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Initial Oxidation Reaction on Cl-Adsorbed Si Surfaces

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Initial oxidation reactions on Cl-adsorbed Si(111) surfaces in various atmospheres are studied with surface analysis methods. Adsorbed Cl atoms on Si(111) has a passivation effect suppressing oxidation in dry atmospheres, while the surface is easily oxidized in wet environments. Adsorbed Cl atoms can be removed by heating in vacuum. Reactions with Cl_2 are disturbed by adsorbed O and oxide on Si surfaces. These results reveal important surface characteristics for the control of surface reactions and stability, during and after Cl-related processes.

I. Introduction

Adsorption of halogen atoms and halogen-composed molecules often occurs on surfaces during various processes of VLSI fabrication, such as dry etching and photo cleaning. These surfaces are highly reactive due to the adsorbed halogens. Because of this, air exposure, after completion of the processes, easily causes surface reactions with ingredients in the air, producing oxide and complicated surface reaction products. In order to avoid undesigned surface reactions and to maintain high controllability and reliability of processes, such reactions on halogen-adsorbed surfaces need to be well controlled throughout device fabrication and inter-process surface preservation.

There are some approaches to controlling the halogen-adsorbed surface conditions: the suppression of natural oxidation, the removal of adsorbed halogens, or the utilization of properties of adsorbed halogens. For the purpose of achieving various surface-controlling processes, we studied reactions involved in natural oxidation, thermal oxidation on Cl-adsorbed Si surfaces, and Cl desorption from the surfaces.

Additionally, it has been reported that the halogen incorporation in the gate-oxide film and at the oxide/Si interface improves device characteristics.[1,2] From this view point, we also studied the Cl incorporation reaction and the role of Cl through thermal oxidation in the presence of Cl_2.

Here, Cl-related reactions were examined, since Cl is a typical halogen utilized in device processes. These Cl-related reactions were examined with surface analysis methods, by studying changes in surface composition, adsorpants and their bindings.

II. Experiments

An ultra-high vacuum (UHV) system, constructed of three chambers, was employed for surface reactions and "in situ" surface analysis. Background pressure was 2×10^{-8} Pa, both in chambers for low-pressure reactions and for surface analysis. It was 1×10^{-6} Pa in a chamber for high-pressure reactions and the sample introduction.

The samples were Si(111) surfaces, p-type, with 3 - 6 $\Omega \cdot cm$ resistivity. The Si surfaces, whose natural oxide layers were removed in a diluted HF solution before sample mounting, were cleaned in the analysis chamber by flashing up to 1000°C.

Cleaned bare-Si(111) surfaces were exposed to a Cl_2 atmosphere of 1.3×10^{-4} Pa for 100-1000 seconds, i.e.
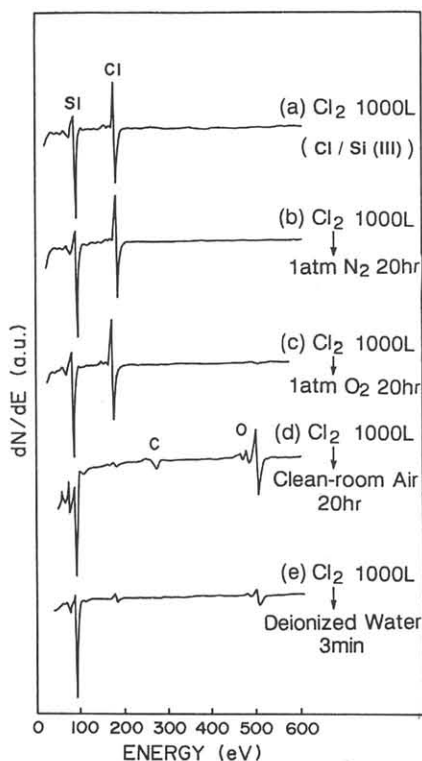
Fig.1 AES spectra for Cl/Si(111) surfaces treated in various environments.

Fig.2 Normalized AES-signal intensities of Cl and O on Cl/Si(111) surfaces exposed to 1 atm N_2 (□,■), 1 atm O_2 (△,▲) and clean-room air (○,●), vs. exposure time.
I_{Cl}, I_{Si}, I_O: Signal intensities of Cl(LMM), Si(KLL) and O(KLL).
f_x: Sensitivity factors. f_{Cl}=1.02, f_{Si}=0.02, f_O=0.51.

100 - 1000 L (1 L = 1.3 x 10^{-4} Pa s), to provide Cl-adsorbed Si(111) surfaces with the saturation level.[3] This surface is denoted as Cl/Si(111) in this paper.

The Cl/Si(111) surfaces were subsequently exposed to or heated in various atmospheres: exposed to 1 atm O_2, 1 atm N_2, and clean-room air, or heated in UHV and in O_2 atmospheres of 1.3 x 10^{-4} - 1.3 x 10^{-2} Pa.

Some cleaned Si surfaces were treated in O_2 atmospheres before Cl_2 treatments. These experiments reveal the reactivity of oxidized Si surfaces with Cl.

Surfaces after reactions were analyzed by Auger electron spectroscopy (AES) and x-ray photoelectron spectroscopy (XPS), with a double-pass cylindrical mirror analyzer (CMA, PHI 15-255 GAR). X-ray of MgKα line was employed in the XPS measurement.

III. Results and Discussion

Figure 1 shows AES spectra indicating alteration of the composition on Cl/Si(111) surfaces under exposure to 1 atm N_2, 1 atm O_2 and clean-room air, and during dipping in deionized water.
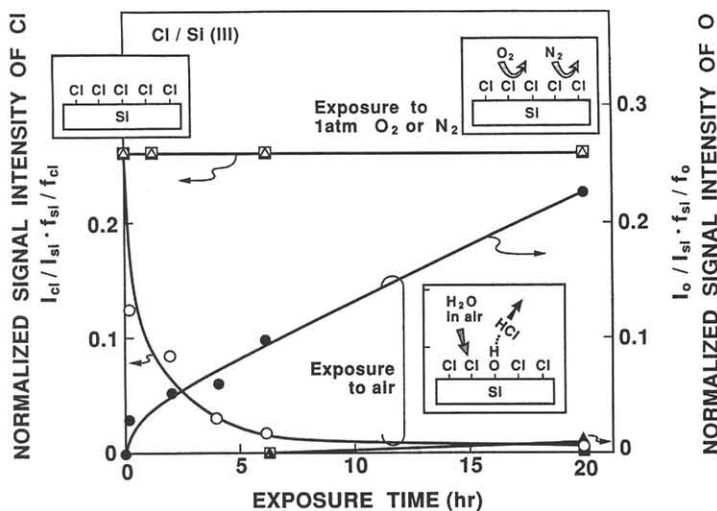
Time-dependent changes in the composition on the atmosphere-exposed surfaces are shown in Fig.2, in terms of AES-peak intensities normalized with the intensity of Si(KLL) peak (1606 eV). The surface composition showed no or very little changes even after 20 hrs exposures to dry N_2 or O_2, while immediate Cl-desorption and oxidation took place under humid clean-room air exposure. The change occurred more rapidly during dipping in deionized water.

These surface changes were caused by humidity or moisture in the environments. The surface reactions are thought to be analogous to those reported by Takahagi et al., on F- adsorbed Si surfaces. They showed that the surface Si-F bonds, formed by diluted HF dipping, are hydrolyzed by subsequent dipping in deionized water to produce Si-OH on the surfaces.[4] It is suggested in our study that the Si-Cl bonds on the Cl/Si(111) surfaces are hydrolyzed to produce Si-OH and to desorb HCl, thereby initiating surface oxidation. Therefore the Si surfaces after Cl-related processes should be kept in a dry atmosphere in order to avoid surface change. In dry atmospheres, the adsorbed Cl has the passivation effect against surface oxidation.

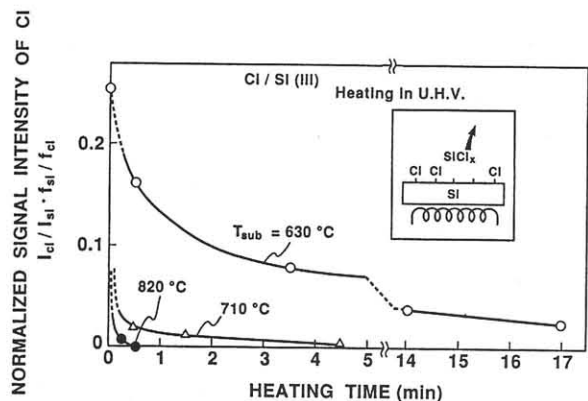Adsorbed-Cl atoms can be removed through

Fig.3 Normalized AES-signal intensities of Cl on Cl/Si(111) surfaces heated in UHV, vs. heating time.

Fig.4 Normalized AES-signal intensities of Cl and O on Cl/Si(111) and bare-Si(111) surfaces heated in O_2 and UHV.

exposure to wet atmospheres. However, the Si surfaces are oxidized under Cl desorption. For the Cl removal without oxidation, heating of Cl-adsorbed surface in a vacuum is effective. It has been previously reported that desorption of $SiCl_x$ ($SiCl_4$ and/or $SiCl_2$) occurs during heating.[5,6] We examined heating of Cl/Si(111) to determine the temperature at which complete Cl desorption is achieved, without causing surface oxidation. Figure 3 shows the Cl composition change on Cl/Si(111) surfaces under heating in UHV. Heating at 820°C for 30 seconds removed most of the surface Cl atoms.

Next, the influence of surface Cl atoms on surface reactions with O_2 was examined. Figure 4 shows the Cl- and O- compositions on Cl/Si(111) and bare-Si surfaces, after heating in UHV and in low-pressure O_2 atmospheres. Cl composition after heating in relatively high pressure O_2 (Figs.4 (d) and (e)), was a little lower than that after heating in UHV (Fig.4 (b)). On the other hand, the O composition gradually increased with the increase in O_2 pressure during heating.

These results indicate that the presence of O_2 atmospheres did not greatly enhance Cl desorption, but caused surface oxidation. It is suggested that oxidation took place first at adsorpant-free surface areas, where Cl had been desorbed under heating, and then progressed from the surface down to the bulk-Si. In the case of a bare-Si heated in an O_2 atmosphere (Fig.4 (f)), the surface O composition was higher than
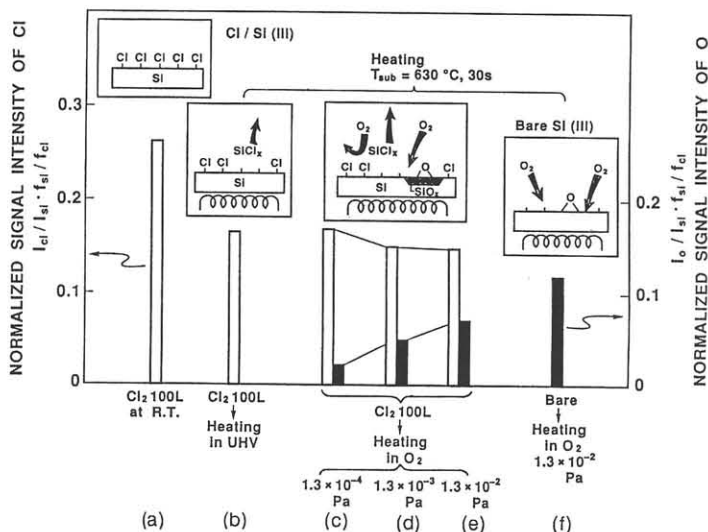
those shown in Figs.4 (c) - (e). It is evident that the adsorbed-Cl atoms suppressed Si surface oxidation under heating in O_2 atmospheres, as well as under exposure to dry atmospheres.

The reactivity of oxidized Si surfaces with Cl_2 was examined as indicated in Fig.5. Si surfaces after O_2 exposure and oxidation were subsequently exposed to or heated in Cl_2 atmospheres. Figure 5 shows the surface Cl composition as a function of the O composition before Cl_2 treatments. Under O_2 exposure of 1000 L, a Si(111) surface adsorbs O with more than mono-layer coverage, i.e. with no dangling bonds. Even on the O/Si(111) surface without dangling bonds, Cl adsorption took place under Cl_2 treatments. Cl adsorption also occurred on suboxide layers (SiO_x, x<2) produced by high-pressure O_2 exposure, while it did not occur on thicker SiO_2 surfaces formed by low-pressure oxidation. The amount of Cl adsorption decreased, depending on the increase in surface O composition before Cl_2 treatments.

It is thought that, after bindings between Si and high-electro-negative O have been achieved to form a surface SiO_2 layer, there are no surplus electrons to be supplied for bindings between surface atoms and Cl. On the other hand, surfaces of suboxide, SiO_x, have different compositions and/or different Si-O-Si binding
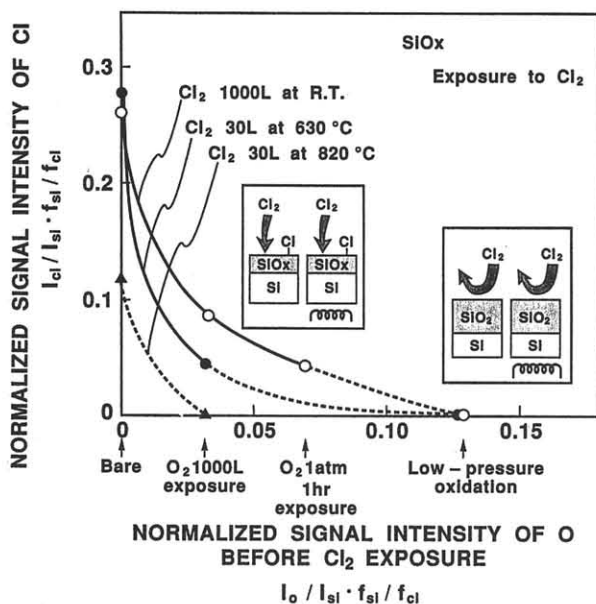
Fig.5 Normalized AES-signal intensities of Cl on O-adsorbed Si or Si oxide surfaces, exposed to or heated in Cl_2, vs. primary O-signal intensities.

Fig.6 Angular-resolved XPS spectra for a Cl/Si(111) surface heated in $1\%Cl_2/O_2$.

angles from those on the SiO_2 surface. Such surface difference may cause an electron distribution variance on surface atoms, resulting in a rather high reactivity of SiO_x surface atoms with Cl. Our results suggests that the removal of any natural oxide layer on a Si surface is necessary to achieve high reactivity of surfaces with Cl.

The thermal oxidation reaction under low-pressure O_2 in the presence of Cl_2 was also examined. Figure 6 shows angular-resolved XPS spectra for a Cl/Si(111) surface, after heating in $1\%Cl_2/O_2$ (1.3×10^{-2} Pa). These spectra indicate that there exists an oxide layer without Cl incorporation, under a Cl-included oxide layer. No Cl segregation was observed at the oxide/Si interface within the limit of XPS sensitivity. Although an improvement in electronic properties has been previously reported on halogen-incorporated SiO_2/Si interfaces[1], our results showed no Cl incorporation at the interface.

In view of the results shown in Figs.1 - 5, the surface reaction indicated in Fig.6 is explained as follows: Cl atoms, which were not desorbed from Cl/Si(111) and remained on the surfaces even under heating, and/or the Cl atoms which were additionally adsorbed on SiO_x during oxidation, are incorporated into the shallower region of the surface oxide layer.
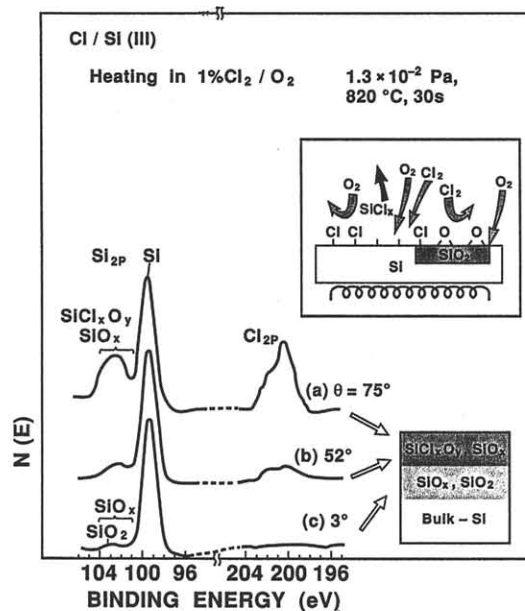
IV. Conclusion

We investigated roles of adsorbed Cl atoms on Si surfaces under reactions involved in initial stage of oxidation. The adsorbed Cl atoms on Cl/Si(111) have a passivation effect suppressing oxidation in dry atmospheres, while the Cl atoms are easily removed in wet environments. These results suggest that Cl-adsorbed Si surfaces should be kept in dry atmospheres in order to maintain surface stability. Adsorbed Cl atoms can be removed by heating in vacuum. Since Cl_2 does not react with surface oxide but with bare Si, removal of the surface oxide layer is necessary to achieve high reactivity on Si surfaces. Cl incorporation at the SiO_2/Si interface was not observed by XPS. These results reveal various characteristics of Cl-adsorbed Si surfaces for the control of surface reactions and stability, during and after Cl-related processes.

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