Quantum Chemical Study on the Interaction of NF3 with Si

Akira Endou, Aruba Yamada, Momoji Kubo, Kazuo Teraishi, S. Salai Cheettu Ammal, Akira Miyamoto, Masahiro Kitajima¹, Thomas W. Little² and Fumio S. Ohuchi²

Department of Materials Chemistry, Graduate School of Engineering, Tohoku University, Aoba-yama 07, Sendai 980-8579,

Japan.

Phone: +81-22-217-7233, Fax: +81-22-217-7235, E-mail: miyamoto@aki.che.tohoku.ac.jp

¹National Research Institute for Metals, 1-2-1 Sengen, Tsukuba, Ibaraki 305-0047, Japan.

²Department of Materials Science and Engineering, University of Washington, Box 352120, Seatle, WA 98195-2120.

1. Introduction

The high-aspect ratio, submicron diameter contact openings that are essential in modern microelectronic fabrication are of considerable importance. An NF3 plasma is particularly attractive because of its chemical reactivity to Si and SiO2 [1-3]. In addition, NF3 plasma etching has the advantage of no deposition of polymer films commonly found with CFx plasmas [4]. A significant amount of work has been reported on etching rate and reaction mechanism in NF3 plasma etching of Si and SiO₂ [5-8]. Recently, from the point of view of surface science, Little et al. [1] studied the interaction of NF3 with Si surface by x-ray photoelectron spectroscopy (XPS) and found that nitridation of silicon is possible using NF3. They also suggested the presence of both Si-F and Si-N bonding for NF3 ion beam interaction and probably F-N-Si moieties. However, the exact nature of the bonding has not been clarified and theoretical investigations concerned with this system have not appeared yet whilst various theoretical works aimed at F/Si system have been published [9, 10].

In our present work, possible cases of NF₃ interaction with Si that may be useful to understand the mechanism of the plasma interaction of NF₃ with Si have been investigated by quantum chemical calculations.

2. Computational Details

All calculations in this work were carried out using selfconsistent Kohn-Sham procedure [11] as implemented in DMol program package [12] of MSI. As the approximation for the exchange-correlation potential, we applied local density approximation (LDA) using Vosko-Wilk-Nusair (VWN) local functional [13]. We chose double numerical plus polarization functions (DNP) basis set [14] for all calculations.

Our model representing H-Si(111) or H-Si(100)-1x1 surface was modeled by Si10H16 cluster, where the number of H atoms bonded to Si are selected such that Si retains the sp3hybridization in its bonds (Fig. 1).

3. Results and Discussion

To determine the stable position of F or NFx species on Si



Fig. 1 Si10H16 cluster model.

Table I. Cal	culated values	of stabilization	energies
	with LE	Alevel.	

Reaction patterns				
(a): H-Si(111) + (1/2)F ₂ \rightarrow Si ₁₀ H ₁₅ F + (1/2)H ₂				
(b): $\text{H-Si}(111) + (1/2)\text{F}_2 \rightarrow \text{Si}_{10}\text{H}_{16}\text{F}$: Td site	+0.07			
(c): H-Si(111) + (1/2)F ₂ \rightarrow Si ₁₀ H ₁₆ F: Hex site	-0.32			
(d): H-Si(100)-1x1 + (1/2)F ₂ \rightarrow Si ₁₀ H ₁₅ F + (1/2)H ₂	-3.69			
(e): H-Si(100)-1x1 + $F_2 \rightarrow Si_{10}H_{14}F_2 + H_2$	-7.66			
(f): H-Si(111) + NF ₃ \rightarrow Si ₁₀ H ₁₅ NF + HF + (1/2)F ₂	+2.93			
(g): $\text{H-Si}(111) + \text{NF}_3 \rightarrow \text{Si}_{10}\text{H}_{15}\text{NF}_2 + \text{HF}$	-1.75			
(h): H-Si(100)-1x1 + NF ₃ \rightarrow Si ₁₀ H ₁₄ NF + 2HF (starting with bent F-N-Si bond)				
(i): H-Si(100)-1x1 + NF ₃ \rightarrow Si ₁₀ H ₁₄ NF + 2HF (starting with linear F-N-Si bond)	-1.9()			
(j): H-Si(100)-1x1 + NF ₃ \rightarrow Si ₁₀ H ₁₄ N(NF ₂) + H ₂	-2.89			

¹ ΔH=Eproducts - Ereactants

	(bound directly with F or N).								
	F	Ν	Si	dF(N) ¹	dF(Si)	đN	dSi		
(a)	-0.45	-	+0.40	-0.39	-0.08	-	-1.06		
(b)	-0.41	-	-	-0.36	-0.05	1 M	-		
(c)	-0.41		-	-0.35	-0.05	-	-		
(d)	-0.45	-	+0.45	-0.39	-0.09	-	-1.01		
(e)	-0.42	-	+0.80	-0.37	-0.06	-	-0.66		
(f)	-0.30	-0.15	+0.24	-0.24	+0.06	-0.32	-1.22		
(g)	-0.20	+0.06	+0.19	-0.15	+0.16	-0.11	-1.27		
(h)	-0.23	-0.19	+0.32	-0.18	+0.13	-0.36	-1.14		
(i)	-0.23	-0.19	+0.39	-0.17	+0.14	-0.36	-1.07		
(j)	-0.20 (-NF) -0.43 (Si-F)	+0.09	+0.66	-0.15 (-NF) -0.37 (Si-F)	+0.16 (-NF) -0.06 (Si-F)	-0.08	-0.80		
NF3	-0.06	+0.17			-		-		
SiF4	-0.37	-	+1.46	-	-	-	-		

Table II. Mulliken atomic charges for F, N and Si (bound directly with F or N)

¹ difference from the charge on F of NF3.

surface or at the tetrahedral (Td) and hexagonal (Hex) sites in the bulk, full geometry optimization calculations were performed. Table I shows the stabilization energies in the formation of various Si-F or Si-NFx bonds on Si surface ((a), (d)-(j)) and in the incorporation of F atom as an interstitial ((b) and (c)). From Table I, we can clearly understand that fluorine atom in Td site is not stable in the ground state. Energetically, F/H-Si(111) and F/H-Si/(100)-1x1 systems are equally favorable and also have almost the same Si-F bond lengths (1.640 Å and 1.638 Å for (a) and (e), respectively). In the case of NF₃/Si systems the ΔH values are larger than those of F/Si systems. It should be noted here that this fact alone is not sufficient to prove that NF3/Si is less stable because in the present work the activation processes for such reactions are not taken into account.

Next, the atomic charges on various atoms involved in the interaction are compared. Table II presents the Mulliken atomic charges on F, N, and Si and the differences from the charges on F of NF₃ (dF(N)) or SiF₄ (dF(Si)), N of NF₃ (dN) and Si of SiF₄ (dSi), respectively. The analysis of charge on F atom shows that the F atom adsorbed on Si surface as well as in Td and Hex sites ((a)-(e)) possess significantly larger negative charges (-0.41 ~ -0.45), which is viewed as F anion. These results qualitatively agree with the reported *ab initio* results [9]. The dF values shows that the F atoms resemble those in SiF₄ molecule rather than NF₃ molecule.

Now let us consider the situation of the formation of Si-N-F and Si-NFx bonds. The nature of Si-N bond formed on H-Si(111) surface is totally different from that of H-Si(100)-1x1 surface. The nitrogen atom in Si-N-F has radical character in the former case (f) whereas it forms a double bond as Si=N-F in the latter cases ((h) and (i)). In all these cases, the negative charges on F atoms are found to be much less compared to those of Si-F bonds and they approach almost neutral state. The states closest to neutral F atoms are observed in the cases (g) and (j). These results reveal the possibility for the presence of almost neutral F atoms in Si-N-F moieties and is in full agreement with the recent XPS results by Little et al. [1].

4. Conclusions

Quantum chemical calculations based on self-consistent Kohn-Sham procedure were carried out to determine (a) the adsorption states of F atom on H-Si(111) and H-Si(100)-1x1 surface, (b) stability of F atom at two kinds of interstitial sites (Td and Hex), (c) atomic charges of several states of F atoms. Our results show that fluorine atom in Td site is not stable at ground state. Adsorbed F atom on Si surface as well as F at the interstitial sites have large negative charges and the Si-F bonds formed on silicon surface resemble those of SiF4 molecule. In the case of NF3/Si system, the negative charges on the F atoms bound to Si=N or Si-N< were found to be less and this is in full accordance with the reported experimental results.

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