Extended Abstracts of the 1992 International Conference on Solid State Devices and Materials, Tsukuba, 1992, pp. 114-116

In-situ Characterization of Si Surface Oxidation by High-Sensitivity Infrared Reflection Spectroscopic Method in Vacuum Chamber

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Adsorption and oxidation on Si surface in vacuum chamber for CVD has been characterized by high-sensitivity infrared reflection spectroscopy. Oxidation time dependence of the absorption peak intensity shows step-like increase and is attributed to layer by layer oxidation. It is considered from difference of oxidation between Si (111) surface etched by 5%HF and that by buffered HF (BHF), that the surface etched by BHF is flatter than that of 5%HF. Moreover it is observed in-situ that VUV light irradiation of D_2 lamp promotes the oxidation.

1. Introduction

Recently, behavior of atomic bonding and morphology on Si surface has gathered much attention from viewpoint of microfabrication of Si integrated devices. Because control of surface condition and surface reaction become the key to improve the device performance. But in fine surface treatment, such as atomic flattening of Si surface and ultrathin film growth, it is very difficult to monitor atomic states on the surface in-situ during the process. Especially in the chemical vapor deposition (CVD), molecules prevent electron or ion beams for surface analyses from approaching the substrate. From this view point, light probing is superior to the other proving using the electron or ion beams. Infrared optical spectroscopy has much advantage for monitoring the chemical states in vapor or on surface even during the CVD process. Because atomic bonding state can be easily monitored even in gas ambience of any pressure, and nondestructive characterization is possible. However conventional infrared transmittance is not appropriate method to characterize ultrathin film of some atomic layers or surface because of low absorbance. High-sensitivity infrared reflection spectroscopy has not only the advantage similar to the infrared transmittance but also high sensitivity, and gives detailed information of chemical state in-situ.

In this paper, we have investigated Si(111) surface by using high-sensitivity infrared reflection spectroscopy when Si surface has been treated by O_2 and / or F_2 gas, and etching.

2. High-sensitivity infrared reflection spectroscopy and measuring system

When infrared beam polarized parallel to the incident plane (p polarized light) is applied to the Si substrate at large angle of incidence more than 80 degree, a strong electric field exists on its surface vertically. This strong electric field of the infrared light excites oscillators perpendicular to the surface and the infrared light can be absorbed effectively. Therefore, this method can give infrared absorption spectrum of thin layer on Si surface sensitively[1]. Measuring system for the high-sensitivity infrared reflection is shown in Fig. 1.

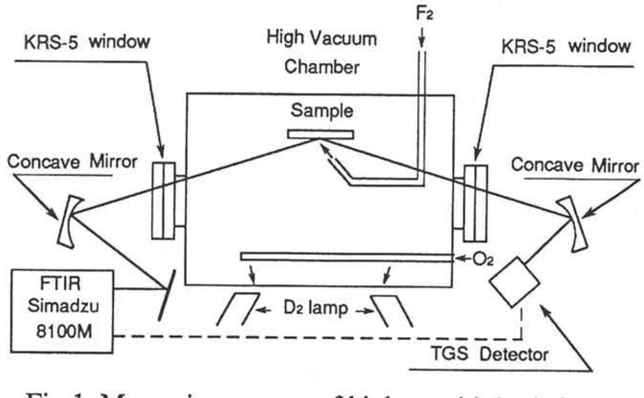

Fig.1. Measuring system of high-sensitivity infrared reflectance.

Infrared beam from Fourier-transformation infrared (FT-IR) spectrometer was concentrated by a concave mirror and applied to the Si wafer through a KRS5-window in a vacuum chamber evacuated to $\sim 10^{-7}$ Torr. After taken out again through the other KRS5-window and concentrated by a concave mirror, reflected infrared beam was defected by TGS-Detector. Output signal of this detector was analyzed by the FT-IR. The absorption induced by atoms and molecules on the Si substrate can be obtained by dividing spectrum measured after the treatment by that before the treatment. A Si(111) wafer was etched by 5% HF solution or BHF(NH_4F:HF:H_2O:NH_4OH=7:1:6:1) solution after RCA cleaning, and set on the sample holder in the vacuum chamber.

3. Surface oxidation in O_2 ambience.

Figure 2 shows reflectance spectrum of the Si(111) wafer which was treated at 200℃ in 5Torr O_2 ambience for 100min after 5%HF etching. The absorption peaks of SiO_2 film exist mainly around 800 ~ 1200 cm^{-1}, and three peaks in the spectrum are attributed to absorptions corresponding to SiO stretching ($\sim 1080 cm^{-1}$)[2,3], SiOH deformation ($\sim 950 cm^{-1}$)[4] or SiO bending ($\sim 840 cm^{-1}$)[2,3]. Intensities of the three absorption peaks as a function of O_2 treatment time are shown in Fig.3. Layer-by-layer oxidation may proceed as step-like increases of the absorption intensities appear obviously. The plateaus in the step-like behavior are found more clearly and their values are smaller in the sample etched by BHF (Fig.3 (b)) in comparison with that by 5%HF (Fig.3 (a)). It is considered that there are many atomic steps on Si (111) substrate surface etched by HF or BHF solution. Oxygen can attack reactive sites, such as step edges and dislocations, whose chemical bondings are weak. The nearest neighbor atoms to the reactive site are also attacked easily by oxygen due to the stress and oxidized successively. If the nearest neighbor parallel to the substrate surface suffers stress and oxidizes easier than that toward the bulk, the substrate surface is oxidized by one layer and becomes quasi-stable till next oxygen's attack. Resultantly a delay of the oxidation happens, and causes the plateaus shown in Fig.3. Moreover, Fig.3 indicates that the plateaus obtained in the surface etched by BHF are longer than that of 5%HF, and the surface of the BHF etching is more flattened atomically than that of the 5%HF. Figure 4 shows the reflectance spectra of the samples etched by BHF and treated in 1Torr O_2 gas with and without

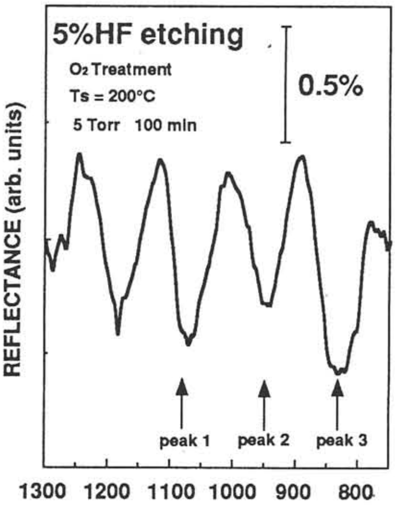

Fig.2. Reflectance spectrum of the oxidized Si wafer.

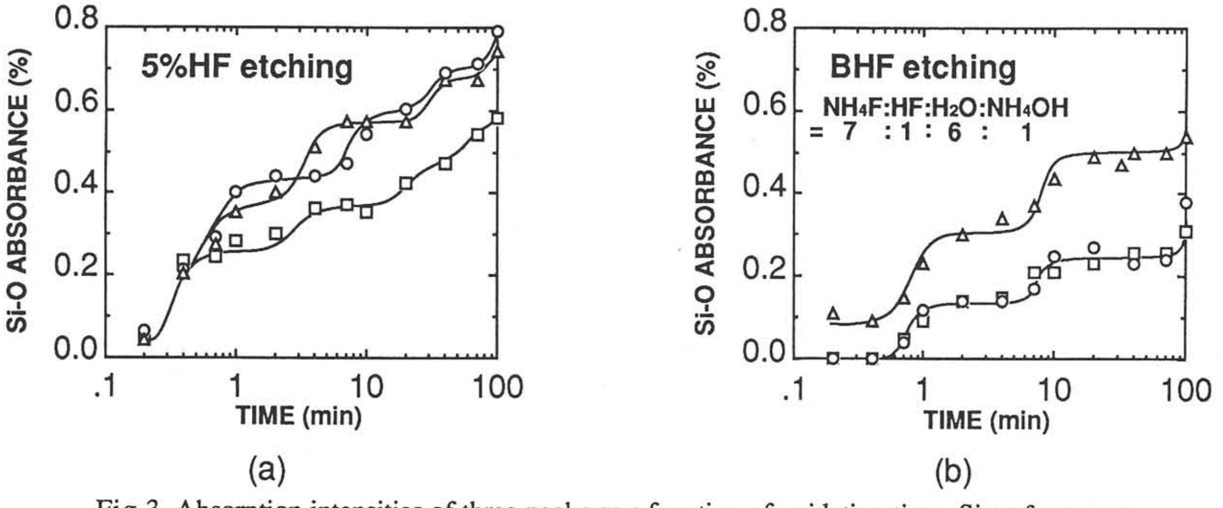

Fig.3. Absorption intensities of three peaks as a function of oxidation time. Si wafers were etched by (a) 5%HF and (b) BHF. Circles, squares and triangles are absorption intensities at $\sim 840\ cm^{-1}$, $\sim 950\ cm^{-1}$ and $\sim 1080\ cm^{-1}$ respectively in Fig. 2.

VUV irradiation of D_2 lamp. It is known from Fig.4 that VUV light promotes the oxidation.

4.Effect of Si surface by F_2 treatment

Figure 5 shows absorption intensity of Si-F around 860 cm^{-1} with increasing F_2 treatment time. This means that fluorine terminated Si surface when Si (111) substrate was treated by F_2 gas[5]. Figure 6 shows intensity of the absorption peak at 1080 cm^{-1} of the Si wafers which were treated in some combinations of HF etching, BHF etching and F_2 treatment before the oxidation. The F_2 treatment suppresses the oxidation on the Si surface obviously. It is supposed that when Si substrate was exposed by F_2 gas, fluorine terminated step edges on Si surface which were reactive sites, and chemical bonds around fluorine became stronger and kept off oxidizing.

5.conclusions

Si surface treated by various process such as etching, O_2 and F_2 gas treatment has been characterized in-situ by high-sensitivity infrared reflection spectroscopy in the CVD vacuum chamber. The absorption intensities of Si (111) surface have shown step-like increase by O_2 treatment and may correspond to layer-by-layer oxidation. Reflectance spectrum corresponding to flat surface has been measured by changing etching solution from 5%HF to BHF. BHF etching and F_2 treatment have suppressed the oxidation on Si (111) surface, but has oxidized with VUV irradiation of D_2 lamp.

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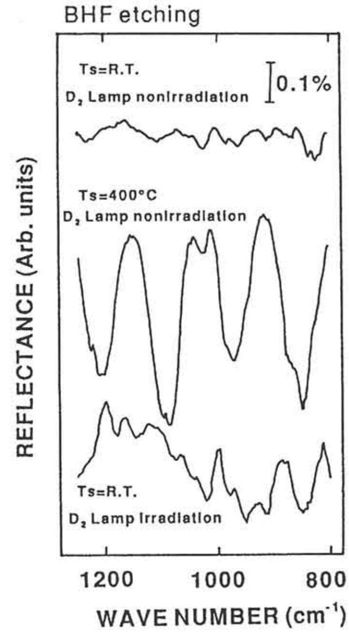

Fig.4. Reflectance spectra of the Si treated with and without VUV irradiation of D_2 lamp.

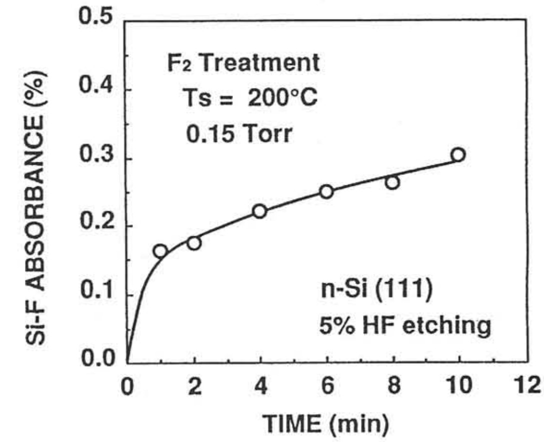

Fig.5. Absorption intensity of Si-F around 860 cm^{-1} as a function of F_2 treatment time.

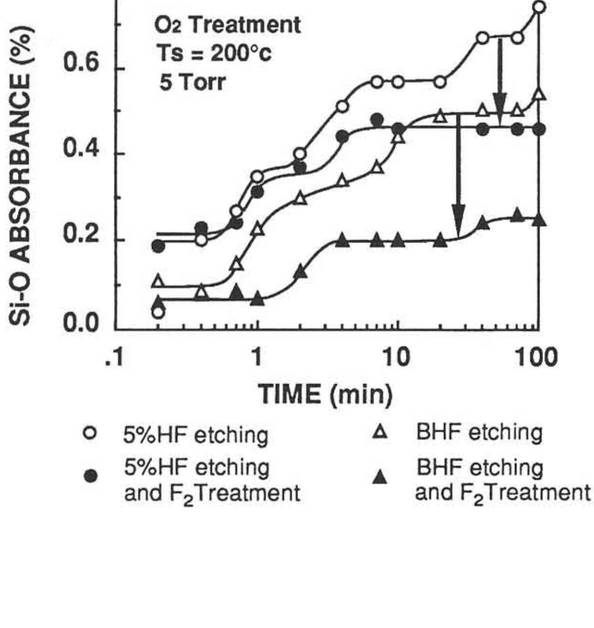

Fig.6. Absorption intensity of the peak at 1080 cm^{-1} as a function of oxidation time in the Si wafer treated with some conbination of etchings, O_2 and F_2 gas treatment.