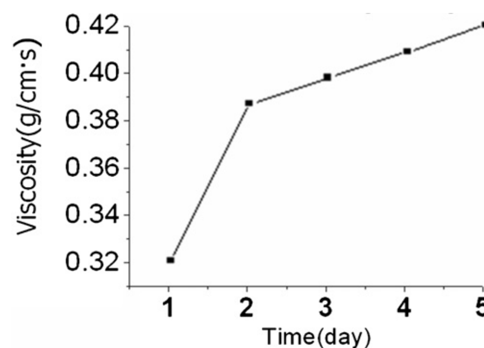

Figure 10. Viscosity measurement data of the $Pd(PPh_3)_4$ compound (100 °C).

absorption of the ultrasonic signal due to the property change of the $Pd(PPh_3)_4$ compound occurred while decomposition took place.

A change in viscosity during degradation (for 0–5 days at 100 °C) was observed. Prior to decomposition, the viscosity value was 0.32 poise but this value had increased to 0.41 poise after decomposition (5 days). Therefore, it can be said that viscosity increased due to decomposed byproducts, and ultrasonic wave was interfered or absorbed by decomposed byproducts, causing the peak intensity to decrease and round trip time to increase (figure 10).

4. Conclusion

Technology for the measurement of real-time decomposition monitoring of TDMAT for the MOCVD process has been developed by utilizing ultrasonic devices. As the velocity and peak strength of the ultrasonic waves change due to the decomposition of TDMAT over the course of time, the degree of decomposition of the precursor can be measured by monitoring this. The demand for a precursor for the MOCVD process will increase sharply as the integration of semiconductors increases. It can be considered that an enhancement of yield can be made through the usage of the real-time decomposition monitoring of precursors as presented by this study and through stable precursor management by

semiconductor fabrication companies and precursor supply companies.

References

[1] Bonitz J, Schulz S E and Gessner T 2003 CVD TiN layers as diffusion barrier films on porous SiO_2 aerogel *Microelectron. Eng.* **70** 330

[2] Lan J K, Wang Y L, Lo K Y, Liu C P, Liu C W, Wang J K, Cheng Y L and Chau C G 2001 Integration of MOCVD titanium nitride with collimated titanium and ion metal plasma titanium for 0.18-μm logic process *Thin Solid Films* **544** 398–9

[3] Leistner T, Lehmbacher K, Harter P, Schmidt C, Bauer A J, Frey L and Ryssel H 2002 MOCVD of titanium dioxide on the basis of new precursors *J. Non-Cryst. Solids* **303** 64

[4] Yun J, Park M and Rhee S 1999 Comparison of tetrakis(dimethylamido)titanium and tetrakis(diethylamido)titanium as precursors for metal-organic chemical vapor deposition of titanium nitride *J. Electrochem. Soc.* **145** 1804

[5] Jeffries M, Lai E and Hull J B 2003 A new approach to process control for a bottling plant *J. Mater. Process. Technol.* **133** 122

[6] Yun J, Park M and Rhee S 1998 Effect of the gas-phase reaction in metal organic chemical vapor deposition of TiN from tetrakis(dimethylamido)titanium *J. Electrochem. Soc.* **145** 2453

[7] Yun J, Chung K and Moon D 2005 Real time quantitative diagnostic technique for measuring chemical vapor deposition precursors *J. Vac. Sci. Technol.* A **23** 1267

[8] Raaijmakers I J 1994 Low temperature metal-organic chemical vapor deposition of advanced barrier layers for the microelectronics industry *Thin Solid Films* **247** 85

[9] Sun S C and Tsai M H 1994 Comparison of chemical vapor deposition of TiN using tetrakis-diethylamino-titanium and tetrakis-dimethylamino-titanium *Thin Solid Films* **253** 440

[10] Kunte G V, Shivashankar S A and Umarji A M 2008 Thermal analysis and vapour pressure of a new series of tungsten (VI) oxo-alkoxide-β-ketoesterate complex precursors for the chemical vapour deposition of tungsten oxide *Thermochim. Acta* **474** 12

[11] Workman J Jr *et al* 1999 Process analytical chemistry *Anal. Chem.* **121** 71