

A Study on Pumping Effect of Oxygen in Polysilicon Gate Etching

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This article presents the experiments and considerations possible about gate etching in polysilicon when oxygen gas is added in chamber. We propose the novel study with optical emission spectroscopy in polysilicon etching. It is shown that added oxygen gases play an important role in enhancement of density in chlorine gases as a scavenger of silicon from SiCl_x . And a small amount of Si-O bonds are deposited and then the deposited thin film protect silicon dioxide against reaction chlorine with silicon in SiO_2 . Consequently, we can improve the selectivity of polysilicon to silicon dioxide, which is clearly explained in this model.

Keywords : polysilicon gate etching, pumping effect, scavenger, optical emission spectroscopy

1. INTRODUCTION

As the devices shrink further and the gate oxide continues to be thinner, the requirements for high selectivity polysilicon etching (e.g., >100 for polysilicon with respect to silicon dioxide) with high etch rate have been increased [1]. There was widely used in polysilicon etching by Cl-containing gases due to the anisotropic characteristics and relatively high selectivity to silicon dioxide compared with other gas chemistries [2]~[4]. However, it often has a limit in selectivity and the loss of anisotropic characteristic. It has been reported that the additive gases, such as HBr, N_2 , O_2 , compensate for the drawbacks of Cl-containing gases, but no discussion on why both etch rates of polysilicon and silicon dioxide changed while O_2 gas added has been reported [5].

In this article, we investigated the etch rates of polysilicon gate and silicon dioxide as a variation of O_2 gas additions in Cl_2/O_2 or $\text{Cl}_2/\text{HBr}/\text{O}_2$ gas mixtures. Optical emission spectroscopy (OES) was employed to determine the reason for the change on both etch rates of polysilicon gate and silicon dioxide by inspecting the radical density when O_2 gas was added. We have used the X-ray photoelectron spectroscopy (XPS) to examine the surface changes which caused the etch rates to change. Consequently, we proposed the experimental model of polysilicon gate etching with underlying gate oxide by addition of O_2 gas.

2. EXPERIMENTAL DETAILS

An inductively coupled plasma (ICP) etching system was used in this study. A planar inductive coil of rectangular cross-section is placed on the top of the dielectric windows. RF power of 13.56 MHz is applied to both the inductive coil and the bottom electrode and wafers were placed on the bottom electrode. The 6 inch, 10-40 Ω -cm B-doped p-type Si (100) wafers were used for this study. These Si substrates with thermally grown oxides of approximately 1000 Å were coated with 2500 Å-thick layer of polysilicon grown by low pressure chemical vapor deposition (LPCVD). The chemistries were Cl_2/O_2 or $\text{Cl}_2/\text{HBr}/\text{O}_2$ gas mixtures. The plasma characteristics were extracted from OES with a resolution of 1 Å. An OES was used to monitor plasma species and etch by-products as a variation of O_2 gas additions through a quartz window of the chamber. After etching and transfer of the etched samples to the analysis chamber, XPS analysis was performed to quantify the surface composition and identify the chemical binding states.

3. RESULTS AND DISCUSSION

Figure 1 shows an etch rate of silicon in Cl_2/O_2 chemistry. The polysilicon etch rate is enhanced from 2100 Å/min for a pure Cl_2 plasma to 2500 Å/min for

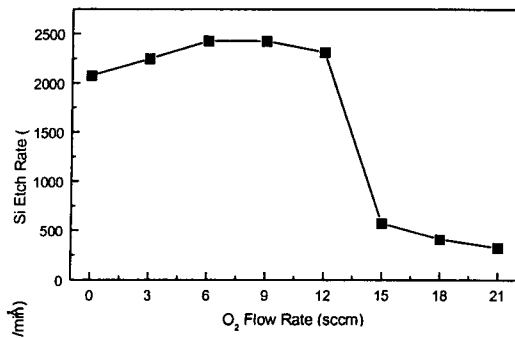
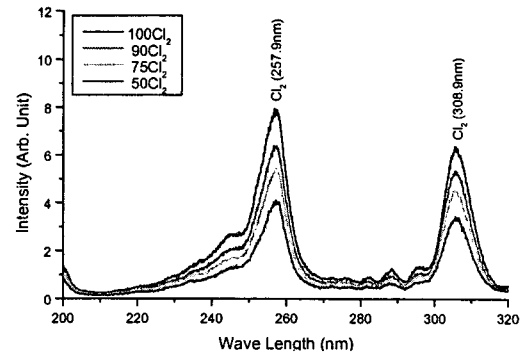


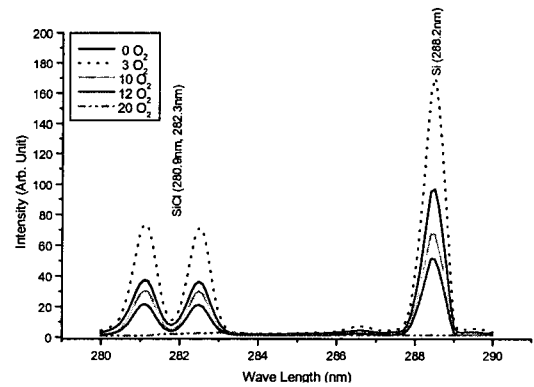
Fig. 1. Etch rate of polysilicon as various partial pressures of oxygen.

6 sccm O₂ gas addition. The etch stop occurs when a flow rate of O₂ gas addition is over 10 sccm. That is the similar trend with the previously documented reports [6]. Gavin C. H. Zau, *et al.* reported the reason that the oxychloride film, formed by reaction between the etching products and the additive O₂, passivates the interior etcher surfaces against Cl surface recombination, and therefore reduces the major Cl loss mechanism [7]. However, there has been little discussion on polysilicon etching mechanism and especially no information regarding on characteristics of plasma in etching by O₂ gas addition. We measured the etch rates of silicon dioxide in order to observe the effects of O₂ gas addition and the remarkable differences in each condition such as Cl₂/O₂, Cl₂/HBr/O₂ and no-PR. As a flow rate of oxygen gas increases, the etch rates of silicon dioxide in all etching conditions gradually decrease while the flow rate of main etchant (i.e., Cl₂ gas) was maintained. Similar results were also reported by several groups in a recent study. It is observed that the etch rate of PR samples is higher than that of no-PR samples in each etching condition. That means carbon contamination which carbon atoms from photoresist react with oxygen atoms prevent the oxygen atoms from recombining with silicon and depositing on silicon dioxide. It can be inspected that the passivation layer formed by additive O₂ gas effected the reduce of etch rates. Compared to the etch rate in Cl₂/O₂ gas chemistry, it is half of the etch rate in Cl₂/HBr/O₂ gas chemistry because the passivation film of SiBr_xO_y at surface is formed to keep silicon dioxide from reacting with its etchant as mentioned above [8].

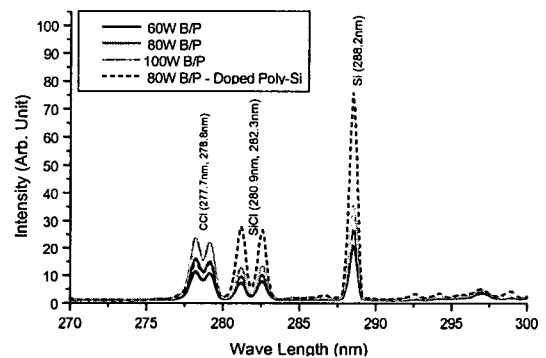
To better understand how these changes occur and then demonstrate the etching mechanism while O₂ gas was added, we investigated the several species by mainly using OES in polysilicon etching with an addition of O₂ gas into Cl₂/HBr gas mixture. Figure 2 (a) shows the OES analysis in silicon dioxide etching as a variation of the Cl₂ gas flow rates. It is generally known that no by-



(a)



(b)



(c)

Fig. 2. Signal intensities by OES analysis in etching of (a) silicon dioxide as a variation of Cl₂ gas flow rates (b) polysilicon as a variation of O₂ gas additions and (c) undoped polysilicon as bias power rise up.

products were created in silicon dioxide etching by Cl₂ gas, any peaks of by-products such as Si (288.2 nm) and SiCl (280.9 nm, 282.3 nm) were not observed. The peaks of Cl₂ (257.9 nm, 308.9 nm) increased in proportional to the flow rate of Cl₂ gas. Figure 2 (b) shows the peak intensities of by-products in etching the polysilicon. In

figure 2 (b), both peaks of Si and SiCl had the similar trend as a function of O₂ gas addition. As increasing the flow rate of O₂ gas addition, the peak intensities of above by-products decreased from O₂ gas addition of 10 sccm and any peak increase was not shown at O₂ gas addition of 20 sccm after etch stop. The peak intensities of by-products below O₂ gas addition of 10 sccm increased as O₂ gas was added though we showed the only one case of 3 sccm O₂ gas addition. It is very the same result of polysilicon etching as shown in figure 1. It is confirmed that the etch rate is proportional to the intensities of by-products. To clarify these results again, we diagnosed the plasma by OES as a function of bias power in etching of polysilicon. It is generally known that the etch rate of polysilicon increases as the bias power rises [9]. Figure 2 (c) shows the peak intensities of several by-products such as Si and SiCl in etching of undoped polysilicon with PR mask. As the bias power rised up, the peak intensities of etching by-products increased as mentioned above. The peak intensities of etching by-products in doped polysilicon are much higher than the case of undoped polysilicon though the bias power was the same. It is confirmed that the etch rate of doped polysilicon is much higher than that of undoped polysilicon and it is published by other research [10].

Figure 3 shows the nomalized signal intensities of etchants and by-products as a function of O₂ gas ratio. It is generally known that the intensities of by-products are enhanced as an etch rate increased. However, the intensity of by-product such as SiCl gradually decreases as the flow rate of oxygen rises from 0.02 to 0.09 while the etch rate of polysilicon increased in figure 3. This means that the by-products of SiCl_x (x=0~4) react with oxygen atoms which have stronger bonding force and then Si-O bonds were recombined and the intensity of Cl atoms increased. These extracted free Cl atoms

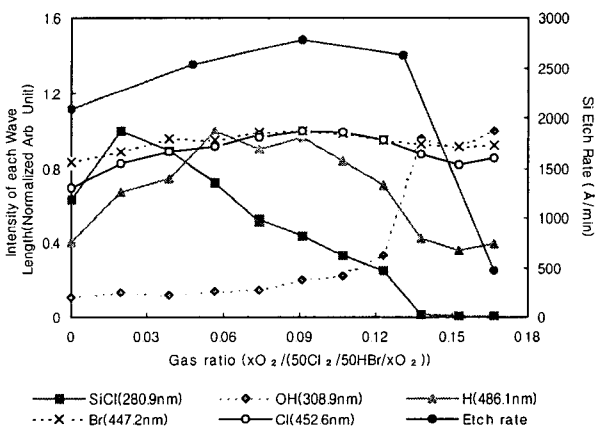


Fig. 3. Signal intensity of etchants and by-products as a function of additive oxygen gas.

repeatedly have concerned with polysilicon etching. As shown in figure 2 which illustrated the etch rates of polysilicon, it is confirmed that the point of maximum peak intensity of Cl atoms agrees with that of maximum etch rate of polysilicon at the O₂ gas addition of 10%. Meanwhile, an intensity of OH is gradually enhanced as a flow rate of oxygen gas is increased. Hydrogen atoms by dissociation of HBr form O-H bond as a flow rate of oxygen rises so they are consumed and OH atoms are created. It is hard to detect the end point if oxygen is used in process. Meanwhile, the peaks of OH show abrupt increase at the end point. According to the previous facts, we infer that this phenomenon can be used the new method for the end point detection due to excellent reproduction in Cl₂/HBr/O₂ gas chemistry.

Figure 4 shows the intensities of by-products in polysilicon etching as a function of etching time. All signals in figure 4(a) were illustrated with breakthrough. The signal in the case of no O₂ gas addition gradually increased and then rapidly decreased at the etching time of 43secs. It means that the etch rate of polysilicon gradually increased and then the etch stop was occurred at the etching time of 43secs. The signal with O₂ gas addition of 10sccm, however, more rapidly increased respect to the signal without additive O₂ gas and then the etch stop was occurred at 39secs. It is inferred that pumping effect helps the etch rate of polysilicon to increase. On the contrary, the signals of the samples with additive O₂ gas over 15sccm hardly increased and/or the etch stop was occurred immediately after polysilicon etching. Figure 4(b) shows the intensities of both Si(288.2 nm) and OH(308.9 nm) in polysilicon etch with Cl₂/HBr/O₂ gas mixture as a function of the etching time. The intensities of Si increased abruptly from the point of etch start to that of etch stop and then decreased rapidly after etch stop. The intensity of OH, on the other hand, decreased abruptly at the etch start and increased at the point of the etch stop. It is the reason that the additive oxygen atoms react with silicon atoms and they cover the surface layer and then surplus oxygen atoms react with hydrogen atoms after the etch stop.

Table 1. Bonding strength(kcal/mol) in Crystal(*), derived from ΔH_f , $D_{0_{298}}$ in diatomic molecule [11].

	ΔH_f	$D_{0_{298}}$		ΔH_f	$D_{0_{298}}$
C-O	257	1076	Si-F	132	552
Si-O	111*	799	Si-C	96	406
Si-Si	54*	326	Si-Br	88	367
Si-Cl	107	451	Si-H	<71	<299
H-Br	87	366	Cl-Cl	57	242
O-O	118	498	H-Cl	102	431
Cl-O	64	269	H-O	101	427
Br-O	56	235	Br-C	66	280
C-Cl	94	397			

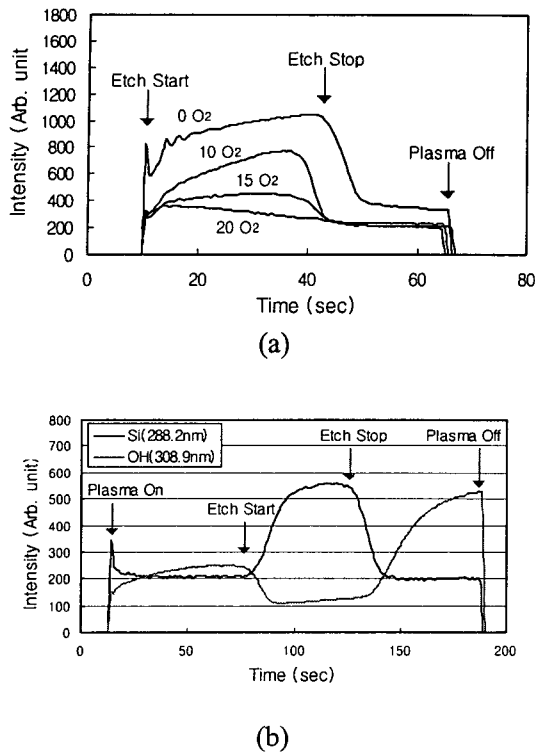


Fig. 4. Signal intensities of (a) Si with various O₂ gas addition and (b) Si and OH in polysilicon etching as a function of etch time.

In figure 3 we can see that SiCl_x (x=0~4) molecules are divided into silicon and chlorine atoms while oxygen gas is used as an additive gas and then oxygen and silicon atoms form passivation layer. XPS narrow scan analysis was carried out to examine the chemical binding states of silicon bonds on the oxynitride. Figure 5(a) shows the XPS analysis of Si 2p peak after deposition and BOE dip. BOE was used in order to remove oxygen rich film on upper layer. Figure 5(b) shows the XPS analysis of the sample exposed silicon through the patterned windows in oxynitride film and then etched by Cl₂/O₂ gas chemistry. It is evident from figure 5(a) that the XPS analysis has the peak of SiN (101.8 eV) and other negligible peaks of Si-O bonds. However, components of oxygen which consist of Si-O bonds are detected considerably at figure 5(b). It is confirmed that oxygen atoms react with silicon remained after scavenging Cl atoms from by-products such as SiCl, etc. and then they are deposited on oxynitride. It is properly agreed that Si-O bonds newly deposited on silicon dioxide layer play a large role as a passivation layer and make the etch rates of silicon dioxide film decrease in figure 3. Therefore, figure 5 is a clear proof of the passivation layer which has Si-O bonds and decreases the etch rate of silicon dioxide.

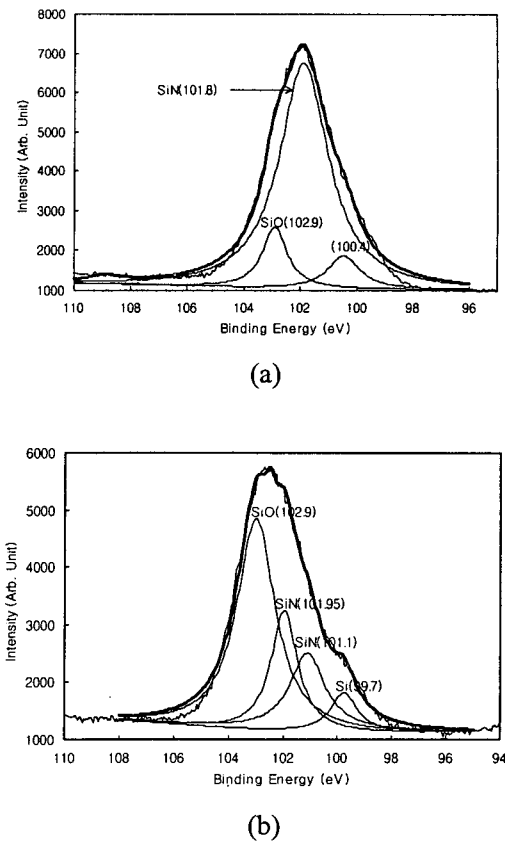
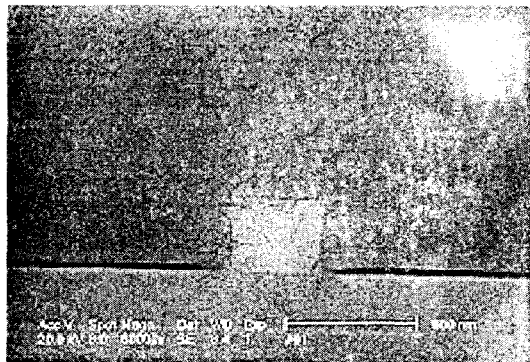
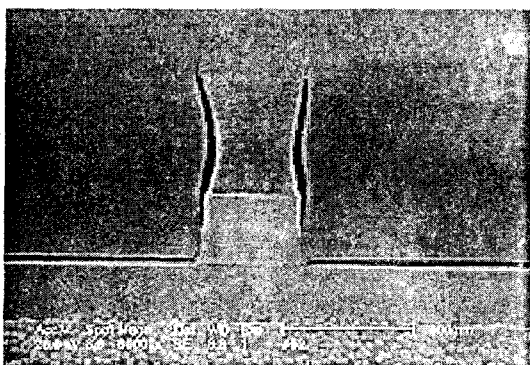


Fig. 5. XPS analysis of silicon on oxynitride surface (a) after BOE dip and (b) after etch polysilicon by BOE dipped and patterned oxynitride mask.

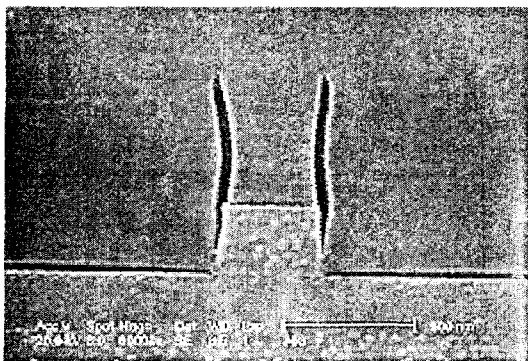
In order to confirm these XPS results, etching of polysilicon with PR mask was performed as a variation of O₂ gas additions. And then these samples were coated by PR. For observing Si-O bonds deposited on pattern sidewall, PR coated samples were cut by cross-sectional and BOE dip was carried out. Therefore, the dark parts which Si-O bonds were removed were observed in SEM photographs if Si-O bonds were redeposited on pattern sidewall. Figure 6 (a) to (d) are the cross-sectional SEM photographs of the samples after several process as mentioned above. In figure 6 (a), it can be observed that any dark part was not on pattern sidewall. That means Si-O bonds were not deposited on pattern sidewall in no additive O₂ gas. However, there are dark parts in figure 6 (b) to (d) which samples were etched by O₂ gas addition of 2.5 sccm, 5.0 sccm and 7.5 sccm, respectively. The dark parts in SEM photographs were more thick as O₂ gas added from 2.5 sccm to 7.5 sccm, that is, Si-O bonds were created by O₂ gas addition and then a little of them deposited on pattern sidewall. It is exactly agreed with the XPS analyses in figure 5.



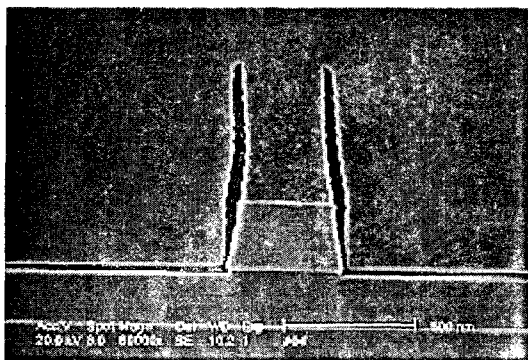
(a) 0 O₂



(b) 2.5 O₂



(c) 5.0 O₂



(d) 7.5 O₂

Fig. 6. Cross-sectional SEM photographs of etched polysilicon samples as variatious O₂ gas addition of (a) 0O₂ (b) 2.5O₂ (c) 5O₂ and (d) 7.5O₂.

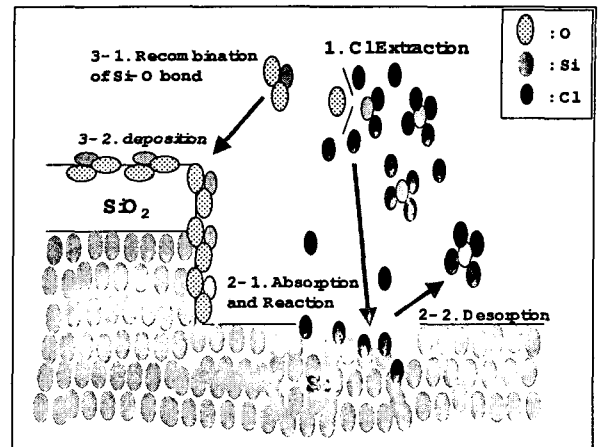
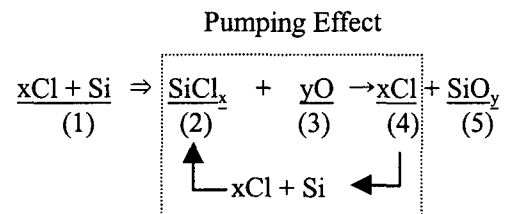


Fig. 7. Model of polysilicon etching reaction by O₂ gas addition.

Figure 7 shows the proposed scheme of the polysilicon etching mechanism by O₂ gas addition. The additive oxygen atoms scavenge the Cl atoms in Si-Cl bonds, and they recombine with Si atoms to make Si-O bond formations. Though most of Si-O bonds are vented from vacuum pump, a little of them is deposited on silicon dioxide as an etch mask. The extracted free Cl atoms enhance the etching of silicon as the reaction with silicon and desorption of themselves. The mechanism explained above can be summarized like this :



(1) Initial surface reaction ; (2) Etch by-product ; (3) Oxygen radical by added oxygen ; (4) Created extra Cl radical by oxygen ; (5) Pumping out & deposition on wafer

4. CONCLUSION

This study makes experiments and considerations possible about gate etching in polysilicon when oxygen gas is added in chamber. One has been found that additive oxygen atoms are adsorbed in chamber wall so a density of etchant becomes enhancing. According to the result in experiments added oxygen gases, however, play an important role in enhancement of density in chlorine gases as a scavenger of silicon from SiCl_x. In other words, the added oxygen atoms scavenge the Cl atoms in Si-Cl bonds, and then they react with Si atoms to form

Si-O bonds. It can be confirmed that etch rate in silicon becomes increasing. Meanwhile, a small amount of Si-O bonds are deposited and then the deposited thin film prevent silicon in silicon dioxide and chlorine atoms from reacting so it reduces etch rate of silicon dioxide. Consequently, we can improve the selectivity of polysilicon to silicon dioxide, which is clearly explained in this model.

REFERENCES

- [1] Semiconductor Industry Association, *The national technology roadmap for semiconductor*, 1997.
- [2] L. Y. Tsou, "High Selective Reactive Ion Etching of Polysilicon with Hydrogen Bromine", *J. Electrochem. Soc.*, Vol. 136, No. 10, p. 3003, 1989.
- [3] C. Cheng, K. V. Guin, V. M. Donnelly, and I. P. Herman, "In situ pulsed laser-induced thermal desorption studies of the silicon chloride surface layer during silicon etching in high density plasma of Cl₂ and Cl₂/O₂ mixture", *J. Vac. Sci. Technol.*, Vol. A12, No. 5, p. 2630, 1994.
- [4] K. V. Guin, C. C. Cheng, and V. M. Donnelly, "Quantitative chemical topography of polycrystalline Si anisotropically etched in Cl₂/O₂ high density plasma", *J. Vac. Sci. Technol.*, Vol. B13, No. 2, p. 214, 1995.
- [5] Marwan H. Khater, Lawrence J. Overzet and Blake E. Cherrington, "Effects of gas distribution on polysilicon etch rate uniformity for a low pressure, high density plasma", *J. Vac. Sci. Technol.*, Vol. B16, No. 2, p. 490, 1998.
- [6] Mutumi Tuda and Kouichi, "Observation of Microscopic Nonuniformity during Overetch in Polysilicon Gate Etching", *Jpn. J. Appl. Phys.*, Vol. 36, p. L518, 1997.
- [7] Gavin C. H. Zau and Herbert H. Sawin, "Effects of O₂ Feed Gas Impurity on Cl₂ Based Plasma Etching of Polysilicon", *J. Electrochem. Soc.*, Vol. 139, No. 1, p. 250, 1992.
- [8] Keiji Koshino, Jiro Matsuo and Moritaka Nakamura, "Chemical States of Bromine Atoms on SiO₂ Surface after HBr Reactive Ion Etching: Analysis of Thin Oxide", *Jpn. J. Appl. Phys.*, Vol. 32, p. 3063, 1993.
- [9] Jung-Hyung Kim, Chang-Jin Kang, Tae-Hyuk Ahn and Joo-Tae Moon, "Characteristics of self bias voltage and poly-Si etching in pulsed helicon wave plasma", *Thin Solid Films*, Vol. 345, p. 124, 1999.
- [10] Dennis M. Manos and Daniel L. Flamm, *Plasma Etching*, Academic Press, 1989, p. 148.
- [11] David R. Lide, *CRC HANDBOOK of CHEMISTRY and PHYSICS*, CRC PRESS, 1996, pp. 9~52.