Extended Abstracts of the 1994 International Conference on Solid State Devices and Materials, Yokohama, 1994, pp. 664-666

Oxygen and Fluorine Treatment Effect on Silicon Surface Characterized by High-Sensitivity Infrared Reflection Spectroscopy

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Atomic bonds on Si(111) such as Si-H, Si-O and Si-F have been precisely measured by high-sensitivity infrared reflection spectroscopy. H on Si terrace of atomic step and H on the Si edge are removed by heat treatment and oxygen treatment at 400℃, respectively. Initial oxidation begins at about 200℃ before H desorption. H desorbs just after F_2 treatment, and Si-F absorption at 850cm^{-1} shifts to higher wavenumber with treatment time. Fluorination of the back bonds might be induced as absorption corresponding to SiF_x(x=2-4) increases with the time.

1. Introduction

Surface reaction on Si is very important in various material processes such as CVD and dry etching, and its mechanism is desired to be elucidated in order to grow good-quality thin film on atomically flat surface or obtain clear surface on etched part. But it is very difficult to characterize atomic bonds on the surface in a vacuum chamber during the process correctively. Because conventional sensitive analyses using electron excitation such as XPS, STM and AES are carried out in a high vacuum chamber which is not used in the process. Infrared attenuated total reflectance(IR-ATR) is sensitive method detecting species on a Si wafer, but it is difficult to use it in a vacuum chamber and detect absorption of species on Si below 1500cm^{-1} because of low transmittance. High-sensitivity infrared reflection spectroscopy(or infrared reflection absorption spectroscopy(IRAS)) has great advantages, because it can be done even at low vacuum in the process and the spectrum could be obtained in wide infrared range where IR-ATR is not available. In recent years, hydrogen termination has been confirmed precisely by IR-ATR method using Si prism of ultra-high purity, which is treated in various kinds of organic solvents, acid and water. We have also succeeded in measuring atomic bond of Si-H, Si-O or Si-F on Si surface and behavior of individual absorption have been studied in the oxidation and for various cleaning treatments.[1,2] In this paper, we present that several atomic bonds of surface Si with hydrogen, fluorine and oxygen have been measured simultaneously in a CVD chamber.

2. Experimental

Figure 1 shows measurement system for high-sensitivity infrared reflection spectroscopy. An infrared light from a fourier-transformation infrared(FT-IR) spectrometer is condensed by a concave mirror in humidity-free space, applied through a

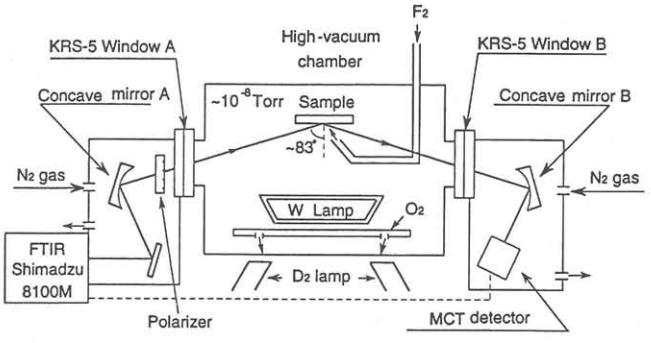

Fig.1. Measurement system for high-sensitivity infrared reflectance spectroscopy.

polarizer and a KRS window to a Si wafer and the reflected light is precisely detected by a MCT detector. Signal of the detector is processed in the FT-IR spectrometer. Absorption of p-polarized light induced by atomic bonds on the Si can be obtained by dividing reflectance after a treatment by reflectance before it, as change of the reflectance is extremely small. Hydrogen terminations on Si(111) and (100) have been clearly found in the range of 2070-2160cm^{-1} by doing adequate etching.[2] Si wafers used in this paper are CZ Si(111) of 7-13 Ωcm. The Si wafers were treated by RCA cleaning, etched by 1%HF solution, oxidized by 50%HNO_3 and treated by various methods described in each experiment.

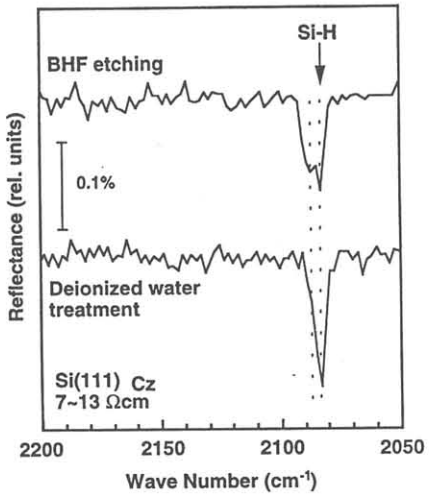

Fig.2. Reflectance spectra of Si(111) (a) etched by BHF and (b) boiled in ultra-pure water. Resolution is 4cm^{-1}.

3. Results

Figure 2 shows reflectance spectra (resolution:4cm^{-1}) of Si(111) wafers (a) etched by buffered hydrofluoric acid (BHF) of NH_4F(40%): HF(50%):H_2O:NH_4OH(28%)=7:1:6:1 for 3 min and (b) boiled in ultra-pure water, respectively. Reference is the reflectance of Si oxidized by HNO_3. A sharp peak at 2083cm^{-1} is attributed to Si-H on S(111). The Si etched by BHF has an additional peak at 2090cm^{-1}, and is attributed to S-H on edge site. So, the boiled Si shows atomically flat surface. Figure 3 shows reflectance spectra(resolution: 8cm^{-1}) of Si(111) after (a) BHF etching, (b) heat-up at 400°C and 3x10^{-7} Torr for 10min and (c) heat up at 400°C in 0.1Torr O_2 for 10 min. The spectrum of Fig. 3(a) is different from that of Fig. 2(a) because the resolutions are different. Si after the etching has a peak around 2085cm^{-1} corresponding to Si-H bond on Si terrace. This peak shifts to 2089 cm^{-1} after the heat-up, corresponding to Si-H at edge of Si atomic step. But it moves back around 2085cm^{-1} after the heat-up in O_2. It is considered that hydrogen goes out from the edge but oxidation happens from the terrace in this condition. In the range of 800-1300cm^{-1}, several absorption peaks

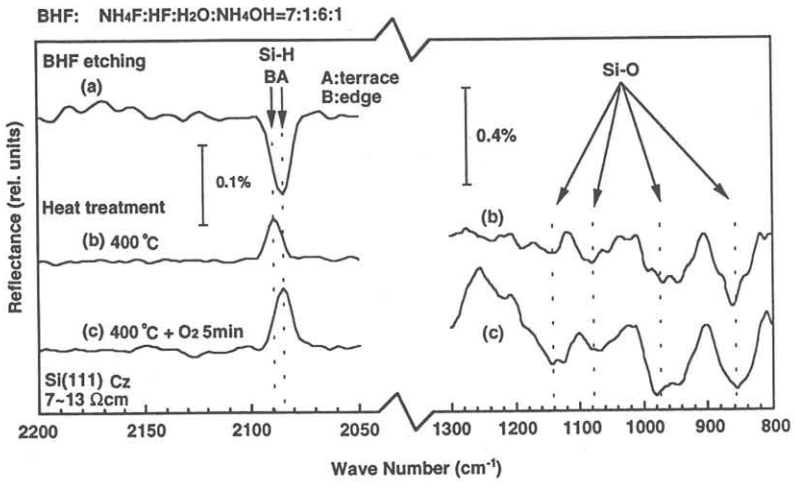

Fig. 3. Reflectance spectra of Si-H and S-O bonds on Si after (a) BHF etching, (b) heat-up at 400°C and 3x10^{-7} Torr for 10min and (c) heat-up at 400°C in 0.1 Torr O_2 for 10min. Resolution is 8cm^{-1}.

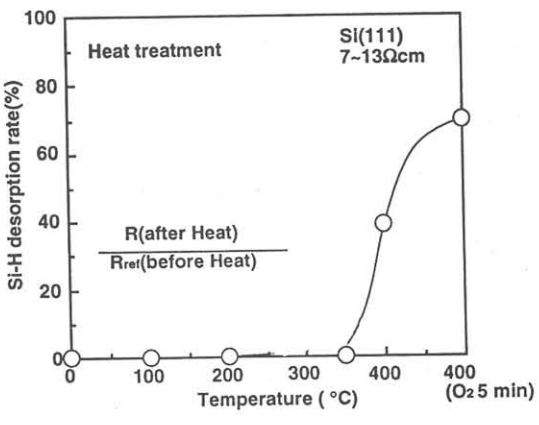

Fig. 4. Si-H desorption as a function of temperature in heat treatment. A value in O_2 at 400°C is also added.

of Si-O stretching, deformation and bending modes are found, and increase by the heat-up and oxygen treatment. Figures 4 and 5 show Si-H reduction and Si-O absorption as a function of temperature. Oxidation starts above about 200℃ but hydrogen desorption begins over 350℃. This means that oxidation occurs without hydrogen desorption at 200-350℃. This behavior is can be understood if initial oxidation might happen at a position where oxygen compounds adsorbs at exposure in air ambient or oxygen is inserted in Si network under the Si-H. But, insertion of oxygen under the Si-H is not plausible because its absorption did not appear around 2250cm^{-1}.

Figure 6 shows the spectral change of Si(111) after F_2 treatment at 0.1Torr at room temperature. The peaks around 2085cm^{-1} are positive, and so adsorbed hydrogen goes out from the surface immediately after exposure in F_2 ambient. Si-F signal around 850cm^{-1} is found in the Si treated for 30sec, shifts to higher wave number with exposure time and finally moves to 880cm^{-1}. Three absorption peaks corresponding to fluorides such as SiF_2, SiF_3 and SiF_4 are also produced. These results show that F goes into Si network and induces fluorination of the back bond.

4. Summary

Atomic bonds on Si, such as Si-H, Si-O and Si-F, could be clearly measured by high-sensitivity infrared reflectance spectroscopy. Heat treatment at 400℃ induces desorption of hydrogen on the Si edge of atomic step, but oxygen treatment at 400℃ induces desorption of hydrogen on the Si terrace. Si-O absorption is found for the Si treated in O_2 above about 200℃, and Si-H absorption decreases over 350℃. Therefore, the initial oxidation might occur at a part of Si terrace where some oxide adsorbs in air ambient. Moreover, hydrogen on Si surface is removed just after the F_2 treatment and Si-F appears. Absorption peaks of SiF_2, SiF_3 and SiF_4 corresponding to fluorination of the back bond under S-H has been observed. It has been shown from these results that this method should be effectively used to clarify the surface reaction mechanism in the process chamber during and after CVD and dry etching.

REFERENCES

1) M.Nishida, Y.Matsui, M.Okuyama and Y.Hamakawa, Jpn.J.Appl.Phys.32(1993)286
2) M.Nishida, M.Okuyama and Y.Hamakawa, to be published in Appl. Surface Science, 1994.

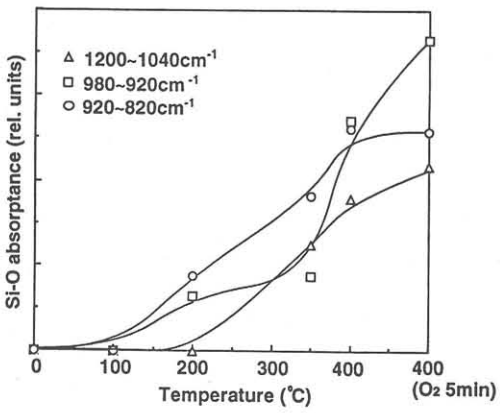

Fig. 5. Si-O absorption as a function of temperature in heat treatment. A value in O_2 at 400°C is also added.

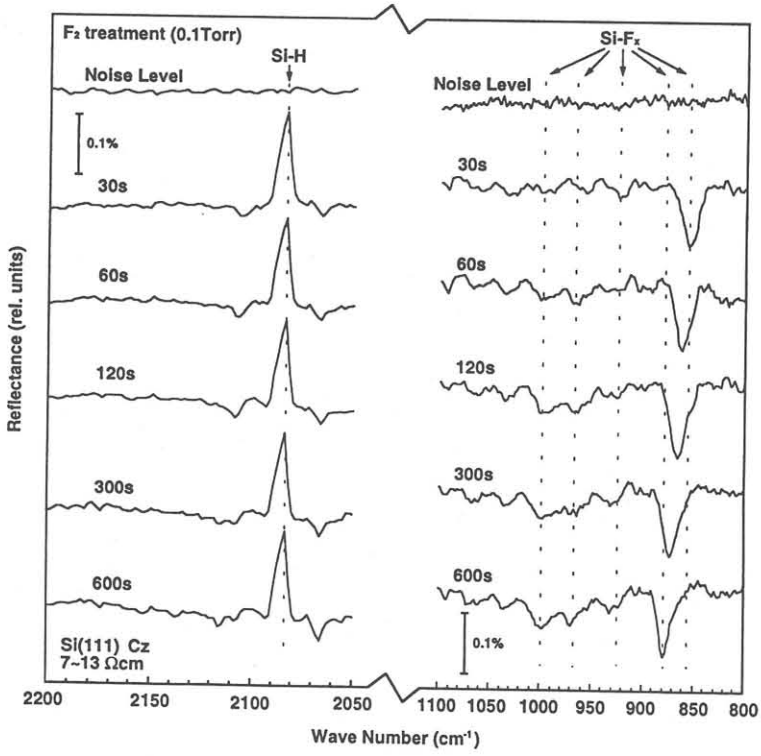

Fig. 6. Reflectance spectra of Si (111) after F_2 treatment at 0.1 Torr as a parameter of exposure time.