Journal of the Korean Ceramic Society
Vol. 49, No. 4, pp. 328~332, 2012.

http://dx.doi.org/10.4191/kcers.2012.49.4.328

Plasma Resistance and Etch Mechanism of High Purity SiC under Fluorocarbon Plasma

Mi-Ran Jang*,*, Yeong-Kyeun Paek**, and Sung-Min Lee*,†**
**Engineering Ceramic Center, Korea Institute of Ceramic Engineering and Technology (Icheon), Icheon 467-843, Korea*
***School of Materials Science and Engineering, Andong National University, Andong 760-749 , Korea*
****Department of Materials Science and Engineering, Korea University, Seoul 136-701, Korea*

(Received May 14, 2012; Revised July 9, 2012; Accepted July 9, 2012)

ABSTRACT

Etch rates of Si and high purity SiC have been compared for various fluorocarbon plasmas. The relative plasma resistance of SiC, which is defined as the etch rate ratio of Si to SiC, varied between 1.4 and 4.1, showing generally higher plasma resistance of SiC. High resolution X-ray photoelectron analysis revealed that etched SiC has a surface carbon content higher than that of etched Si, resulting in a thicker fluorocarbon polymer layer on the SiC surface. The plasma resistance of SiC was correlated with this thick fluorocarbon polymer layer, which reduced the reaction probability of fluorine-containing species in the plasma with silicon from the SiC substrate. The remnant carbon after the removal of Si as volatile etch products augments the surface carbon, and seems to be the origin of the higher plasma resistance of SiC.

Key words : Silicon carbide, Fluorocarbon plasma, Plasma resistance, XPS

1. Introduction

SiC has been widely used as a substrate material for light emitting diodes (LED) and power electronics for electrical vehicles or trains.[1-3] In addition, since SiC maintains mechanical strength at high temperature, it has been extensively used to chamber parts for high temperature chemical vapor deposition (CVD).[4-6] The developed processing route to produce SiC parts as large as over 1 meter with exceptionally high purity has also supported its widespread use in the semiconductor industry.[4,5] Recently, besides the structural aspects of SiC, its electrical conductivity and possibly its enhanced life time under fluorocarbon plasma with less generation of contamination particles are drawing attention for use in applications such as cathodes or focus rings, which have been made of Si for a long time. Compared to Si, SiC was believed to have a better plasma resistance; however, the experimental evidences and the conditions necessary for longer life time have rarely been studied.[7-9] Especially for high purity SiC, which has usually been made by the CVD method, there has been no comparative study with Si.

The etch rate of ceramics strongly depends on the plasma conditions such as the chemistry of the etch gas and bias power.[10,11] Generally, an increased bias power enhances the etch rate, and the chemistry of the etch gas determines the threshold bias voltage to start the erosion of the ceramics.[10-13] The etch products are usually of the formula SiF_n, and are produced by the interaction between radicals or ions of fluorine-containing species and silicon atoms of the materials being etched.[14] The interaction of fluorocarbon plasma with ceramics has been studied using X-ray photoelectron spectroscopy.[12,15-17] The analyses showed that there was a fluorocarbon polymer layer as thin as a few nm on the etched surface, and that this layer affected the etch rate of the ceramics. In terms of this surface polymer layer, SiC has a fundamental difference in comparison to Si because SiC has inherent carbon in its chemistry, which may possibly supply more carbon to the polymer layer. The carbon may retard the interaction between the plasma and the SiC, but a detailed analysis of the various plasma conditions has not yet been conducted.

In this study, we first compared the etch rates of Si and high purity SiC for various plasma conditions. The high purity SiC was made by a conventional CVD method. After the plasma exposure, the etched surface was carefully analyzed using high resolution X-ray photoelectron spectroscopy (XPS) to reveal the interrelationship between the surface polymer layer and the etch rate. In particular, we focused on the C_{1s} spectrum in order to analyze the surface polymer layer. Finally, based on the measured surface carbon content and the polymer thickness, the higher plasma resistance of SiC has been understood and its relative benefits, depending on the plasma conditions, are discussed.

2. Experimental Procedures

High purity SiC (>99.999%, 4.3 kΩ-cm) was prepared

---

†Corresponding author : Sung-Min Lee
E-mail : smlee@kicet.re.kr
Tel : +82-31-645-1441 Fax : +82-31-645-1492

Table 1. Details of Plasma Etch Conditions

Parameters	Condition
RF power (W)	600
DC bias power (W)	50-200
Pressure (mTorr)	10
CF_4, CHF_3 (sccm)	20-40
O_2 (sccm)	0-15
Ar (sccm)	10

Table 2. Details of XPS Conditions

Parameter	Condition
Pass energy (eV)	23.5
Step (eV)	0.05
Time per step (ms)	60
Repeat (#)	10

through a conventional chemical vapor deposition method using methyltrichlorosilane (MTS) as a precursor gas. The etch rate of SiC was compared with that of a reference, a Si wafer. The SiC was polished to a 1 μm surface finish using a diamond paste and, the surface was treated using a colloidal silica suspension. Then, the substrate was cleaned with isopropyl alcohol in an ultrasonic container for 10 min. The prepared Si and SiC were exposed to fluorocarbon plasmas using an inductively coupled plasma etcher (Versaline, Unaxis Co., USA) with CF_4 or CHF_3 as the main etch gas, with or without O_2 at various bias powers. Details of the etch conditions appear in Table 1. Before the plasma exposure, the surfaces of the specimens were masked using a Kapton tape with an opening width of around 1 mm. The plasma exposure time was 10 min for the measurement of etch depth. The etch depths were measured using a surface profiler (Surfcorder ET3000, Kosaka Lab., Japan).

XPS analysis of the etched Si and SiC after the plasma exposure was performed using a monochromated Al K_α X-ray source (PHI 5000 VersaProbe, ULVAC-PHI, Japan) at a pass energy of 23.5 eV. Using fitting software (Avantage, Thermo Fisher Scientific, UK) the photoelectron spectrum resulting from the core energy levels of C_{1s} was deconvoluted to estimate the contributions from the bonds with other elements. Each of the deconvoluted peaks was assigned following the binding energies in the literature for various chemical bonds of carbon on the etched Si or SiO_2.[12,15,16] In order to calculate the thickness of the surface polymer layer, the surface of etched SiC was sputtered for 80 seconds using focused Ar^+ ions (2 kV) and the intensities of Si_{2p} peaks were compared before and after the removal of the surface polymer layer.

3. Results and Discussion

Fig. 1(a) shows the etch rates of Si and SiC as a function of bias power. Bias voltage accelerates positive ions on to the substrates and promotes the reaction probability of fluorine atoms with the silicon of the substrates.[18] With an increasing bias power, the etch rates of both specimens increased but there was a more pronounced effect on the SiC etch rate. Therefore, if the plasma resistance of SiC relative to Si is defined as the etch rate ratio of Si to SiC, the plasma resistance of SiC was the highest at the lowest bias power, gradually decreasing from 4.1 to 1.5 with a bias power increase from 50 to 200 W. The relative plasma resistance of SiC was also a function of the oxygen flow rate (Fig. 1 (b)). When oxygen was additionally introduced to CF_4 etch gas at a bias power of 100 W, the etch rate of Si was practically unchanged, while there was a monotonic increase in the SiC etch rate. Thus, the plasma resistance of SiC decreased from 2 to 1.4 with the increase of the oxygen flow rate from 0 to 15 sccm.

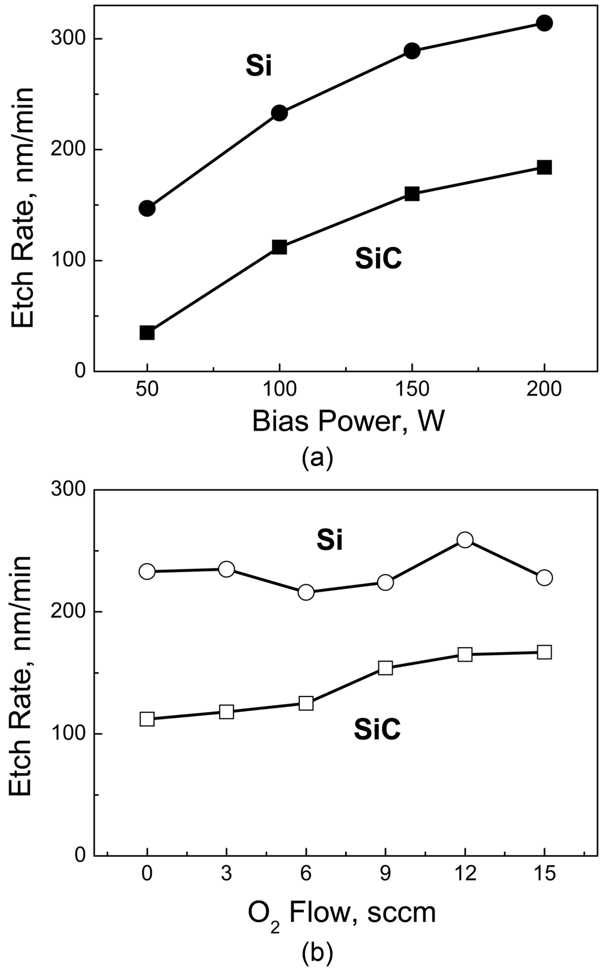

Fig. 1. Etch rates of Si and SiC as functions of (a) bias power without oxygen flow and (b) oxygen flow rate at a bias power of 100 W.

The dependency of the etch rate of Si and SiC on the various plasma conditions indicates that SiC has, in general, a plasma resistance higher than that of Si. The relative resistance varied between 4.1 and 1.4, depending on the bias power and oxygen flow rate. The benefit of SiC over Si, however, was almost lost at certain specific conditions such as a high oxygen flow rate and high bias power.

The etch gas itself also affects the etch rates of Si and SiC.

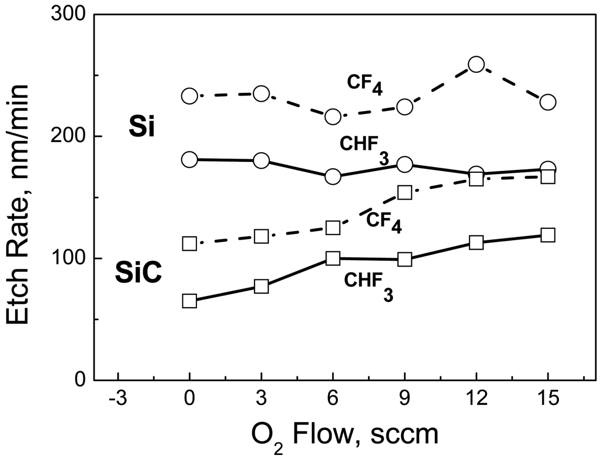

Fig. 2. Etch rates of Si and SiC in CF_4 or CHF_3 plasma as a function of oxygen flow rate at a bias power of 100 W.

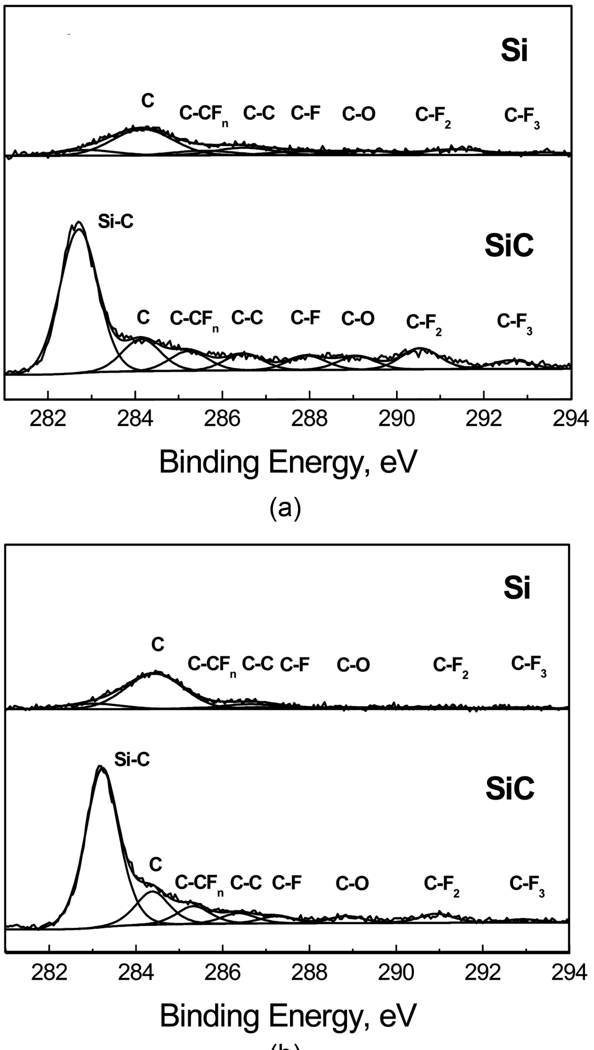

Fig. 3. C_{1s} photoelectron spectra of the Si and SiC surface etched in CF_4 plasma (a) without O_2 flow and (b) with O_2 flow rate of 15 sccm at a bias power of 50 W.

Fig. 2 shows the etch rate variations when CHF_3 was used as the main etch gas; these etch rates were compared to the etch rates when CF_4 was used as the main etch gas. CHF_3 gas lowered the etch rates of both Si and SiC. Since CHF_3 has a hydrogen atom, the hydrogen radicals from plasma discharge can scavenge fluorine radicals to produce hydrofluoric acid, effectively lowering the fluorine to carbon ratio in the plasma.[16,19)] The reduced amount of fluorine may result in a lower etch rate for Si and SiC. On the other hand, the relatively higher carbon content in plasma may also affect the etch rate. The relative plasma resistance of SiC, however, was less affected by the chemistry change of the etch gas. In CHF_3, the plasma resistance of SiC was similar to that of the CF_4 cases for a given oxygen flow rate at a bias power of 100 W.

The dependency of the etch rate on the plasma conditions must be understood based on the surface interaction between the plasma and the substrate. Tatsumi et al.[18)] suggested that the etch rate of SiO_2 is controlled by the thickness of the surface carbon polymer layer. The kinetic energy of ions impinging on the substrate is attenuated by the carbon polymer, resulting in reduced reaction probability. Schaepkens et al.[12)] also reported the dependency of the etch rate of SiO_2 and Si_3N_4 on the surface polymer thickness.

In this regard, the surfaces of etched Si or SiC were analyzed using high resolution XPS. Fig. 3 shows the C_{1s} spectra obtained from Si and SiC etched at 50 W bias power in plasma discharge fed with CF_4, with or without O_2 flow. The spectra consisted of many peaks from Si-C, C-C or C-F_n bonds, whose positions were previously obtained from the literature.[12,15,16)] Among these peaks, the peak at a binding energy of around 284.5 eV may come from adventitious carbon, because the analysis was conducted ex-situ after the etch test.[20)] A peak due to Si-C bonds also strongly appeared in the etched SiC because the photoelectrons can come from the carbon in the substrate SiC. Thus, the peaks, except for the ones due to adventitious carbons and carbons from Si-C bonds, may be more responsible for the surface carbon during the etching of Si and SiC. If Si and SiC are compared, the surface carbon is clearly higher in the etched SiC than in the Si (Fig. 3(a)). The fact that the etch rate of SiC was lower than that of Si, as shown in Fig 1(a), indicates that higher surface carbon content must be related to a lower etch rate, and thus to a higher relative plasma resistance of SiC. This relationship has also been supported when the effects of oxygen flow on the carbon 1s spectra from etched Si and SiC have been investigated. Fig. 3 (b) shows that the oxygen flow resulted in less surface carbon for both Si and SiC, but the reduction due to oxygen introduction was more significant in SiC. Accordingly, the etch rate increase due to oxygen flow, as shown in Fig. 1(b), must be due to the enhancement of the C-F dissociation and the removal of surface carbon atoms in the form of CO and CO_2.

In contrast to the effects of oxygen introduction on the reduction of surface carbon, the etch gas change from CF_4 to CHF_3 produced a strong enrichment of surface carbon on the etched Si or SiC (Fig. 4). As mentioned, CHF_3 has an effec-

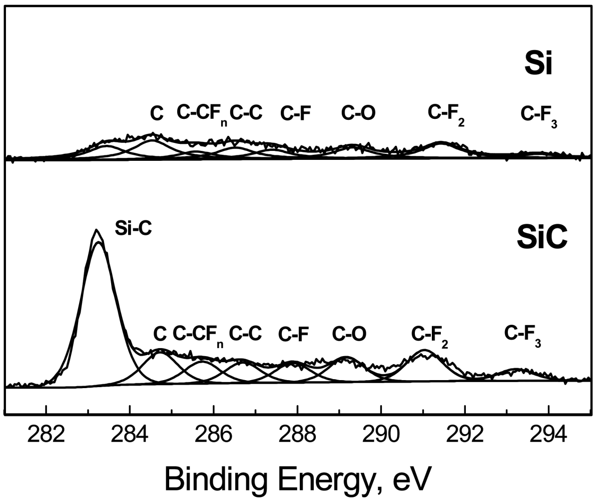

Fig. 4. C_{1s} photoelectron spectra of the Si and SiC surface etched in CHF_3 plasma at a bias power of 50 W.

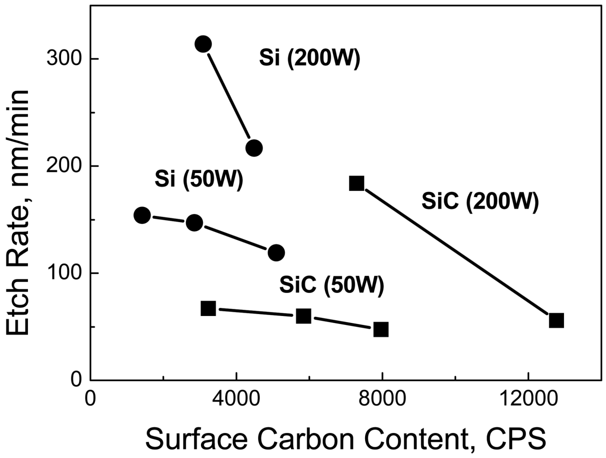

Fig. 5. Etch rates as a function of surface carbon content of Si and SiC for various plasma conditions.

tively lower F/C ratio due to the scavenging effect of hydrogen. Thus, at the same flow rate of CF_4 or CHF_3, the total amount of fluorine-containing radicals or ions may be less in CHF_3, possibly resulting in a lower etch rate. This possibility, however, was rejected because the flow rate of CHF_3 did not affect the etch rate at the investigated flow range between 20 and 40 sccm. Instead, the reduction of the etch rate may be a result of the higher surface carbon content, which is produced from the plasma with a lower F/C ratio. The lower F/C ratio of CHF_3 resulted in a thick carbon polymer layer on the etched Si and SiC surfaces as shown in Fig. 4, and thus led to the lower etch rate. In terms of the relative plasma resistance of SiC, however, the surface carbon increments on both Si and SiC seem to have little effect.

The surface carbon contents on the etched specimens were quantitatively measured and compared with the etch rates. For the carbon intensity calculation, we excluded the peak at around 284.5 eV due to the formation of adventitious carbon, and the peak due to carbon from Si-C bonds on the etched SiC. Fig. 5 shows that the higher surface carbon contents always resulted in lower etch rates for the given materials and bias powers. In addition, SiC has a generally higher surface carbon and lower etch rate than Si, thus providing better plasma resistance.

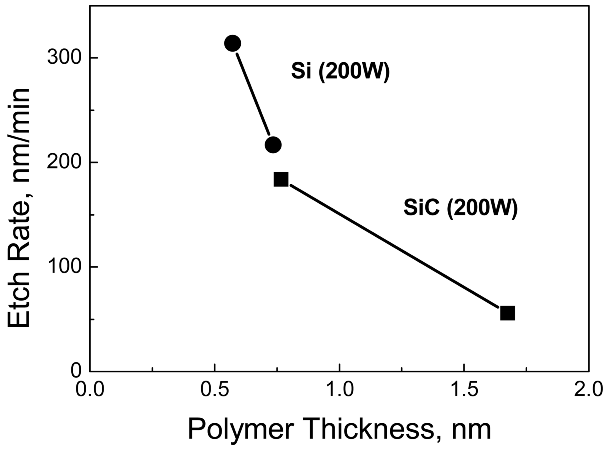

Fig. 6. Etch rates as a function of surface polymer thickness at a bias power of 200 W.

Surface carbon seems actually to be a part of a complex fluorocarbon polymer layer, because the carbon has diverse bond characteristics with fluorine and other elements, as shown in Figs. 3 and 4. The peak intensity due to C-F_2 bonds was the greatest, indicating that the carbon is in the chain structure of a fluorocarbon polymer. The fluorine and carbon in the polymer layer on the etched Si may mostly come from plasma, but additional carbon can be supplied from the substrate SiC in the etched SiC. When Si is removed from the SiC with a volatile etch product, SiF_n, the remnant carbon from SiC must contribute to the surface carbon. Closer examination of the deconvoluted peaks of carbon 1s spectra reveals the relatively higher intensity of the C-CF_n peak for the etched SiC compared to that for Si. However, since our analysis was conducted ex-situ, the contamination effect impeded a further analysis.

The thickness of the polymer layer was semi-quantitatively calculated by comparing Si_{2p} peak intensities before and after the sputtering removal of the surface polymer layer. The photoelectrons from the Si or SiC substrates are attenuated by inelastic scattering through the polymer layer. Assuming a mean free path λ, 3 nm,[15)] of photoelectrons, the polymer thickness, d, was calculated using the following equation:

$$\frac{I}{I_0} = \exp\left(-\frac{d}{\lambda\cos\theta}\right)$$

where I and I_0 are the intensities before and after polymer layer removal and θ is an emission angle of the photoelectron, 45°. Then, the calculated polymer thickness varied between 0.5 and 1.7 nm and these values were plotted with respect to the etch rates at a bias power of 200 W. Fig. 6 shows that the etch rate varied inversely with the polymer thickness at a bias power of 200 W, which is similar to the relationship reported for SiO_2 and Si_3N_4 etching.[12)] In terms of these surface polymer layers, the effects of the plasma condition on the plasma resistance of SiC can be understood. With an increasing bias power, the kinetic energy of ions impinging on the surface being etched increases and promotes the physical etching of the surface polymer layer. The physical etching results in thinner polymer layers on both Si and SiC, which decrease the plasma resistance of SiC. The effects of oxygen flow rate can also be understood with respect to the reduced polymer thickness due to the oxidation of carbon, weakening the protection effects of the polymer layer on the etched SiC, as shown in Fig. 3 (b).

4. Conclusion

The etch rates of Si and SiC, which are widely used as parts for semiconductor processing chambers, were compared after exposure to typical fluorocarbon plasmas. If the relative plasma resistance of SiC is defined as the etch rate ratio of Si to SiC, SiC has a plasma resistance generally higher than Si. The plasma resistance decreased with an increasing bias power and oxygen flow rate. The etch rates were also a function of the chemistry of the etch gas. High resolution X-ray photoelectron analysis showed that there was a thin fluorocarbon polymer layer on the etched surface and that the surface carbon content from the polymer layer was highly correlated to the etch rate of Si and SiC. SiC always had higher carbon content on the etched surface, with a lower etch rate than that of Si. The increased carbon content on the etched SiC was inferred to come from the remnant carbon after evaporation of the etch product, SiF_n. Hence, the enriched surface carbon, which is from a thicker fluorocarbon polymer layer on the etched surface of SiC, may, reduce the kinetic energy of the incident ions, reducing the probability of the etch reaction and finally resulting in a higher plasma resistance for SiC. In terms of this etch mechanism, the effects of plasma conditions on the plasma resistance of SiC were qualitatively understood.

REFERENCES

1. S. I. Vlaskina, “Silicon Carbide LED,” *Semiconductor Physics, Quantum Electronics & Optoelectronics*, **5** [1] 71-5 (2001).
2. A. Elasser and T. P. Chow, “Silicon Carbide Benefits and Advantages for Power Electronics Circuits and Systems,” *Proc. IEEE*, **90** [6] 969-86 (2001).
3. B. Ozpineci, L. M. Tolbert, S. K. Islam, and M. Hasanuzzaman, “Effects of Silicon Carbide (SiC) Power Devices on HEV PWM Inverter Losses,” pp. 1061-6 in the Proceeding of the Industrial Electronics Soc. Annu. Conf., IEEE, Denver, Colorado, 2001.
4. S. S. Hwan, S. W. Park, J. H. Han, K. S. Han, and C. M. Kim, “Mechanical Properties of Porous Reaction Bonded Silicon Carbide,” *J. Kor. Ceram. Soc.*, **39** [10] 948-54 (2002).
5. B. V. Manoj Kumar, M. H. Roh, Y. W. Kim, W. J. Kim, S. W. Park, and W. S. Seo, “Effect of Additive Composition on Microstructure and Mechanical Properties of SiC Ceramics Sintered with Small Amount of RE_2O_3 (RE: Sc, Lu, Y) and AlN,” *J. Mater. Sci.*, **44** 5939-43 (2009).
6. G. M. Kim, G. S. Cho, and S. W. Park, “Effects of β-SiC Particle Seeds on Morphology and Size of High Purity β-SiC Powder Synthesized using Sol-Gel Process,” *J. Kor. Ceram. Soc.*, **46** [5] 528-33 (2009).
7. L. Jiang, R. Cheung. R. Brown, and A. Mount, “Inductively Coupled Plasma Etching of SiC in SF_6/O_2 and Etch-induced Surface Chemical Bonding Modifications,” *J. Appl. Phys.*, **93** [3] 1376-83 (2003).
8. N. J. Dartnell, M. C. Flowers, R. Greef, and J. Zhu, “Reactive Ion Etching of Silicon Carbide (Si_xC_{1-x}),” *Vac.*, **46** [4] 349-55 (1995).
9. B. W. Kim, S. M. Kong, and B. T. Lee, “Modeling SiC Etching in C_2F_6/O_2 Inductively Coupled Plasma Using Neural Networks,” *J. Vac. Sci. Technol. A*, **20** [1] 146-52 (2002).
10. Ho, Pauline, Johannes, E. Justine, Buss, J. Richard, and Meeks, Ellen, “Modeling the Plasma Chemistry of C_2F_6 and CHF_3 Etching of Silicon Dioxide, with Comparisons to Etch Rate and Diagnostic Data,” *J. Vac. Sci. Technol.* A, **19** [5] 2344-67 (2001).
11. A. J. van Roosmalen, “Review: Dry Etching of Silicon Oxide,” *Vac.*, **34** 429-36 (1984).
12. M. Schaepkens, T. E. F. M. Standaert, N. R. Rueger, P. G. M. Sebel, and G. S. Oehrlein, “Study of the SiO_2-to-Si_3N_4 Etch Selectivity Mechanism in Inductively Coupled fluorocarbon Plasmas and a Comparison with the SiO_2-to-Si mechanism,” *J. Vac. Sci. Technol. A*, **17** [1] 26-37 (1999).
13. M. Matsui, T. Tatsumi, and M. Sekine, “Observation of Surface Reaction Layers Formed in Highly Selective SiO_2 Etching,” *J. Vac. Sci Technol. A*, **19** [4] 1282-8 (2001).
14. K. Kurihara, Y. Yamaoka, K. Karehashi, and M. Sekine, “Measurements of Desorbed Products by Plasma Beam Irradiation on SiO_2,” *J. Vac. Sci. Technol. A*, **22** [6] 2311-14 (2004).
15. N. R. Rueger, J. J. Beulens, M. Schaepkens, M. F. Doemling, J. M. Mirza, T. E. F. M. Standaert, and G. S. Oehrlein, “Role of Steady State Fluorocarbon Films in the Etching of Silicon Dioxide using CHF_3 in an Inductively Coupled Plasma Reactor,” *J. Vac. Sci. Technol. A*, **15** [4] 1881-9 (1997).
16. T. E. F. M. Standaert, C Hedlund, E. A. Joseph, and G.S. Oehrlein, “Role of Fluorocarbon Film Formation in the Etching of Silicon, Silicon Dioxide, Silicon Nitride, and Amorphous Hydrogenated Silicon Carbide,” *J. Vac. Sci. Technol. A*, **22** [1] 53-60 (2004).
17. D. M. Kim, S. H. Lee, W. B. Alexander, K. B. Kim, Y. S. Oh, and S. M. Lee, “X-ray Photoelectron Spectroscopy Study on the Interaction of Yttrium-Aluminum Oxide with Fluorine-Based Plasma,” *J. Am. Ceram. Soc.*, **94** [10] 3455-9 (2011).
18. T. Tatsumi, M. Matsui, M. Okigawa, and M. Sekine, “Control of Surface Reactions in High-Performance SiO_2 Etching,” *J. Vac. Sci. Technol. B*, **18** [4] 1897-1902 (2000).
19. A. J. van Roosmalen, J. A. G. Baggerman, and S. F. H. Brader, “Dry Etching for VLSI,” pp. 99-135, Plenum Press, New York and London, 1991.
20. B. Vincent Crist, “Advanced Peak-Fitting of Monochromatic XPS Spectra,” *J. Surf. Anal.*, **4** [3] 428-34 (1998).