Journal of Korean Institute of surface Engineering
Vol. 32, No. 3, Jun., 1999

INFRARED ABSORPTION MEASUREMENT DURING LOW-TEMPERATURE PECVD OF SILICON-OXIDE FILMS

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Abstract

In situ measurement of infrared absorption spectra has been performed during low-temperature plasma-enhanced chemical vapor depositiion of silicon-oxide films using tetramethoxysilane as a silicon source. Several absorption bands due to the reactant molecules are clearly observed before deposition. In the plasma, these bands completely disappear at any oxygen mixing ratio. This result shows that most of the tetramethoxysilane molecules are dissociated in the rf plasma, even C-H bonds. Existence of Si-H bonds in vapor phase and/ or on the film surface during deposition has been found by infrared diagnostics. We observed both a decrease in Si-OH absorption and an increase in Si-O-Si after plasma off, which means the dehydration condensation reaction continues after deposition. The rate of this reaction is much slower than the deposition ratio of the films.

Key words : *in situ diagnostics, infrared spectroscopy, organosilicon compound, plasma-enhanced chemical vapor deposition.*

1. INTRODUCTION

It has been strongly needed to deposit silicon dioxide (SiO_2) films on polymeric materials for various purposes, abrasion-resistance coating, anti-reflection coating, oxygen gas barrier, etc. Generallty polymeric materials have poor heat resistance, so that low process temperature, near room temperature, is necessasry for the deposition of SiO_2 films. Therefore, plasma-enhanced chemical vapor deposition (PECVD) using organosilicon compounds at low temperature has been extensively studied[1-9], since this process can work at much lower temperature has been extensively studied[1-9], since this process can work at much lower temperature than thermal CVD and PECVD using SiH_4 as a reactant. However, the deposition mechanism of SiO_2 films at low temperature, especially near room temperature, has not been elucidated. In this study, we have performed in situ measurement of infrared (IR) absorption spectra during low-temperature PECVD of SiO_2 films using an organosilicon reactant. Reactions in the plasma, dissociation and

oxidation process of the reactant molecules, are discussed.

2. EXPERIMENTAL

We used a remote-type rf PECVD system assembled with a Fourier transform infrared spectrometer (FTIR : FTS-175, Bio-Rad). Fig. 1 illustrates the system for the IR transmittance measurement. A 13.56 MHz generator supplied rf power of 75 W which was transferred to the gas in the discharge tube with an impedance-matching network terminating in a 3.5 turn inductively-coupled coil. Tetramethoxylsilane (TMOS) was used as a silicon source. After evacuating the deposition chamber below 0.3 Pa, the organosilicon gas was introduced from a gas inlet on a side wall of the deposition chamber, whereas oxygen gas from the top of the discharge tube. The partial pressure ratio of oxygen to the organosilicon gas, R, was varied 0~90% with a constant total pressure of 10 Pa. Si (100) single crystal windows were used as substrates, which were held at room temperature during deposition. Therefore the acquired IR spectra contain the absorption from the vapor phase, deposited films and surfaces on the two windows. Experimental conditions are summarized in Table 1.

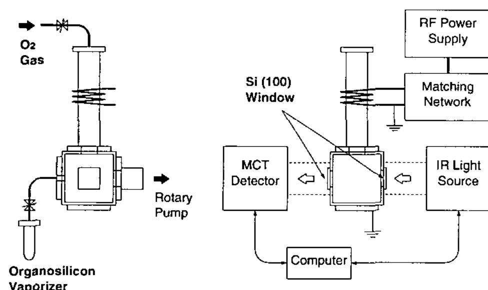

Fig. 1 Schematic diagram of the rf PECVD-FTIR system. IR light path legnth in the deposition chamber is 75mm.

3. RESULTS AND DISCUSSION

3. 1 Before Deposition

Fig. 2(a) shows the transmission spectrum measured at R=0% before dischasrge on. We can observe several absorption bands, which are identified as described in Table 2 When the TMOS pressure dereases from 10 to 1 Pa, the absorption become weaker. Plotting the absorbance due to Si-O-C asymmetric stretching vibration at 111 cm^{-1}, we can clearly recognize a linear-dependence of the absorbance on TMOS

Table 1. Deposition conditions.

Reactant	
Tetramethoxysilane (TMOS)	$Si(OCH_3)_4$
Oxtygen	O_2
Deposition Chamber	
Base Pressure	0.3 Pa
Total Pressure	10 Pa
O_2 Partial Pressure Ratio R	0~90%
R = PO_2/P Total 100 [%]	
RF Power	75 W
FT-IR System : Bio-Rad FTS-175S	
Michelson-type Interferometer	
MCT Detector (10000~700cm^{-1})	
Resolution > 0.5cm^{-1}	

Table 2. Identified absorption bands in the transmission spectrum of TMOS gas.

a. C-H astm str	2958 cm^{-1}
b. C-H stym str	2854 cm^{-1}
c. atmospheric CO_2	~1350 cm^{-1}
d. $-CH_3$ rocking	1200 cm^{-1}
e. Si-O-C asym str	1111 cm^{-1}
f. Si-O-C sym str	843 cm^{-1}

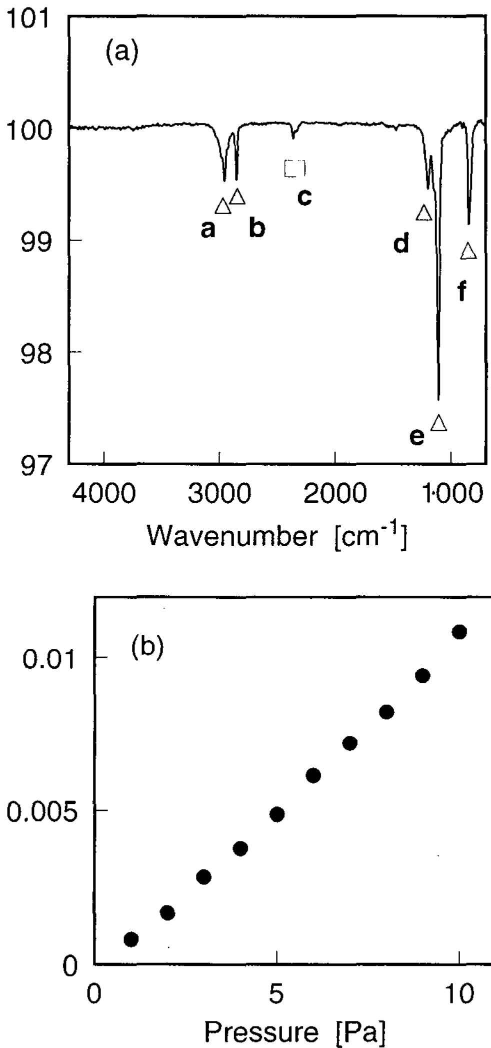

Fig. 2 (a) Transmission spectrum measured at 10 Pa of TMOS before dischasrge on. See Table II for the identification of each absorption band. (b) Dependence of the absorbance due to Si-O-C asymmetric stretching vibration at 1111cm^{-1} on TMOS partial pressure.

pressure (Fig. 2(b)). This means that the absorption bands detected in these spectra are originated in the TMOS molecules in vapor phase, not those absorbed on the substrate surface. Therefore when we need to use more than two kinds of organosilicon compound as gas sources, IR transmittance measurement can be a simple and useful method to control their partial pressure since each organosilicon molecule has its identical absorption peak position.

3. 2 During Deposition

Fig. 3 shows R-dependence of the spectra measured in the plasma after 1 minute deposition. At any oxygen mixture ratio, the absorption bands due to TMOS molecule are not observed. That is to say, the most of TMOS molecules introduced into the chamber are dissociated in the rf plasma, even C-H bonds. This result is consistent with our previous reports which deals with in situ plasma diagnostics of TMOS-O_2 system by using mass spectroscopy[8, 9].

Furthermore, we can observe small but distinct absorption bands due to Si-H bond around 2200 wavenumber. As illustrated in Fig. 4(a), the Si-H bands are independent of deposition time. Therefore Si-H bonds are not included in the de-

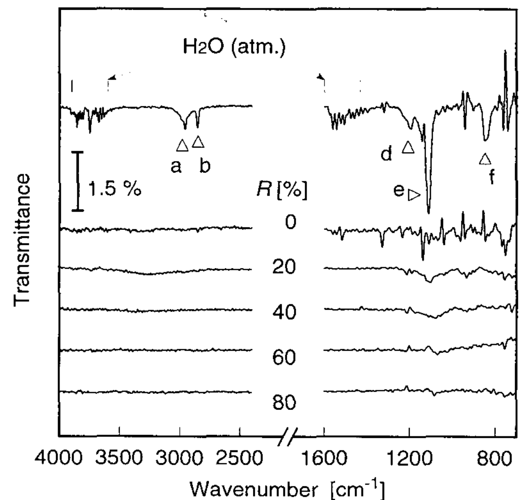

Fig. 3 R-dependence of IR transmission spectra during deposition.

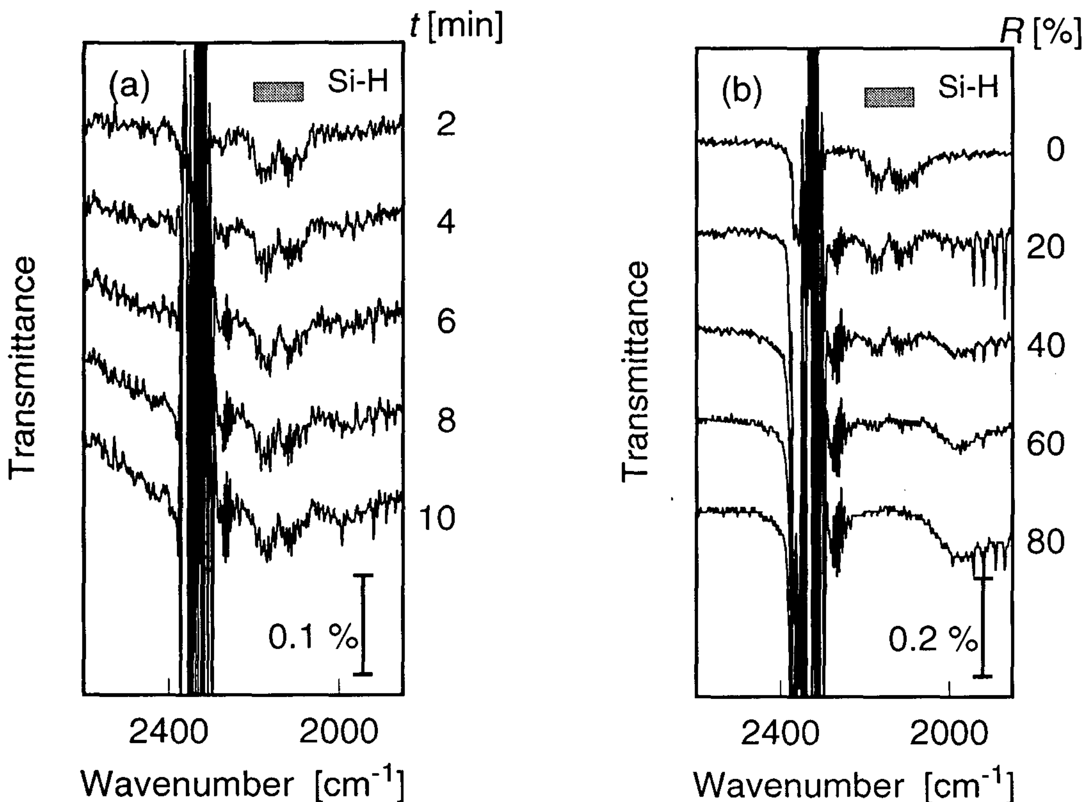

Fig. 4 Dependeces of the Si-H absorption bands on (a) deposition time and (b) oxygen mixing ratio R.

posited film but in the vapor phase and/or on the film surface. The R-dependence of the Si-H bands shows a decrease of absorption intensity with oxygen mixing ratio (Fig. 4(b)). However, from only this R-dependence result, we cannot make clear that the Si-H bonds exist in vapor phase or on the surface. It is necessary to separate the absorption of vapor phase from that of the surface by using other in situ IR techniques, e.g., infrared reflection-absorption spectroscopy (IR-RAS) and polarization modulation infrared spectroscopy (PMIR).

3. 3 After Deposition

Just after plasma off, the Si-H absorption completely disappears within a several seconds (Fig. 5). This result also proves that the Si-H bonds do not exist in the deposited film. Fig. 6 shows a difference spectrum between a transmission spectrum measured in the plasma at 10 minutes deposition and that acquired more 10 minutes after plasma off. This difference spectrum cleasrly shows not only the disappearence of Si-H and the reappearence of the absorption bands due to TMOS reactant, but also a decrease in Si-OH absorption and an increase in Si-O-Si. From this result, the dehydration condensation reaction continues after deposition even at room temperature in the deposited film. However, this reaction is much slower compared to the deposition rate of the

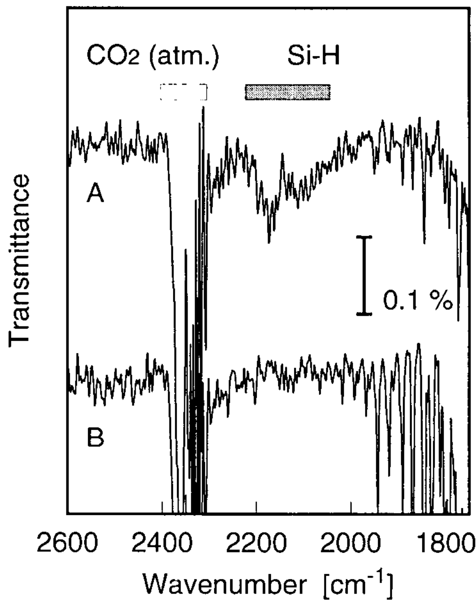

Fig. 5 Si-H absorption bands during deposition(A) and just after plasma off (B). The spectrum B was acquired within 5 seconds after plasma off.

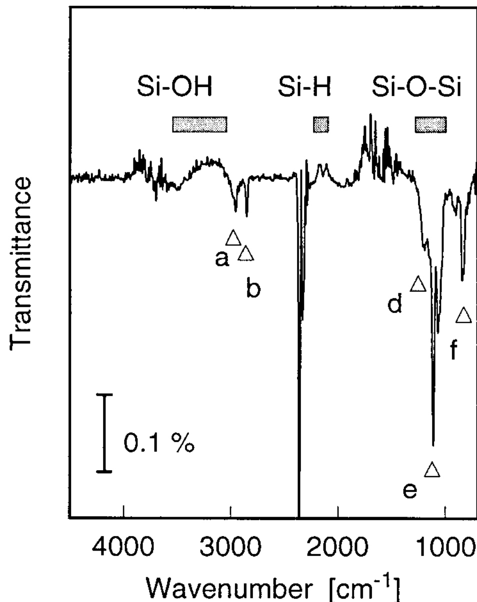

Fig. 6 The difference spectrum between a transmission spectrum measured in the plasma at 10 minutes deposition and that acquired more 10 minutes after plasma OFF.

films. Therefore we must consider the surface reaction during deposition which is much faster than such dehydration condensation in the film. For this purpose, further investigation using IR-RAS and PMIR diagnosing method is needed.

4. CONCLUSIONS

In situ IR diagnostics have elucidated that the reactant organosilicon molecules can be dissociated even in relatively low-density plasma used in this study. Si-H bonds exist in the vapor phase and/or on the film surface only during discharge, and they disappear rapidly after discharge off. Dehydration condensation of Si-OH continues after discharge off to produce Si-O-Si network. Further investigation using IR-RAS and PMIR will make cleaar the surface reaction in PECVD of silicon-oxide films.

ACKNOWLEDGEMENT

This work was supported by a Grant-in-Aid for Scientific Research from The Ministy of Education, Science, Sports and Culture, Japan.

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