

## Diagnostics of Hydrogen Role in the Si Surface Reaction Processes Employing In-situ Fourier Transform Infrared-Attenuated Total Reflection

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The oxidation process of H-terminated amorphous Si film on Ge and the reaction mechanism of the triethylsilane (TES)/H system which allows us to deposit an organic Si film conformably have been investigated employing in-situ FTIR(Fourier transform infra red)-ATR(attenuated total reflection). This measurement was demonstrated to be a sensitive and simple method to inspect the role of H(hydrogen) in their surface reactions. In the Si oxidation case, the H-terminated Si is readily oxidized by O(oxygen) atoms. The oxidation with O<sub>2</sub> molecules proceeds gradually as the breaking of Si-H bonds and forming of H-Si-O bonds due to binding of O atoms with the back bond of Si for 700 min. After about 700 min, dissociated O atoms rapidly penetrate the Si film, and oxidize the bulk Si, leaving both Si-H and H-Si-O bonds still on the Si surface. Next, in the TES/H reaction system, gas phase FTIR spectra obtained by reactions of H atoms or H<sub>2</sub> molecules with TES do not show appreciable change in a wide range of pressure. Nevertheless, in-situ FTIR-ATR reveals that TES reacts easily with H atoms on the surface, desorbing H<sub>2</sub>, methyl and ethyl groups.

**KEYWORDS:** hydrogen role, oxidation, triethylsilane, diagnostics, in-situ FTIR-ATR, surface reaction

### §1. Introduction

With continual shrinkage in the minimum feature size of ULSI devices, atomic order controls are required increasingly for the surface reaction processes which dominate growth of very thin Si(silicon) dioxide (SiO<sub>2</sub>) film and a variety of CVD(chemical vapor deposition) processes. Especially, H(hydrogen) plays an important role in the reaction processes such as initial layer-by-layer oxide growth phenomena<sup>1)</sup> of the H(hydrogen)- and F(fluorine)-terminated Si surface,<sup>2,3)</sup> the Al-selective CVD employing DMAIH(dimethylaluminumhydride) which occurs only on the H/F-terminated Si surfaces,<sup>4)</sup> and the digital CVD of SiO<sub>2</sub><sup>5)</sup> which is carried out by the repetitive process of firstly deposition of thin Si film as a result of a reaction of H atoms with TES(triethylsilane) and subsequent oxidation of the Si film. The reaction mechanisms of these processes are not understood well. Much attentions has been placed recently on a FTIR(Fourier transform infrared)-ATR(attenuated total reflection) method which can easily detect H bonding with high sensitivity.<sup>2)</sup> This paper reports diagnostics of both surface reactions of the oxidation process of the H/F-terminated Si and TES/H reaction employing in-situ FTIR-ATR and discusses both reaction mechanisms.

### §2. Experimental

An in-situ FTIR-ATR system is shown in Fig. 1. A small reactor which consisted of a gas inlet, an ATR prism and an evacuation outlet connected to a turbomolecular pump (50 l/s) system was set in an ATR accessory mounted on a FTIR system (Perkin Elmer 1640). The reactor was evacuated up to  $1 \times 10^{-6}$  Torr. Since a Si ATR prism is not transparent for IR light lower than  $1500 \text{ cm}^{-1}$ , because of Si self-absorption, a Ge(n type,  $60 \Omega \cdot \text{cm}$ , (100)) wafer was used as the prism for the Si oxidation experiment.

The Ge prism was prepared as follows. Both edges of the Ge sample with  $20 \text{ mm} \times 50 \text{ mm}$  were polished by sandpaper and then finished by fine polishing on a velvet cross with #1500 aluminum oxide powder. Finally it was cleaned by organosolvent boiling and subsequent water rinsing. A  $1\text{-}\mu\text{m}$ -thick Si film was deposited at room temperature by electron beam evaporation of Si on one side of the Ge prism under a pressure of  $1 \times 10^{-6}$  Torr. Eventually an amorphous Si surface was investigated for the oxidation experiment. These Si films were dipped in 5% HF solution and subsequently processed by N<sub>2</sub> blowing. Heating of the Ge prism up to  $250^\circ\text{C}$  is available by installing a small ceramic heater on the back surface. IR rays were incident normally on one side surface of the 45-degree cut edge plane of the prism. Then the surface was exposed to hydrogen (H) or oxygen (O) atoms which were generated by upstream microwave (2.45 GHz) discharge of H<sub>2</sub> and O<sub>2</sub> gases in an Al<sub>2</sub>O<sub>3</sub> tube. A CaF<sub>2</sub> window which is set in the opposite side of the Ge prism allows us to introduce D<sub>2</sub> UV light irradiation. As inset in Fig. 1, an electrode coupled with RF (13.56 MHz) power

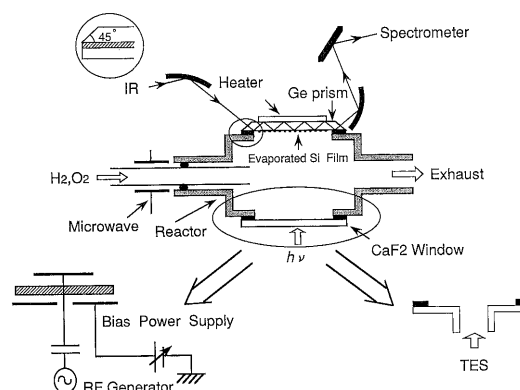


Fig. 1. A schematic diagram of the in-situ FTIR-ATR system.

which provides a plasma in a reactor can be equipped by replacing the  $\text{CaF}_2$  window. Negative DC bias voltage can also be added to the prism of the substrate.

### §3. Results and Discussion

#### 3.1. Oxidation of the H/F-terminated Si surface

##### 3.1.1 Behavior of Si-H and Si-F bonds during oxidation

As shown in Fig. 2, the use of the Ge prism enables us to detect the Si-F stretching mode around  $830\text{ cm}^{-1}$ <sup>6)</sup> as well as the Si-H<sub>x</sub> stretching mode at  $2100\text{ cm}^{-1}$ <sup>2)</sup> for the Si surface after 5% HF solution treatment and N<sub>2</sub> blowing. Then the FTIR spectrum of the Si surface subjected to the following exposure processes was studied as shown in Fig. 3: (a) 60-min exposure of O<sub>2</sub> at 160 Torr, (b) 5-s exposure of O atoms generated by O<sub>2</sub> plasma at 1 Torr, (c) 10-s exposure of O atoms generated from 1 Torr O<sub>2</sub> under irradiation of D<sub>2</sub>-UV lamp with main wavelength of 161 nm. In the case of (a), appreciable oxidation was not observed after slight oxidation in the early stage. In-

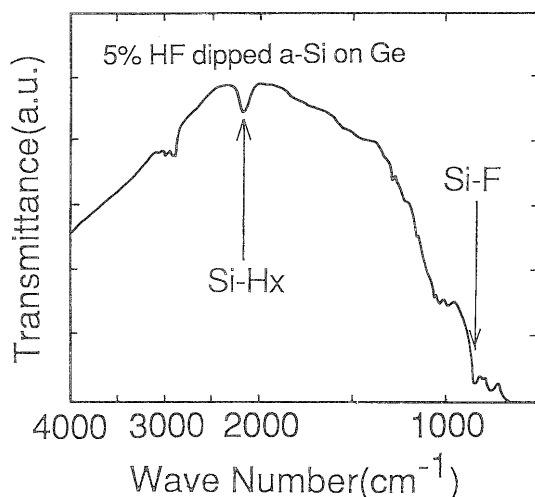


Fig. 2. FTIR-ATR spectrum of the H/F-terminated surface of a-Si after 5% HF dipping, which was deposited by EB evaporation on a Ge prism.

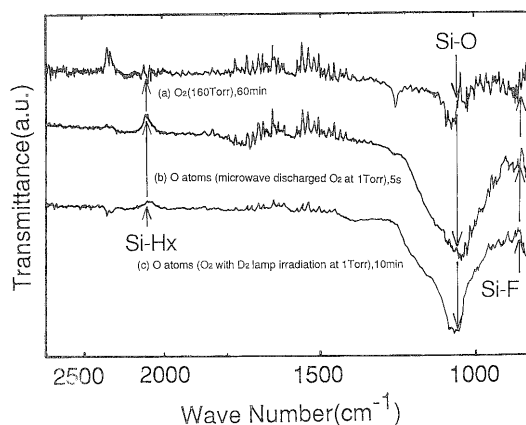


Fig. 3. FTIR-ATR spectra of the oxidizing process; (a) 60-min exposure of O<sub>2</sub> at 160 Torr, (b) 5-s exposure of O atoms generated by microwave discharge of O<sub>2</sub> at 1 Torr, (c) 10-min exposure of O atoms generated from O<sub>2</sub> under irradiation of D<sub>2</sub>-UV lamp at 1 Torr.

creasing peak of the Si-O stretching mode ( $1050\text{ cm}^{-1}$ ) for the (b) and (c) cases shows that rapid oxidation takes place for both processes. In addition, the Si-F peak is not varied and the Si-H peak decreases, while a small peak of the Si-H is still seen. This results demonstrate that oxygen atoms predominate to oxidize the Si surface sufficiently and the F bond remains on the Si surface due to the strong Si-F bond with 129 kcal/mol.

Figure 4 shows variations in the integrated intensity of the Si-O stretching band, Si-H stretching band and H-Si-O stretching band observed around  $2250\text{ cm}^{-1}$ <sup>7)</sup> as a function of O<sub>2</sub> exposure time at room temperature. The O<sub>2</sub> pressure is 160 Torr. The integrated intensity of the Si-H stretching band proportionally decreased with increasing O<sub>2</sub> exposure time and, simultaneously, the integrated intensity of the Si-O stretching band obviously increased rapidly from O<sub>2</sub> exposure time longer than about 700 min. Although an amorphous Si is used in our experiment, the results are quite similar to the previous paper<sup>8)</sup> that reports that the rapid Si(100) oxidation after about 800 min of growth in an air ambient. This exposure time when the Si-O peak rapidly increases is considered as the incubation time when O<sub>2</sub> molecules adsorb and then dissociate to O atoms on the H-terminated Si surface.<sup>9)</sup> Corresponding to the change, the integrated intensity of the H-Si-O stretching band also increased from the exposure time of about 700 min. However the integrated intensity of H-Si-O stretching band was saturated at exposure time longer than about 800 min. The result is considered to be as follows: since the number of H atoms which terminate the Si dangling bond is limited to the Si surface atoms, the number of O atoms bound with the Si back bond is also limited to the same number of Si-H bonds. The present rapid increase in the integrated intensity of Si-O stretching over 700-min O<sub>2</sub> exposure time suggests that the oxidation proceeds inside the Si film, leaving Si-H and H-Si-O bonding on the Si surface.

##### 3.1.2 Study on removal of H and F bonds

H and F atoms bound with the Si surface have to be eliminated prior to processes such as oxidation, CVD and metallization. Although H atoms are removed by heating the substrate at a temperature of more than

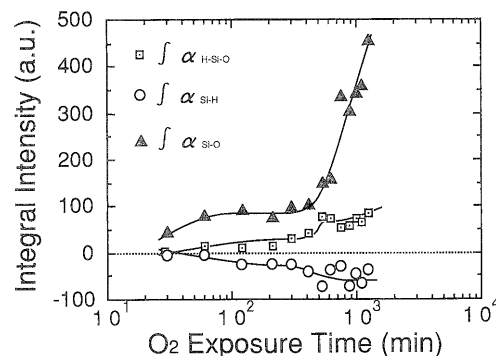


Fig. 4. The variation in the intensity of Si-O stretching band ( $1050\text{ cm}^{-1}$ ), Si-H stretching band ( $2100\text{ cm}^{-1}$ ) and H-Si-O stretching band ( $2250\text{ cm}^{-1}$ ) as a function of O<sub>2</sub> (160 Torr) exposure time at room temperature.

Table I. A comparison of ability to remove Si-F bonds in variety of processes.

Substrate treatment	Addition of bias voltage (-30 V)	Exposure of radicals	Exposure in plasma	UV-Light Irradiation
Gas				
H <sub>2</sub>	no experiment	no change	no change	no change
H <sub>2</sub> + Ar	disappears Si-F bond	no change	no change	no experiment

about 400°C, F atoms remains after even 1000°C heating.<sup>10)</sup> The strongly bonded F atoms were removed successfully using a process of Xe lamp irradiation at 700°C.<sup>11)</sup> In our work, the removal of H and F atoms was also investigated, as summarized in Table I. A variety of exposure methods of downstream H or H/Ar atoms, H<sub>2</sub> or H<sub>2</sub>/Ar plasma and assistance of D<sub>2</sub> lamp irradiation for these processes were applied for the H/F-terminated Si surface by expecting strong H-F bond energy (153 kcal/mol). However, no reduction in Si-F peak was observed. When bias voltage of -30 volts was applied to the Ge substrate in the H<sub>2</sub> + Ar plasma, F atoms were eliminated completely, while the Si-OH bond newly appeared due to oxidation by O atoms which might be generated by H<sup>+</sup> ion bombardment to the inner wall of the reactor.

### 3.2. Discussion on reaction mechanism of the Si film CVD with the TES/H system

It was found that simultaneous reaction of TES and H atoms provided conformal CVD of a Si film involving methyl and ethyl groups. However, the TES/H reaction was not understood to occur in the gas phase or on the surface. In order to study which reaction is dominant, spectra were measured employing in-situ FTIR for the gas phase reaction and in-situ FTIR-ATR for the surface reaction. The typical spectra of the gas phase (a) in TES/H<sub>2</sub> and (b) in TES/H atom are shown in Fig. 5. The gas phase spectrum was obtained by introducing TES and H<sub>2</sub> or H atoms into a reactor with a set of Si wafer windows which was arranged in an optical path of IR light. TES gas was introduced at 2 Torr. For wide range variation of H<sub>2</sub> partial gas pressure from 3 to 20 Torr, almost the same spectrum was measured for both TES/H<sub>2</sub> and TES/H reactions. This suggests that H atoms do not react with TES in the gas phase. For the goal of investigating the role of H atoms in this system, the spectrum which was obtained by substitution of H<sub>2</sub> by D<sub>2</sub> gas was measured. A Si-D peak newly appeared around 1500 cm<sup>-1</sup> at a D<sub>2</sub> pressure of more than 10 Torr, as shown in Fig. 6. The amount of the Si-D bonds was almost equal to the decreased amount of Si-H bonds. The result also demonstrates that no reaction occurs besides the substitution reaction between the Si-H bond of TES molecules and D atoms.

Next, in-situ FTIR-ATR of the TES/H reaction was measured at room temperature as shown in Fig. 7(b). The result of the gas phase reaction for the TES/H system is also shown in Fig. 7(a). Figure 7(b) shows the difference

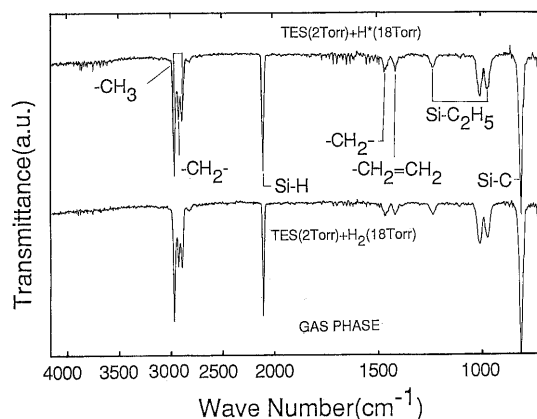
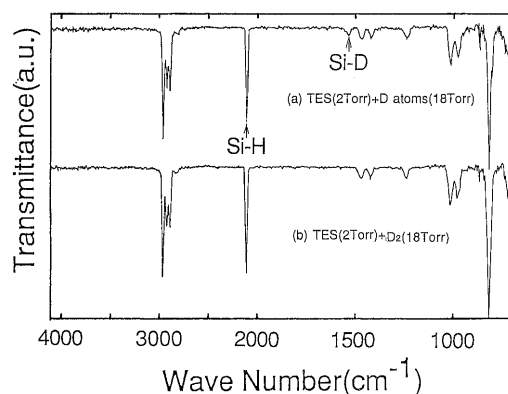
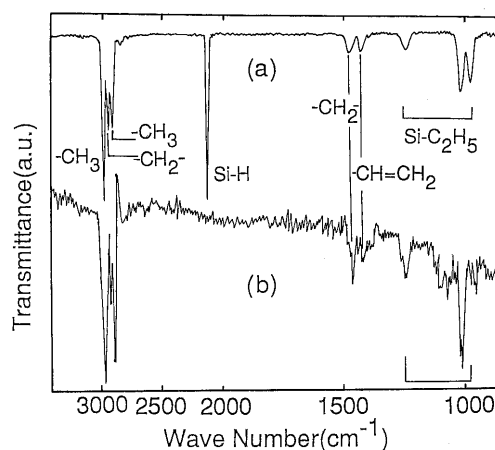
Fig. 5. The typical FTIR spectra of the gas phase (a) in TES (2 Torr) /H<sub>2</sub>(18 Torr) and (b) in TES (2 Torr)/H(18 Torr) atoms.Fig. 6. The FTIR spectra of gas phase (a) in TES(2 Torr)/D<sub>2</sub>(18 Torr) and (b) in TES(2 Torr)/D(18 Torr) atoms.

Fig. 7. FTIR spectra of the TES/H reaction (a) in the gas phase and (b) on the H/F-terminated Si surface.

spectrum of the H/F-terminated Si on Ge prism before and after TES/H reaction on the same surface. TES and H atoms were introduced simultaneously to the H/F-terminated Si surface. Partial gas pressures of TES and H<sub>2</sub> were 2 Torr and 8 Torr, respectively. Thus the Si-H peak which results in H termination is not observed because of

the compensation of both Si-H peaks. However, the Si-H bond of the adsorbed TES is also not observed. This indicates that H atoms react with methyl or ethyl groups of the adsorbed TES on the H/F-terminated Si surface, releasing as CH<sub>4</sub>, C<sub>2</sub>H<sub>6</sub> and H<sub>2</sub> even at room temperature.

The effect of exposure of H atoms to the Si film including a rich amount of organic species such as CH<sub>2</sub>, CH<sub>3</sub> and C<sub>2</sub>H<sub>5</sub> was investigated. Figure 8 shows a FTIR-ATR difference spectrum which is measured from spectra before and after H-atom exposure on the organic Si film deposition at room temperature. These organic species were reduced drastically by H-atom exposure. The result gives us valuable information that additional H-atom exposure after CVD of the present Si film leads to effective improvement of the Si film quality. Indeed, the effectiveness of this process was investigated in the digital CVD of SiO<sub>2</sub> film. The film quality was checked by wet etch rate with buffered HF (HF:H<sub>2</sub>O=1:9) solution at room temperature. Eventually, the etch rate of SiO<sub>2</sub> film which was fabricated at 250°C by repeating the process of the TES/H reaction, 10-s H-atom exposure

and 10-s oxidation, was reduced to 250 Å/min, which was about 3 times that of the thermal SiO<sub>2</sub>.\*

Figure 9 shows a FTIR-ATR difference spectrum between a spectrum of the organic Si film deposition on the H/F-terminated surface and one before heating this sample at 250°C. Desorption of methyl and ethyl groups can be observed, and the Si-H bond disappears at the same time. This result also elucidates that H atoms on the H/F-terminated Si surface react with these organic species, desorbing as CH<sub>4</sub> and C<sub>2</sub>H<sub>6</sub>.

Based on these results, TES/H reaction at the actual deposition temperature of 250°C is considered to result from a process in which H atoms react with predominantly H atoms in TES and the reaction with CH<sub>3</sub> and C<sub>2</sub>H<sub>5</sub> occurs insufficiently, depositing the organic Si film. However, the most important question of why the TES/H reaction takes place only on the surface is still unanswered.

#### §4. Conclusions

The in-situ FTIR-ATR method is a very powerful tool for detecting the H bond, which is important in Si surface reactions. This was applied to elucidation of both the oxidation of Si and the TES/H CVD system. In the oxidation process, the terminated H atoms showed a tolerance for attack by O<sub>2</sub> (160 Torr) for up to 700 min at room temperature. In the TES/H atom system, H atoms react with TES only on the surface even at room temperature, desorbing Si-H bonds of TES in the deposited Si film. However, the reason why the reaction occurs only on the surface is not understood.

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#### References

- 1) M. Morita, T. Ohmi, E. Hasegawa, M. Kawasaki and M. Ohwada: *J. Appl. Phys.* **68** (1990) 1272.
- 2) T. Takahagi, I. Nagai, A. Ishitani, H. Kuroda and Y. Nagasawa: *J. Appl. Phys.* **64** (1988) 35.
- 3) G. S. Higashi, Y. J. Chabel, G. W. Trucks and K. Raghavachari: *Appl. Phys. Lett.* **56** (1990) L656.
- 4) H. Kawamoto, H. Sakaue, S. Takehiro and Y. Horiike: *Jpn. J. Appl. Phys.* **29** (1990) 2657.
- 5) H. Sakaue, M. Nakano, T. Ichihara and Y. Horiike: *Jpn. J. Appl. Phys. Lett.* **30** (1991) L124.
- 6) W. C. M. Claassen, R. W. A. H. Schmitz and J. Dieleman: *Appl. Surf. Sci.* **43** (1989) 292.
- 7) G. Lucovsky: *Solid State Commun.* **29** (1979) 571.
- 8) N. Hirashita, M. Kinoshita, I. Aikawa and T. Ajioka: *Appl. Phys. Lett.* **56** (1990) L451.
- 9) M. Grundner and H. Jacob: *Appl. Phys.* **39** (1986) 73.
- 10) T. Sunada, T. Yasaka, M. Takakura, T. Sugiyama, S. Miyazaki and M. Hirose: *Extended Abstracts of the 22nd Conf. on Solid State Devices and Materials*, (Business Center for Academic Societies of Japan, Tokyo, 1990) p. 1071.
- 11) T. Ohmi, M. Morita, M. Takakura, M. Kosugi, H. Kumagai and M. Itoh: *Appl. Phys. Lett.* **52** (1988) L1173.

\*T. Ichihara, S. Miyazaki, H. Sakaue and Y. Horiike: in preparation for publication.

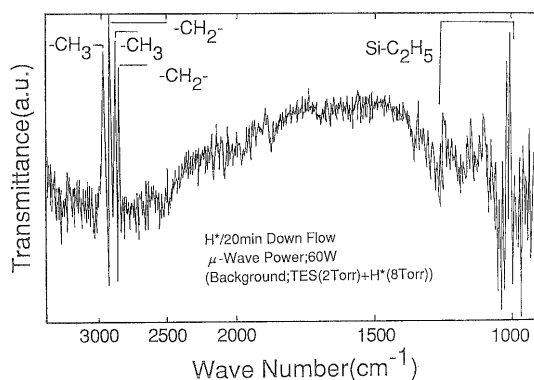


Fig. 8. FTIR-ATR difference spectrum between before and after exposure of H atoms at 20 Torr on the organic Si film deposition which was deposited by reaction between TES at 2 Torr and H atoms generated by microwave discharge of H<sub>2</sub> at 8 Torr. Microwave power was 60 W and exposure time of H atoms was 20 min.

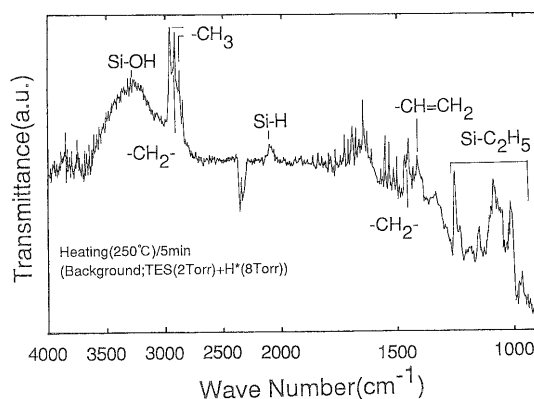


Fig. 9. FTIR-ATR difference spectrum between before and after heating of the organic Si film on the H/F terminated Si surface for 5 min at 250°C. The organic Si film was deposited in the same condition as the film described at Fig. 8.