## Electron Spectroscopy Study of Cl/Si Reaction on Si(111), Si(100) and Si(110) Surfaces

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Si(111), Si(100) and Si(110) surfaces were characterized after Cl adsorption and after Ar ion-assisted  $Cl_2$  etching by means of Electron Energy Loss Spectroscopy, Auger Electron Spectroscopy, X-ray Photoelectron Spectroscopy and Reflection High Energy Electron Diffraction. Cl atoms did not resolve surface Si dimers but adsorbed on Si dangling bonds. Conspicuous EELS peaks on Cl-adsorbed surfaces were thought to be due to the overlayer plasmon excitations. After etching, an electron excitation, resembling that took place on Cl-adsorbed surfaces, remained in deeper surface layers. Si surfaces after etching showed another EELS peak which was related to the existence of surface reaction products, SiCl<sub>2</sub> and SiCl<sub>3</sub>.

## I. Introduction

Cl adsorption on clean Si surfaces is of interest in forming stable chemisorbed monolayers by Cl<sub>2</sub> dissociation on surfaces. Its adsorption sites and the local-densityof-states have been previously investigated 1-7, mainly for Si(111) surfaces. Additionally, the reaction between Si and Cl plays an important role in VLSI manufacturing processes such as dry etching and gas phase epitaxial growth. In order to obtain fundamental knowledge about Cl/Si reactions, Si(111), Si(100) and Si(110) surfaces after Cl adsorption and after Ar ion-assisted Cl<sub>2</sub> etching are characterized in this paper. Ar ion-assisted Cl<sub>2</sub> etching was employed as an example of the Si/Cl-system process. The electronic structure of Cl-reacted surfaces were analyzed with Electron Energy Loss Spectroscopy (EELS), in which various incident electron energies were employed to profile the electronic structures in depth.8) Auger Electron Spectroscopy (AES) and X-ray Photoelectron Spectroscopy (XPS) were also employed for the analysis of surface reaction products. On the basis of the results, Si/Cl

bonding states and reaction products resulting from Ar ion-assisted Cl<sub>2</sub> etching as well as from Cl adsorption will be discussed.

### II. Experimental

Figure 1 shows the experimental apparatus. The background pressure was under  $2 \times 10^{-8}$  Pa in the analysis and treatment chambers, and  $1 \times 10^{-6}$  Pa in the preparation chamber. The samples were Si(111), Si(100), and Si(110), each of the p-type, with 10~20  $\Omega$ -cm resistivity.After flashing up to 110°C in the analysis chamber, clean surfaces, showing no AES contamination, were obtained. The surfaces exhibited reconstructed patterns of 7x7 on Si(111), 2x1 on Si(110) and weak 16x2 on Si(110) when observed with Reflection High Energy Electron Diffraction (RHEED).





Cl adsorption and Ar ion-assisted Cl<sub>2</sub> etching were carried out in the treatment chamber. Cl adsorption was produced in Cl<sub>2</sub> gas atmospheres of 0.1~1000L (1L= $1.3 \times 10^{-4}$  Pa·s) at room temperature. Ar ion-assisted Cl<sub>2</sub> etching was carried out under Cl<sub>2</sub> atmospheres of  $1.3 \sim 5.3 \times 10^{-6}$  Pa for 1000s(10~ 40L Cl<sub>2</sub> supply), with an Ar ion beam of 1kV acceleration energy and of 0.4  $\mu$ A/cm<sup>2</sup> current density under 7.0×10<sup>-7</sup> Pa Ar partial pressure.

After both Cl adsorption and etching, the samples were transported to the analysis chamber in about  $1.0 \times 10^{-7}$  Pa and then analyzed using EELS, AES and XPS techniques, with a double-pass Cylindrical Mirror Analyzer (CMA), and by means of RHEED. EELS and AES spectra were measured using lock-in detection.

# III. Results and Discussions

Figure 2 shows relative Cl concentration on Si surfaces, evaluated using the AES peaks of Si(LMM) and Cl(LMM), after exposure to various Cl<sub>2</sub> atmospheres. No contamination peaks were observed after Cl<sub>2</sub> exposure. The Cl concentration was saturated at about 10L on Si(100), and at about 100L on Si(111) and Si(110). After saturation, the 2x1 reconstructed RHEED pattern on Si(100) persisted clearly, while 7x7 and 16x2 patterns on Si(111) and Si(110) weakened. The low saturate Cl concentration and the persistence of clear 2x1 pattern on Si(100) indicate that the dimers, which construct the are not resolved by the 2x1 structure.







Fig.3 EELS spectra of clean and Cladsorption-saturated Si surfaces.  $S_1, S_2, S_3$ :transitions from surface states  $E_1, E_2$ :bulk interband transitions thws, hwp:surface- and bulk-plasmons

chemical attack of the Cl. It has been reported that steps and irregularly arranged surface atoms are of high density on Si(100)2x1 surfaces.9) Cl atoms are expected to adsorb at dangling bonds found on these spots. In the case of Si(111), the high saturate Cl concentration and the weakening of the 7x7 pattern indicate that the 7x7 structure resolves partially because of Cl adsorption. Applying the DAS model<sup>10)</sup> which describes the 7x7 structure comprised of dimers, adatoms, and stacking faults, we expect that Cl atoms adsorb at dangling bonds on the DAS structure, and that the dimers of the structure persist as suggested by the case of Si(100). On the Si(110)16x2 surface, Cl atoms are thought to adsorb on regularly-arranged steps<sup>11)</sup> of the reconstructed structure.

Figure 3 shows the EELS spectra of clean and Cl adsorbed Si(111), Si(100) and Si(110) surfaces. The spectra of adsorption-saturated surfaces (b), (d) and (f) show conspicuous peaks at about  $7 \sim 9 \text{eV}$  energy loss. These



Fig.4 Depth profile of EELS spectra of a Cladsorption-saturated Si(111) surface.

peaks did not change after heating up to 400 °C. Because of the high intensity of these peaks, it is thought that the peaks are not due to simple one-electron-type interband excitations which have been reported.4,5) Rather they are due to the overlayer plasmons and/or its collective-interband-transition modes as in the case of alkali adsorption on metals and on Si, 12) and as was suspected for other adsorption systems.<sup>13)</sup> Employing the photoemission and calculation previous reports $^{1-7)}$ , the interband transitions, which have the possibility to merge with the overlayer plasmons, are expected as follows: a transition of about  $8 \sim 10 \, \text{eV}$  from the  $Cl(p_{\pi})$ state, which makes a o-like bonding state with  $Si(p_{\pi})$ , to the  $Cl(p_{\pi})$  antibonding state, and a transition of about  $6 \sim 8 \text{ ev}$  from the  $Cl(p_x, p_y)$  bonding state, which makes a  $\pi$ -like bonding state, to the Cl(pz) antibonding state. It has been speculated that Cl adatoms on Si(100) do not sit on top of Si atoms; rather, the covalent Si-Cl bonds are tilted<sup>1)</sup>, in contrast to the on-top site Cl adsorption on  $Si(111)^{7}$ . The difference in the energy and the intensity of the  $7 \sim 9 \text{eV}$ peaks among (b), (c) and (d) are due to both their different Cl adsorption sites and the surface Cl concentrations.

Figures 4 and 5 show the incidentelectron-energy dependence of EELS spectra for Cl adsorbed Si(111) and Si(100) surfaces. The probing depth on this type EELS



Fig.5 Depth profile of EELS spectra of a Cladsorption-saturated Si(100) surface.

measurement is reported to be about 2.0Å for an incidence electron energy of 100eV, 2.7Å for 200eV, 4.0Å for 400eV, 5.7Å for 600eV, and 7.0Å for  $800 eV^8$ ). In contrast to the steady decrease of the 8.8eV peak seen in Figure 4, the 7.2eV and 8.8eV peaks in Figure 5 vary differently depending on the probingdepth increase. When the probing depth is on the increase, the 7.2eV peak decreases more quickly than the 8.8eV peak decreases. If the excitation-cross-sections of these peaks do not change differently depending on the incident electron energy, it is indicated that the electron states causing 7.2eV electron excitation are confined more closely to the surface than the states causing 8.8eV excitation.

Figure 6 shows the EELS spectra of the Si(100) surfaces after Ar ion-assisted Cl2 etching. With an increase in Cl<sub>2</sub> supply, a new peak, which does not appear on the C1adsorbed surface, comes to appear at 6.3eV, while the 9.0eV peak persists. Etched Si(111) surfaces, under the same conditions as Figure 6 (c), showed a similar EELS spectrum to Figure 6 (c). The depth profile of the Figure 6 (c) is shown in Figure 7. The 9.0eV peak remains until the incident electron energy comes to be 600eV, while the 6.3eV peak appears at less than 400eV. This indicates that the electron states which produce the 6.3eV peak exist more superficially in the surface layers than those of the 9.0eV peak



Fig.6 EELS spectra of Si(100) surfaces after Arion-assisted  $Cl_2$  etching with various  $Cl_2$  supply.

and that both states remain in deeper regions than those observed on Cl-adsorbed surfaces. These peaks, especially the 6.3eV peak, indicate the formation of new electron states on etched surfaces. There is a possibility that the cause of the 9.0eV peak may be assigned to the same excitation as that of the 8.8eV peak for the Cl-adsorbed surface.

Figure 8 shows a Si(2p) XPS spectrum of the same surface as Figures 6 (c) and 7. It shows chemical shifts of the reaction products SiCl, and SiCl, as well as SiCl. On the other hand, XPS spectra of the same surfaces as Figure 6 (a) and (b) show smaller amounts of these chemical shifts. Consequently, it is expected that the peaks at 6.3eV and 9.0eV in Figures 6 and 7 are related to the electron states formed by the reaction products of SiCl<sub>2</sub> and SiCl<sub>3</sub>. When the 9.0 eV peak is assumed to have the same origin as that of the 8.8eV peak of the C1adsorbed surface, it is thought that the excitation originating from surface reaction products, SiCl<sub>2</sub> and SiCl<sub>3</sub>, takes place more superficially than the excitation which originates from the SiCl type bonding.

### IV. Conclusion

After Cl adsorption on Si surfaces, EELS spectra show Cl-related EELS peaks which are thought to be due to overlayer plasmon excitations or to its collective interband



Fig.7 Depthprofile of EELS spectra of a Si(100)surface after Ar ion assisted Cl<sub>2</sub> etching.



ENERGY (eV) Fig.8 An Si<sub>2p</sub> XPS curve-fitted spectrum of the samesurface as Figure 7.

modes. The difference in the energies and depth profiles of peaks at different substrate orientations is expect to depend on the Cl adsorption site and on the surface Cl coverage; i.e., on surface dangling bonds for Si(111) and Si(110) with high Cl coverage, and not at dimers but at steps and irregularly-arranged surface atoms for Si(100) with low Cl coverage. After Ar ionassisted Cl<sub>2</sub> etching, two EELS peaks, which change differently in depth, appear. One is related to the formation of the surface reaction products, SiCl<sub>2</sub> and SiCl<sub>3</sub>, and another is possibly due to the same excitation as that on the Cl-adsorbed surface. The latter excitation remains in a deeper region on the etched surface indicating the possibility of its persistence in the interface region between the bulk and the reaction product layers.

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