

The Role of Hydrogen, Oxygen and Water in Oxidation of Hydrogen Terminated Silicon Surface

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The role of hydrogen, oxygen and water in oxidation of HF cleaned silicon surface is investigated in the low pressure region by thermal desorption spectroscopy(TDS). The oxidation of the hydrogen terminated silicon surface proceeds by two steps at about 500°C and 800°C. The first step reaction might occur by desorption of hydrogen and adsorption of oxygen and water. The second step might occur by the formation of SiO. Oxidation reaction changes by the presence of the native oxide. The consumption quantities of water do not change with increasing those of oxygen.

1. Introduction

An HF cleaned silicon surface is terminated with hydrogen and has remarkable passivation effect against surface oxidation¹⁾. Native oxide does not grow for a week at room temperature unless both water and oxygen are present on the HF cleaned surface²⁾. However it is still unknown whether this surface is stable or not for oxidation in the high temperature region. On the other hand, hydrogens on the HF cleaned silicon surface are desorbed from about 400°C by heating with some desorption activation energies³⁾. Consequently, it is expected that the oxidation of the surface begins with the hydrogen desorption.

The purpose of this paper is to clarify the oxidation mechanism of the HF cleaned silicon surface when the temperature is elevated. We have investigated the relationship between hydrogen desorption and consumptions of oxygen and water in the low pressure using thermal desorption spectroscopy (TDS). X-ray photoemission spectroscopy (XPS) study is also performed in order to confirm the oxidation after heating.

2. Experimental

The samples were cut to the size of 2cm x 5cm from n-type CZ Si(100) wafers with 3-5 Ω .cm. One type of the samples was dipped in a 1% HF solution and rinsed in de-ionized(DI) water to terminate the silicon surface by hydrogen, after washings in H₂SO₄-H₂O₂, diluted HF, NH₄OH-H₂O₂-H₂O and HCl-H₂O₂-H₂O. The other was dipped in a 30% H₂O₂ solution and rinsed in DI water to cover the surface by the native oxide.

TDS was carried out at a heating rate of 20°C/min under a base pressure of less than 1×10^{-8} Torr. The spectra of hydrogen(M/e=2), water(18) and oxygen(32) were measured by a quadrupole mass analyzer. The partial pressure of oxygen was measured by an ionization vacuum gauge. That of water was estimated by using Ehlert's values of ion transmission efficiency of the mass analyzer⁴⁾ and the mass ion intensity ratio of water/oxygen. The sample signals were distinguished from the background signals by the reported methods⁵⁾. TDS was performed leaking about 4×10^{-9} Torr oxygen in the TDS system to investigate the differences of the consumptions of oxygen and water between the HF cleaned surface and the H₂O₂ treated

surface. For the HF cleaned samples, the consumption quantities of oxygen and water were measured for leakage oxygen quantities.

The XPS spectra of O1s were measured watching the change of the surface after heating to various temperatures in the TDS system. The samples were transferred in the nitrogen atmosphere from the TDS to the XPS, but they were in contact with air for several minutes during enclosing.

3. Results

The thermal desorption spectra of hydrogen, oxygen and water from the HF cleaned silicon surface are shown in Fig. 1. The solid lines are from the sample and the dotted lines are from the background. Hydrogen is desorbed with peaks at 400 and 520°C. The spectra of oxygen and water do not change at 400°C for the first hydrogen desorption peak. Oxygen and water decrease at about 500°C in the first step and at about 800°C in the second step. They are consumed by oxidation reaction with silicon.

Figure 2 shows the thermal desorption spectra of hydrogen, oxygen and water for the H₂O₂ treated silicon surface. The spectra of this sample differ from those of the HF cleaned sample. Main difference is that the

consumptions of oxygen and water at about 500°C disappear. The temperature in the second step of the H₂O₂ treated sample move 80°C higher than that of the HF cleaned sample. Other difference is observed on the desorptions of hydrogen and water. The desorption of water is observed from 200 to 830°C with a peak at 340°C. The desorption quantity of hydrogen is about 1/3 of the HF cleaned surface.

The intensity of O1s XPS spectra was measured for the HF cleaned surface which was heated to various temperatures in the TDS system. The results of XPS measurement coincided with those of TDS in the change at about 500°C, but didn't coincide at about 800°C. Figure 3 shows the heated temperature dependence of the O1s relative intensity. The O1s intensity at each temperature was normalized by that at room temperature. The O1s relative intensity does not change till about 500°C. It increase to 2-3 in the more than about 500°C region. The increase of O1s at about 500°C coincides with the consumption of oxygen and water. However, O1s does not increase in the more than 800°C region where the consumption quantities of oxygen and water increase.

The oxygen consumption quantity (ΔP_{O_2})

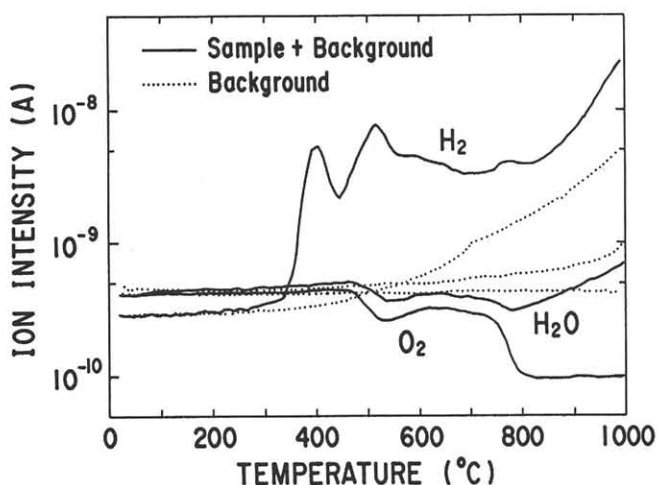


Fig. 1 TDS spectra of hydrogen, oxygen and water from the HF cleaned silicon surface. The partial pressures of O₂ and H₂O are about 4×10^{-9} and 3×10^{-9} Torr, respectively.

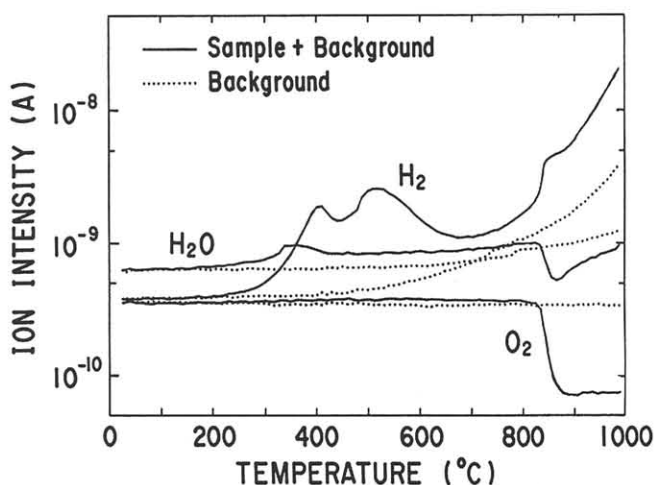


Fig. 2 TDS spectra of hydrogen, oxygen and water from the H₂O₂ treated silicon surface. The partial pressure of O₂ and H₂O are 4×10^{-9} and 5×10^{-9} Torr, respectively.

at 500 and 800°C were measured in the TDS experiment by leaking oxygen from 2×10^{-10} to 1×10^{-7} Torr (Fig.4). ΔP_{O_2} at 500°C is inclined to be saturated with increasing oxygen pressure. ΔP_{O_2} at 800°C is proportional to oxygen pressure. Therefore, it is expected that the oxidation reactions occurred at about 500°C and about 800°C are different.

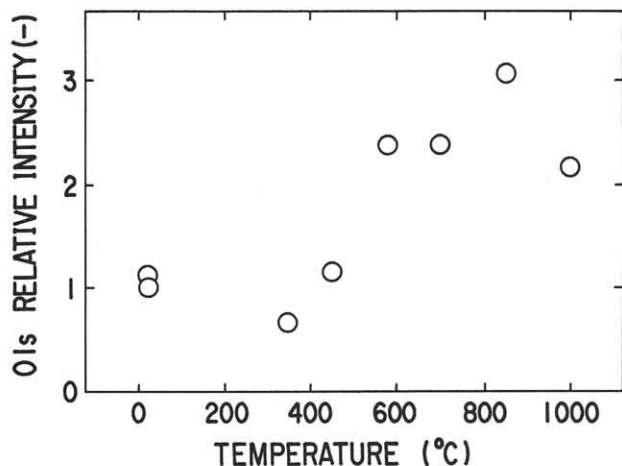


Fig. 3 Temperature dependence of O1s XPS spectra normalized by O1s intensity at room temperature. XPS was measured after heating to each temperature in the TDS apparatus.

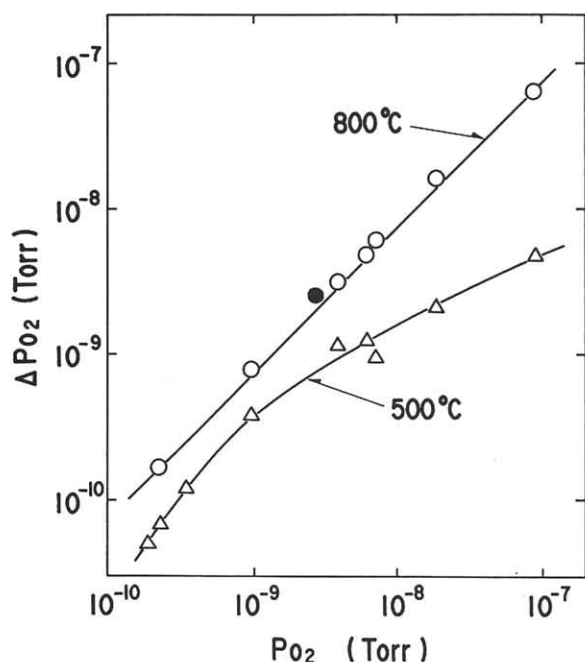


Fig. 4 O_2 consumption quantity (ΔP_{O_2}) for the O_2 leakage quantity (P_{O_2}). The closed circle is plotted by the TDS result of the H_2O_2 treated silicon surface.

From Fig.1 and Fig.2, oxygen and water react with Si at the same temperature. In other words, oxygen and water consumes at the same time in the oxidation procedure. The relationship between the consumption quantity of water and that of oxygen at 500 and 800°C are shown in Fig.5. Here, ΔI_{H_2O} and ΔI_{O_2} are the decrease quantity of mass intensity from the background level. ΔI_{H_2O} hardly changes for ΔI_{O_2} at both 500°C and 800°C. Consequently, water may act as the catalyst in the oxidation reaction.

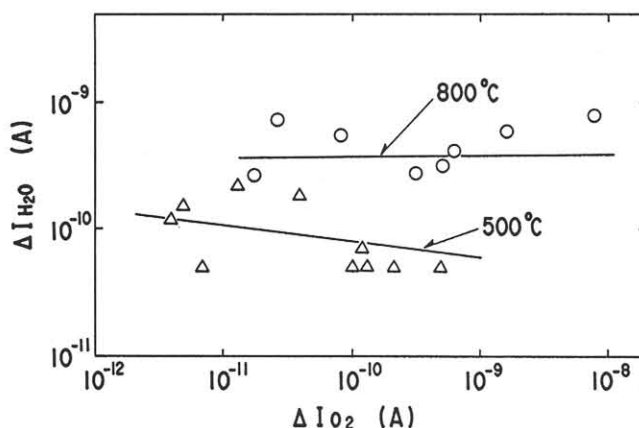


Fig. 5 Relationships between the consumption quantity of H_2O (ΔI_{H_2O}) and that of O_2 (ΔI_{O_2}). Here, ΔI_{H_2O} and ΔI_{O_2} are the mass intensity decrease quantity from the background level.

4. Discussion

TDS and XPS results showed that HF cleaned silicon surface was not oxidized till about 500°C. Consequently, Oxidation does not occur until hydrogen at the 520°C peak begins to be desorbed. This is because the surface is still passivated for oxidation by hydrogen at the 520°C peak even after hydrogen desorption at 400°C. When bare silicon appears at over 500°C, oxygen and water attack it, and then oxidation proceeds.

TDS result of H_2O_2 treated surface supported this consideration. When the native oxide covers the silicon surface, oxygen and water don't adsorb on the surface. The native

oxides formed by various chemical treatments are desorbed at 750 to 950°C⁶). If the bare silicon begins to appear at 830 °C by desorbing the native oxide formed by H₂O₂ treatment, it is explained that oxygen and water react with this surface.

XPS results coincided with TDS results that oxidation started from 500°C, but didn't coincide with them that the oxide film growth obtained from O1s relative intensities ought to increase with the consumption quantities of oxygen over 800°C region. Kado et. al. reported that the boundary of oxygen pressure between 7x7 remained and 7x7 vanished region at 780°C in the Si(111) surface was 3.5×10^{-6} Torr. In our experiments, as the heat treatments were performed less than 3.5×10^{-6} Torr oxygen pressure, silicon would be etched by oxygen and no oxide film would be formed over 800°C region. Oxygen might adsorb on the surface during reducing temperature in the TDS apparatus and during several minute in the air before enclosing the sample by nitrogen.

ΔP_{O_2} at 500°C was inclined to be saturated for oxygen pressure, while ΔP_{O_2} at 800°C was proportional to it. This means that oxidation reaction between 500°C and 800°C is different. The reaction at 500°C might be adsorption of oxygen on the bare silicon surface occurred with hydrogen desorption. If we assume that oxygen was not adsorbed except on the bare silicon surface, the saturation tendency of ΔP_{O_2} can be explained. The reaction at over 800°C might be the formation of SiO. As this SiO is evaporated from the surface, oxygen can always attack bare silicon and form SiO. It is considered that the same reaction occurs on the H₂O₂ treated surface, too, after desorption of the native oxide. The closed circle in the Fig. 4 is plotted from the result of Fig. 2. The fact that this closed circle almost exists on the

800°C line of HF cleaned surface supports this assumption.

4. Conclusion

- (1) The oxidation of the hydrogen terminated silicon surface in the low oxygen pressure region proceeds by two steps at about 500°C and 800°C.
- (2) Oxidation reaction on the native oxide covered surface differs from that on the hydrogen terminated surface.
- (3) The consumption quantity of water don't increase with increasing those of oxygen.

Acknowledgments

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