

## Quantum Chemical Investigation of Metal Adsorption Mechanism onto Silicon Surface in Cleaning Solution

Moriya MIYASHITA, Hiroyasu KUBOTA, Yoshiaki MATSUSHITA

Reiko YOSHIMURA\* and Tsukasa TADA\*

Semiconductor Materials Engineering Dept., Toshiba Corporation

72, Horikawacho, Saiwai-ku, Kawasaki-shi, 210, Japan

\* Research and Development Center, Toshiba Corporation

Quantum chemical approach was adopted to investigate metal adsorption mechanism onto silicon surface in cleaning solution.  $Fe^{3+}$  and  $Al^{3+}$  complex ion structures in aqueous solution were estimated by ab initio molecular orbital theory. The reactivity between metal complex ions and silicon surface depends on the pH value of solution, which was well explained by the frontier orbital theory. Based on the result of theoretical estimation, a metal adsorption suppressing procedure, which is an addition of chelating reagent to basic solution to prevent  $OH^-$  ion from coordinating to metal ions, is proposed.

### 1. Introduction

Ultra clean technologies for semiconductor device manufacturing are becoming more and more important as the VLSI device integration is progressing. Wet cleaning processes are desired for high ability of contamination removal, but it is well known that metal ions, such as Fe and Al ions, become to be easily adsorbed onto a silicon surface as the pH value in aqueous solution is increased<sup>1)</sup>. This metal adsorption provides a serious problem for VLSI devices because alkaline cleaning solutions, such as ammonium and hydrogen peroxide mixed solution, which is recommended as RCA cleaning<sup>2)</sup>, are frequently used in VLSI fabrication processes. Many experimental approaches, such as electrochemical<sup>3)</sup>, chemical kinetics<sup>4)</sup> or chemical equilibrium approaches<sup>5)</sup>, have been adopted to reveal the metal adsorption and desorption mechanism.

The metal complex ion and its  $OH^-$  ligand number are known to be changed with pH value<sup>6)</sup>. So the adsorbed metal quantity change is expected to be attributed to the reactivity change of the metal complex ions due to their structure and electronic state change with pH value. In this paper, a quantum chemical approach has been employed to analyze the dependence of Fe and Al ions adsorption on the pH value of the cleaning solution. Based on the analysis, an effective method of suppressing metal adsorption is proposed.

### 2. Methods

#### 2.1 Experimental

Wafers used in this study were n-typed, (100) oriented, 125mm in diameter and cut from a crystal

grown by CZ method. Concentrations of metal adsorbed on silicon surface after wet cleaning process were quantitatively analyzed by wafer surface analysis (WSA) method<sup>9)</sup>. Wafers were initially cleaned by mixed solution of hydrogen chloride and hydrogen peroxide to make a hydrophilic surface. Wafers were immersed in various pH standard solutions containing with  $50 \mu g/l$  Fe and Al for 10 minutes at room temperature and rinsed by deionized water for 15 minutes as described in the previous paper<sup>1)</sup>.

#### 2.2 Theoretical

Structures of  $Fe^{3+}$  and  $Al^{3+}$  complex ions coordinated with  $OH^-$  and/or  $H_2O$  were estimated by ab initio MO theory. Calculations were carried out at the Hartree-Fock level with the MINI-4 basis set<sup>7)</sup> using the HONDO 7 program<sup>8)</sup>.  $(SiH_3)_2Si(H)OH$  was adopted as a (100) hydrophilic Si surface model cluster.

### 3. Results and discussion

The dependence of adsorbed Fe and Al concentration on pH value of aqueous solution is shown in Fig.1. This figure clearly indicates that the adsorbed quantities of Fe and Al are increased with an increase in the pH value of the aqueous solution. The adsorbed Al quantity is also shown to be larger than that of Fe in the figure.

#### 3.1 Theoretical analysis

The reactivity difference between  $Fe^{3+}$  and  $Al^{3+}$  can be explained by the difference between the formation free energy of Fe-O-Si and Al-O-Si bonding. Because the formation free energies are -697 and -1581 kJmol<sup>-1</sup> for  $Fe(OH)_3$  and  $Al(OH)_3$  respectively<sup>10)</sup>, the Al-O-Si bond energy is estimated to be much higher than that of

Fe-O-Si bond. On the other hand, the dependence of adsorption on the pH value is interpreted by the next quantum chemical investigation.

The adsorbed metal quantity change for the same metal, on the other hand, is interpreted by the frontier orbital theory<sup>11)</sup>. The number of OH<sup>-</sup> coordinating to metal ion increases with the increase of pH value of aqueous solution<sup>6)</sup>. The minimum energy structures of Fe<sup>3+</sup> and Al<sup>3+</sup> complex ions coordinating with OH<sup>-</sup> and/or H<sub>2</sub>O at each coordination number of OH<sup>-</sup> can be estimated by ab initio MO calculations and are summarized in Table 1. The highest occupied molecular orbital (HOMO) energy levels of each complex ion are also listed in Table 1. The lowest unoccupied molecular orbital (LUMO) energy level of silicon surface model cluster is calculated to be 1.73eV.

In Table 1, it should be noted that the HOMO level of metal complex ions is increased with an increase in the number of OH<sup>-</sup> ligand ion both for Fe<sup>3+</sup> and Al<sup>3+</sup> ions. This indicates that the HOMO(metal complex ion)-LUMO(Si surface) energy gap is decreased with an increase in the OH<sup>-</sup> ligand number. Since the HOMO-LUMO interaction is inversely proportional to the HOMO-LUMO energy gap<sup>11)</sup>, the calculated result in Table 1 means that the orbital interaction between the HOMO of metal complex ions and LUMO of Si surface is increased with an increase in the pH value. Assuming that the metal adsorption proceeds by frontier-controlled reaction<sup>11)</sup> between the HOMO of metal complex ion and LUMO of the Si surface, the metal adsorption is expected to proceed rapidly with the increasing pH value of aqueous solution, which is consistent with the experimental result. This frontier orbital interaction diagram between the HOMO of the metal complex ion and the LUMO of the Si surface is shown in Fig. 2.

Considering that the HOMO of the metal complex ion mainly consists of the lone pair orbital of O atom in the OH<sup>-</sup> or H<sub>2</sub>O ligand, the calculated results strongly suggest that the metal adsorption is initiated by the attack of ligand O atom on the surface Si atom and that the metal ion is adsorbed by a Si-O-metal bond. This reaction is a nucleophilic reaction from metal complex ion to silicon surface as shown in Fig. 3. The increase of HOMO energy level of metal complex ion is mainly due to the increase of the electron-electron Coulombic repulsion energy caused by the increase of the negatively charged OH<sup>-</sup> ligand number.

### 3.2 Suppression method of metal adsorption

Based on the result of the theoretical analysis, a metal adsorption suppressing procedure is proposed. One promising procedure is an addition of chelating reagent to basic solution to prevent OH<sup>-</sup> ion from coordinating to metal ions. Figure 4 shows that Fe concentrations adsorbed on silicon surface as a function

of dipping time in alkaline solution of PH 9 containing with 20 μg/l Fe with or without addition of chelating reagent. This figure clearly indicates that the addition of chelating reagent into cleaning solution is effective in suppressing metal adsorption on Si surface.

## 4. Conclusion

Fe and Al adsorption mechanism onto silicon surface has been investigated by ab initio MO theory. Fe and Al ion adsorption probability dependence on the pH value in aqueous solutions has been explained by the frontier orbital interaction between the HOMO of Fe<sup>3+</sup> or Al<sup>3+</sup> complex ion and the LUMO of silicon surface. An addition of chelating reagent to basic solution to prevent OH<sup>-</sup> ion from coordinating to metal is proposed as an effective suppressing method of metal adsorption.

## References

- 1) H.Hiratsuka, M.Tanaka, T.Tada, R.Yoshimura and Y.Matsushita: *Ultra Clean Technology*, **3**(1991)258.
- 2) W.Kern: *RCA Rev.* **31**(1970)207.
- 3) F.W.Kern Jr., M.Itano, I.Kawanabe, M.Miyashita and T.Ohmi: *Proc. 11th Workshop on ULSI Ultra Clean Technology*, Tokyo, 1991, (Ultra Clean Soc., Tokyo, 1991) p.23.
- 4) J.Ryuta, T.Yoshimi, H.Kondo, H.Okuda and Y.Shimanuki: *Jpn. J. Appl. Phys.*: **31**(1992)2338.
- 5) Y.Mori, K.Uemura, K.Shimano and T.Sakon: *Semiconductor Silicon, 1994*, (The Electrochemical Society, Pennington) p.248.
- 6) C.M.Flynn: *Chem.Rev.*, **84**(1984)31
- 7) Tawewaki et al.: *J. Comp. Chem.* **2**(1981)96
- 8) M.Dupuis et al.: *HONDO 7, QCPE 544*, (Indiana University, 1987)
- 9) A. Shimazaki: *Defects in Silicon 2*, 1991, (The Electrochemical Society, Pennington)
- 10) *Kagaku-binran-Kisohen*: (Maruzen, Tokyo)
- 11) H K.Fukui: *Theory of Orientation and Stereoselection*; (Springer-Verlag, Berlin, 1975)

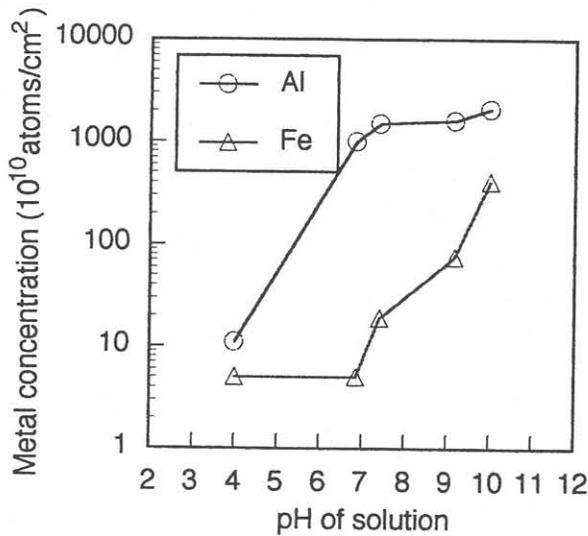
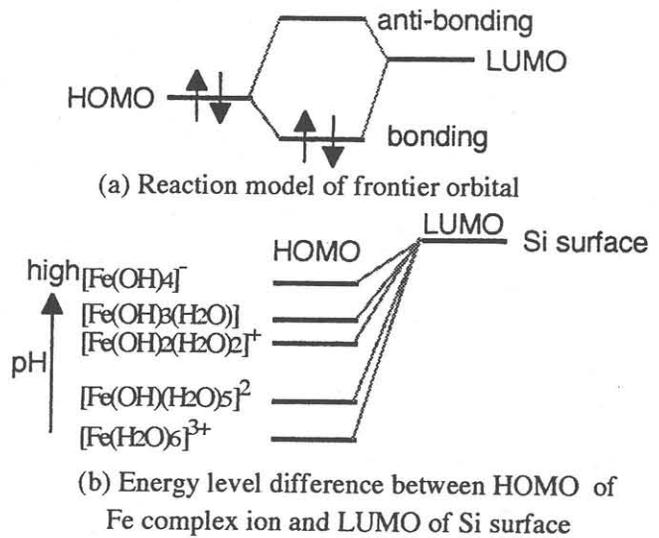


Fig.1 Dependence of adsorbed Al and Fe concentration on pH of solution containing 50ppb Al and Fe.



(a) Reaction model of frontier orbital  
(b) Energy level difference between HOMO of Fe complex ion and LUMO of Si surface

Fig.2 Frontier orbital interaction diagram between the HOMO of the metal complex ion and the LUMO of the Si surface.

Table1 Some properties of various  $Fe^{3+}$  and  $Al^{3+}$  complex ions in Aqueous solution estimated by ab initio MO calculations.

major complex ion	Symmetry	Bond length		HOMO level (eV)
		Fe-OH <sub>2</sub>	Fe-OH	
$[Fe(H_2O)_6]^{3+}$	Th	2.0	-	-28.8
$[Fe(OH)(H_2O)_5]^{2+}$	C <sub>1</sub>	2.1	2.3	-22.7
$[Fe(OH)_2(H_2O)_4]^+$	C <sub>1</sub>	2.1	2.0	-13.9
$[Fe(OH)_3(H_2O)]$	C <sub>1</sub>	2.1	2.0	-10.7
$[Fe(OH)_4]^-$	S <sub>4</sub>	-	1.8	-5.5
		Al-OH <sub>2</sub> Al-OH		
$[Al(H_2O)_6]^{3+}$	Th	1.9	-	-29.2
$[Al(OH)(H_2O)_5]^{2+}$	C <sub>1</sub>	2.0	1.7	-19.6
$[Al(OH)_2(H_2O)_4]^+$	C <sub>1</sub>	2.0	1.8	-14.8
$[Al(OH)_3(H_2O)]$	C <sub>1</sub>	2.0	1.7	-11.9
$[Al(OH)_4]^-$	S <sub>4</sub>	-	1.8	-6.1

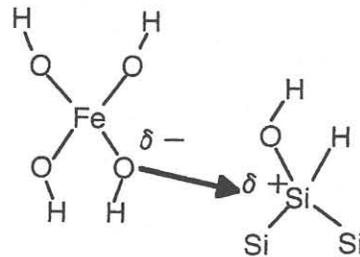


Fig.3 Model of metal adsorption onto silicon surface.

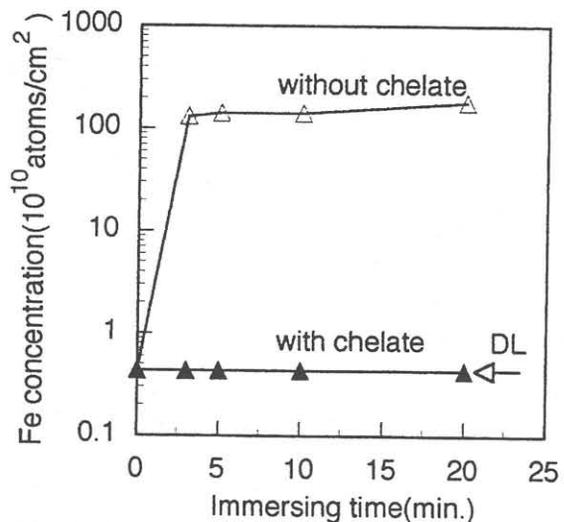


Fig.4 Fe adsorbed on silicon as a function of immersing time in pH9 solution containing 20ppb Fe with or without chelating reagent.