

## Real Time Monitoring of Surface Reactions during Plasma Enhanced CVD of Silicon

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Reacting silicon surfaces in contact with the glow discharge of  $\text{SiH}_4$  has been studied by an FT-IR-ATR (Attenuated Total Reflection) technique. The surface hydrogen bond configurations of a thin silicon layer have been monitored in real time at different substrate temperatures. In the early stages of silicon film growth at a substrate temperature of  $200^\circ\text{C}$ ,  $\text{SiH}_2$  is the major species on the surface although monohydride bonds are predominant in the bulk layer, while at room temperature  $\text{SiH}_3$  and  $(\text{SiH}_2)_n$  chains are the dominant surface species. At a temperature of  $-95^\circ\text{C}$ , polymerization reactions among adsorbates proceeds on the surface to form polysilane consisting of  $(\text{SiH}_2)_n$  chains terminated with  $\text{SiH}_3$ .

### 1. Introduction

In situ or real time diagnostics of surface reactions in a reactive plasma is potentially important for atomic scale control of plasma deposition processes or dramatic improvement of step-coverage of a deposited thin film. Regarding gas phase reactions in a silane plasma the concentration of reactive species has been quantitatively measured<sup>1)</sup>. Real time monitoring of surface reactions during plasma deposition from silane has been made by employing IR-RAS (Reflection Absorption Spectroscopy)<sup>2)</sup> or ellipsometry<sup>3)</sup>. In this paper we report on a newly developed FT-IR-ATR (Attenuated Total Reflection) system by which surface reactions in contact with a plasma can be directly probed. It is demonstrated that ATR sensitively detects the chemical bonding features of reacting surfaces and provides detailed information about surface reactions which are promoted in silane or deuterium plasmas.

### 2. Experimental

A silicon crystal was used as the ATR prism, which was attached to a grounded electrode in a capacitively coupled PECVD reactor. As illustrated in Fig. 1, an infrared beam from an FT-IR spectrometer passed through a polarizer (P-polarized) and a  $\text{BaF}_2$  window before entering the Si prism. Multiple internal reflections in the prism

enabled us to probe surface chemical bonds whose vibrational spectra were obtained by a MCT detector. The resolution of ATR system was  $4\text{ cm}^{-1}$  and the spectral data were obtained in 30 sec or more. For the purpose of monitoring an H/D exchange reaction, an atomically flat, hydrogen-terminated  $\text{Si}(111)$  ATR crystal was employed. In a deuterium plasma the flow rate, the rf power density and the total pressure were maintained at 50 sccm,  $40\text{ mW/cm}^2$  and 0.2 Torr, respectively. The ATR measurements during deuteration reaction were carried out after turning off the discharge because the H/D exchange reaction rate is fast. During PECVD, the flow rate of 3% $\text{SiH}_4$  diluted with  $\text{H}_2$ , the rf power density and the total pressure were kept at 90 sccm,  $20\text{ mW/cm}^2$  and 0.2 Torr, respectively. The deposition temperature was varied from  $200^\circ\text{C}$  to  $-95^\circ\text{C}$ .

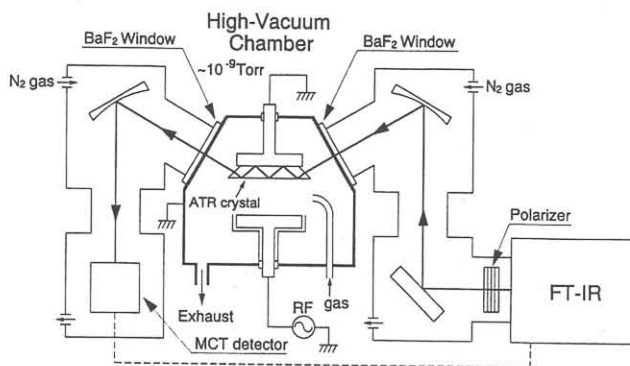


Fig. 1 Schematic of an FT-IR-ATR system for monitoring surface reactions in a UHV chamber.

The deposition rate of a Si thin film was estimated to be about 0.3 nm/min at room temperature and 200°C.

### 3. Results and Discussion

#### 3.1 H/D Exchange Reaction

An H-terminated Si(111) surface is exposed to a D<sub>2</sub> plasma in order to examine the submonolayer sensitivity of ATR and to monitor the exchange reaction of surface SiH bonds with deuterium. The intensity of the optical absorption due to the SiH stretching vibration at 2083cm<sup>-1</sup> is decreased by the D<sub>2</sub> plasma exposure as shown in Fig. 2. Correspondingly, the absorption peaks due to SiD<sub>x</sub> (x=1,2,3) appear. The SiD bond absorption at 1512cm<sup>-1</sup> is predominant at 0.2 sec exposure to a deuterium plasma. Further exposure of the H-terminated surface results in increasing number of SiD<sub>2</sub> (1550cm<sup>-1</sup>) and SiD<sub>3</sub> bonds (1553.5cm<sup>-1</sup>)<sup>4</sup> presumably because the deuteration reaction of SiH bonds on the top surface is followed by further deuteration of the Si backbonds at SiD sites. Figure 3 shows integrated absorption intensities for SiH<sub>x</sub> and SiD<sub>x</sub> stretching vibrational modes as a function of D<sub>2</sub> plasma exposure time. As the exposure time increases, the decrease of SiH<sub>x</sub> (mainly x=1) bonds is accompanied with the corresponding increase of the SiD<sub>x</sub> absorption. This clearly shows that H/D exchange reaction proceeds on the top

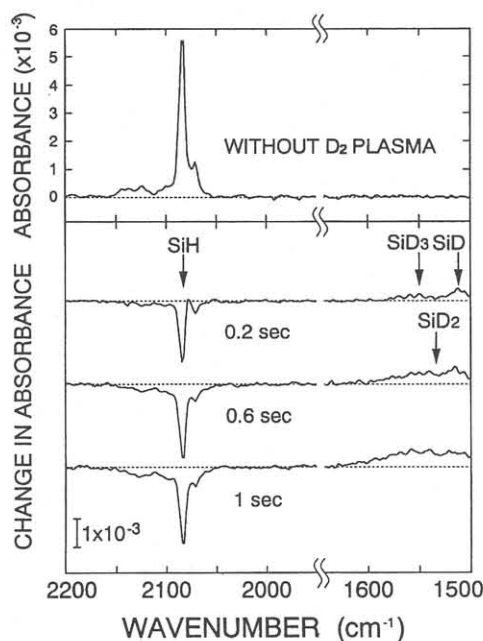


Fig. 2 P-polarized ATR spectrum of a Si(111) surface treated with a BHF solution and the change in the absorbance after D<sub>2</sub> plasma exposure.

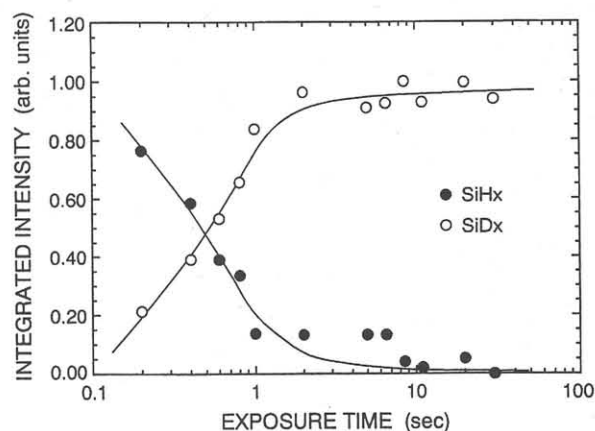


Fig. 3 Integrated absorption intensities for SiH<sub>x</sub> and SiD<sub>x</sub> stretching vibrational modes as a function of D<sub>2</sub> plasma exposure time.

surface and also backbonds of surface Si atoms are partially deuterated. A few seconds of D<sub>2</sub> plasma exposure are enough to completely deuterate a monohydride terminated surface.

#### 3.2 Silicon Deposition Kinetics

ATR spectra due to SiH<sub>x</sub> bonds on silicon deposition surfaces during PECVD are shown in Fig. 4. The time indicated for each of spectra denotes the period needed for the cumulative spectral measurements. In the early stages ( $\leq 30$ sec) of the silicon film growth at 200°C the absorption due to the stretching modes of SiH<sub>3</sub> and (SiH<sub>2</sub>)<sub>n</sub> molecular units are observable around 2140~2120cm<sup>-1</sup>. The absorption due to the surface SiH<sub>2</sub> vibration is increased with deposition time as a consequence of hydrogen desorption reaction at this temperature. Taking into account the fact that SiH bonds are mainly incorporated in the bulk hydrogenated amorphous silicon (a-Si:H) films grown at 200°C, it is likely that silicon network formation reaction in the near surface region is not completed. This is consistent with a previous result of IR-RAS<sup>2)</sup>. At room temperature, a significant increase of the absorption due to (SiH<sub>2</sub>)<sub>n</sub> chains and SiH<sub>3</sub> bonds is clearly observed in the early stages of the growth ( $\leq 30$ sec), reflecting the reduction of thermal desorption reactions of bonded hydrogen in the near-surface region. The H/D exchange reaction after silicon deposition at room temperature also reveals the hydrogen bonding features on the top surface even for a relatively thick film as shown in Fig. 5. Significant reduction of (SiH<sub>2</sub>)<sub>n</sub> chains, SiH<sub>3</sub> and SiH<sub>2</sub> bonds by deuteration clearly shows the existence of such molecular units on the top surface in agreement with the result of Fig. 4.

By lowering the deposition temperature to  $-50^{\circ}\text{C}$  or  $-95^{\circ}\text{C}$ , optical absorption due to  $(\text{SiH}_2)_n$  chains and  $\text{SiH}_3$  units are predominant from the beginning of the deposition and even after long time film growth. Particularly at  $-95^{\circ}\text{C}$ , the absorption band due to  $(\text{SiH}_2)_n$  chains terminated with  $\text{SiH}_3$  is only observed during the film growth and the absorption intensity is increased by a factor of about 20 as compared to that at  $-50^{\circ}\text{C}$ . This agrees very well with the result of a previous paper<sup>5)</sup>, where silicon film growth rate from a silane plasma dramatically increases at temperatures below  $-80^{\circ}\text{C}$  and the deposited films consist of the  $(\text{SiH}_2)_n$

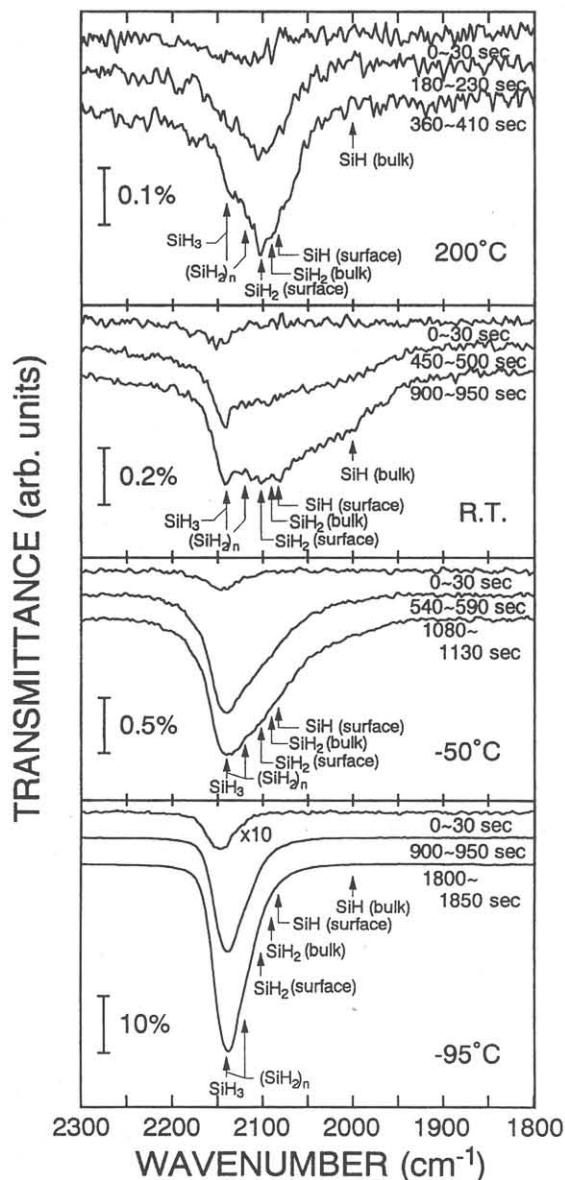


Fig. 4 P-polarized ATR spectra of surfaces of ultra-thin silicon films at different substrate temperatures. The times indicated in the figure refer to sampling time for data acquisition.

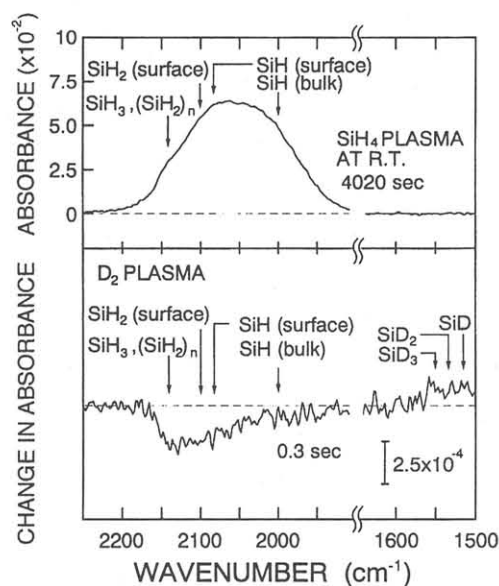


Fig. 5 H/D exchange reaction on a silicon surface after 4020 sec deposition.

chains terminated with  $\text{SiH}_3$  which is a typical structure of polysilane.

#### 4. Conclusions

Chemical bonds on a growing film surface in a silane plasma have been sensitively probed by real-time ATR spectroscopy at substrate temperatures ranging from  $200^{\circ}\text{C}$  to  $-95^{\circ}\text{C}$ . Dramatic change in surface reaction is observable by lowering the substrate temperature. Applications of this technique to investigate the reactions at heterointerfaces, silicon oxidation and etching are now in progress.

#### References

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