Surface Degradation Mechanism During the Fluorine-Based Plasma Etching of a Low-*k* Material for Nanoscale Semiconductors

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The degradation of a low-*k* material surface during the exposure to plasma etching is one of the most serious problems to be solved for the realization of high speed semiconductor devices. In this study, the factors causing the degradation of a low-*k* material surface during the etching using fluorine-based plasma etching have been investigated by using XPS. As the plasma factors, active radicals, bombardment energy, and charge of the ions were considered and, as the low-*k* material, methyl silsesquioxane (MSQ) has been used. The XPS results showed that the ion bombardment during the plasma etching of MSQ affects the breaking of MSQ bone structure by changing the Si–O bonds and Si–C bonds to Si–F mostly, while fluorine-based radicals in the plasma mostly affect the change of Si–CH$_3$ bonds to Si–CH$_x$F$_y$. By removing the charge of the ions during the bombardment, the MSQ properties were further improved. When F intensity which is related to the damage of the MSQ surface is estimated, the bombardment energy, reactive radical density, and charge of the ions were responsible for ∼18%, ∼53%, ∼19% of the F intensity in the MSQ. Therefore, by using the neutral beam etching instead of a conventional ICP etching, the degradation on the MSQ surface estimated by the F intensity remaining on the MSQ surface could be decreased to 10%.

Keywords: Low-*k* Materials, Plasma Etching, Ion Beam Etching, Neutral Beam Etching, Damage.

1. INTRODUCTION

The critical dimension of the semiconductor devices in the advanced integrated circuit is continuously decreasing down to tens of nanometer for lower power consumption, higher speed, higher packing density, etc. As the device dimension is decreased to low tens of nanometer scale, the performance limiting factors such as interconnection delay, cross-talk noise, power dissipation, etc. has emerged as the serious problems in affecting device performance. Among these issues, the parasitic resistance and capacitance of the interconnection affect the device speed and the power consumption. The signal delay (RC time delay) of the

interconnect caused by the capacitance (C) between adjacent interconnect lines and the resistance (R) of the interconnect metal lines are increasing further and further due to the increase of wiring levels and the decreased pitch of the wiring in the advanced integrated circuit.[1] To decrease the RC delay and to improve the performance of the integrated circuit, as the interconnect conducting metal, Cu has been introduced instead of Al to decrease the metal resistance about 35% and, as the inter-metal dielectric (IMD), materials with lower dielectric constant (low-*k*) are being investigated. For IMD, if the IMD is replaced from SiO$_2$ ($k = 4.0$) to air ($k = 1.0$), which is ideal dielectric, it has been theoretically calculated that 75% of RC time delay can be decreased.[2]

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Therefore, many researches have been conducted to investigate the insulating materials with low-*k* that can be applied to the inter-metal dielectric of the advanced integrated circuits.[3, 4] Among those, materials such as hydrogen silsesquioxane (HSQ)[5] and methyl silsesquioxane (MSQ)[6] have been investigated the most widely. In addition, organic polymer materials such as fluorinated silica glass (FSG), hybrids of nanocomposite,[7] poly(arylene) ethers (PAE), benzocyclobutene (BCB), polytetrafluoroethylene (PTFE) have been also investigated.[8]

To apply the low-*k* materials as the inter-metal dielectric of the integrated circuits, in addition to the material properties itself, the other issues related to the processing of the dielectric need to be resolved and one of the most serious issues is the damage and degradation of the material surface caused by the plasma etching or plasma ashing.[9] It is known that the low-*k* materials such as MSQ are known to be very vulnerable to physical and chemical damage during the plasma processing. In the case of MSQ, by the chemical reaction of reactive species in the plasma with the Si–CH$_3$ in the MSQ structure during the plasma processing, the carbon in the hydrophobic bonds of the Si–CH$_3$ is broken and removed by forming volatile compounds such as CF$_4$, CO$_2$, CO, etc. Through these thermodynamically favorable reactions, the MSQ surface damaged by the plasma forms Si–OH bonds and the surface becomes hydrophilic surface.[9] Due to the surface damage, it is known that moisture is absorbed and, due to the high polarizability of absorbed water molecule ($k = 80$), the dielectric constant is abruptly increased and the leakage current is also increased.[10] Especially, when the low-*k* material has a porous structure, the reactive species from the plasma can easily penetrate deeply through the pore to pore of the structure, the sensitivity to the plasma damage is expected to be seriously increased due to the porosity.

Many researches have been also carried out to decrease the degradation of the low-*k* materials caused by the plasma processing. The surface of the low-*k* materials exposed during the plasma processing was passivated by surface treatment or gas absorption, by the deposition of polymer on the sidewall using the polymer-rich gas of the etched low-*k* material,[11] or by controlling the etchant gas itself during the plasma etching.[12] In addition to the researches in decreasing the degradation of the low-*k* materials during the plasma processing, the researches in finding the source of the degradation of the low-*k* material and the methods in removing the source of the degradation were also investigated. In fact, the degradation of the low-*k* materials during the plasma processing is caused by complex phenomena and the degree of damage or the damage mechanism can be different from material to material[13] but the damage is known to be increased by the combined effects of active radicals, ion bombardment, and vacuum ultra violet light, etc.[14] However, for the application of low-*k* materials in the actual integrated circuits, the understanding of the significance and role of the plasma

processing components on the degradation of low-*k* materials such as radical species, ion bombardment, etc. is important in the development of low damage plasma processing or in the development of next generation low-*k* material.

In this study, in addition to a conventional plasma etching technique, by using a neutral beam etching technique and a reactive ion beam etching technique, the role of plasma etching factors possibly responsible for the degradation of low-*k* materials during the plasma etching such as active radicals, ion bombardment energy, charge of the ions has been investigated. Even though the degradation of the low-*k* materials has been investigated by many researchers, the effect of each factor in the plasma such as radical, energy, and charge on the degradation of the low-*k* material has never been investigated.

2. EXPERIMENTAL DETAILS

Methyl Silsesquioxane (MSQ) was used as the low-*k* material to be investigated, and 3200 Å thick MSQ was deposited on *p*-type silicon wafers using chemical vapor deposition (CVD, Applied Materials Inc.). The dielectric constant of the deposited MSQ was 2.7 and the refractive index measured at 632.8 nm was 1.42.

To study the effect of radicals and ions in the plasma during the etching on the degradation of the MSQ, various etching tools such as inductively coupled plasma (ICP) etcher, reactive ion beam etcher, and neutral beam etcher have been used in the etching of MSQ. The ICP etcher is a conventional planar coil-type ICP etcher and was operated by supplying 13.56 MHz rf power to the ICP source and a separate 13.56 MHz rf power to the substrate to supply bias voltage. The schematic diagram of the reactive ion beam etcher used in this experiment is shown in Figure 1. The ion source of the reactive ion etcher was also an ICP-type source operated with 13.56 MHz rf power and three grids were installed in front of the ICP-type ion source for the acceleration of the reactive ions. (1st grid was the acceleration grid for the control the energy of the ions, 2nd grid was the extraction grid for the extracting the ion beam through the potential difference between the 1st grid and the 2nd grid, and 3rd grid was grounded to maintain the energy of the beam close to the 1st grid potential and to prevent the potential leak to the chamber.) For the neutral beam etcher, as shown in Figure 1, a parallel low angle (5°) graphite reflector plates were installed in front of the ion source of the reactive ion etcher for the neutralization of the reactive ion beam extracted from the grids and the source was tilted to have a vertical neutral beam on the substrate. Using the low angle reflector plates installed in front of the reactive ion beam, the most of the reactive ions were neutralized (>99%). The details of the neutral beam source can be found elsewhere.[15]

For the ICP etching, 10 mTorr of operating pressure, 5 sccm/15 sccm of CF$_4$/Ar gas, 30 W of ICP source

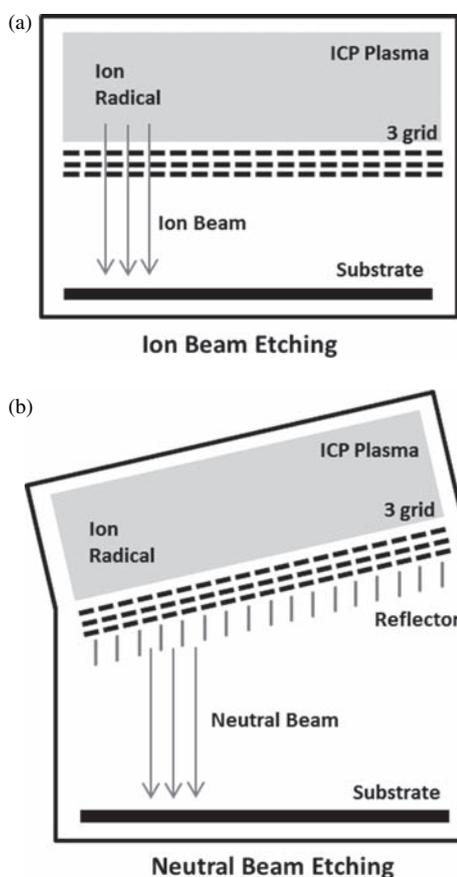(a)

Ion Beam Etching

(b)

Neutral Beam Etching

Figure 1. Schematic diagrams of (a) reactive ion beam etcher and (b) the neutral beam etcher used in the experiment. The ion beam source was composed of a three-grid ICP ion gun and, to change from the reactive ion etcher to the neutral beam etcher, a low angle reflecting plate was installed in front of the ion beam source.
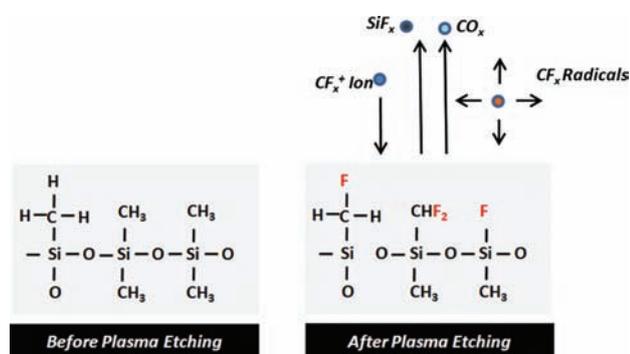

Figure 2. Surface reactions on the MSQ material after the exposure to conventional fluorine-based plasmas.

plasma species consisted of fluorine gas-based radicals and ions. The fluorine-based radicals and ions bombarding the MSQ surface will react with the bondings on the MSQ surface such as C–H (3.5 eV), –Si–C (4.7 eV), etc. to form more chemically stable bondings such as Si–F (11.3 eV), C–F (11.1 eV), etc. because the reactions are thermodynamically favorable. During the etching using CF_4 plasmas, the Si–O (8.3 eV) backbone of MSQ is broken by the ion bombardment and removed as byproducts composed of SiF_x and CO_x. However, in addition to the removal as the byproducts, the fluorine-based radicals/ions remaining on the surface or those penetrated into the MSQ will deform the MSQ surface and degrades the dielectric properties of MSQ by forming the fluorine based bondings. Especially, due to the high electronegativity of fluorine bonded to MSQ surface, the hydrophobic MSQ surface is changed to the hydrophilic surface, and the dielectric constant of the MSQ surface is increased rapidly by the increased absorption of water molecule ($k = 80$) on the hydrophilic surface. In this study, the source factors causing the surface modification and deformation of the low-*k* material, MSQ, during the fluorine-based plasma processing such as energy of bombarding ions, radicals in the plasma, energetic neutrals instead of energetic ions were separated by using various etching methods and the effect of each source factor on the degradation of the MSQ surface has been investigated.

Figure 3 shows the chemical bonding states of (a) F 1s, (b) C 1s, (c) Si 2p, and (d) O 1s measured by XPS for
(i) the reference,
(ii) after the conventional ICP etching with −600 V of dc bias voltage, and
(iii) a low bias ICP etching with −50V of dc bias voltage using 10 mTorr of CF_4 (5 sccm)/Ar (15 sccm).

The ICP source power was 30 W and the etch depth was maintained at 2200 Å. As shown in Figure 3(a), after the etching using CF_4/Ar ICP, significant increase of fluorine-related bonding peaks (C–F: 687.7 eV, Si–F: 685.8 eV) on the etched MSQ surface could be observed. From the C 1s narrow scan data, as shown in Figure 3(b), the deformation of the MSQ surface from C–H_3 boding peak (284.8 eV) originated from MSQ to the fluorinated

power, and −50 V of the substrate bias voltage were used to etch MSQ. In the case of reactive ion beam etching, 5 sccm/15 sccm of CF_4/Ar gas was fed to the ICP ion source, −500 W of ICP source power, +280 V of 1st grid voltage, and −500 V of 2nd grid voltage were applied. In this case, the pressure of the process chamber was maintained ∼1×10^{-4} Torr because it is a remote type plasma. In the case of the neutral beam etching, the same conditions as the reactive ion beam etching was used except for the 1st grid voltage of +700 V due to the lower etch rate compared to the reactive ion etching. By using the above etch conditions, the MSQ etch rates were maintained the same at ∼ 500 Å/min for all three etch methods. The chemical binding states of MSQ surfaces after the etching using the various methods were investigated using X-ray photoelectron spectroscopy (ARXPS, Thermo VG, MultiLab 200, Mg Kα source).

3. RESULTS AND DISCUSSION

Figure 2 shows a cartoon showing the possible chemical bondings on the MSQ surface after the exposure to the
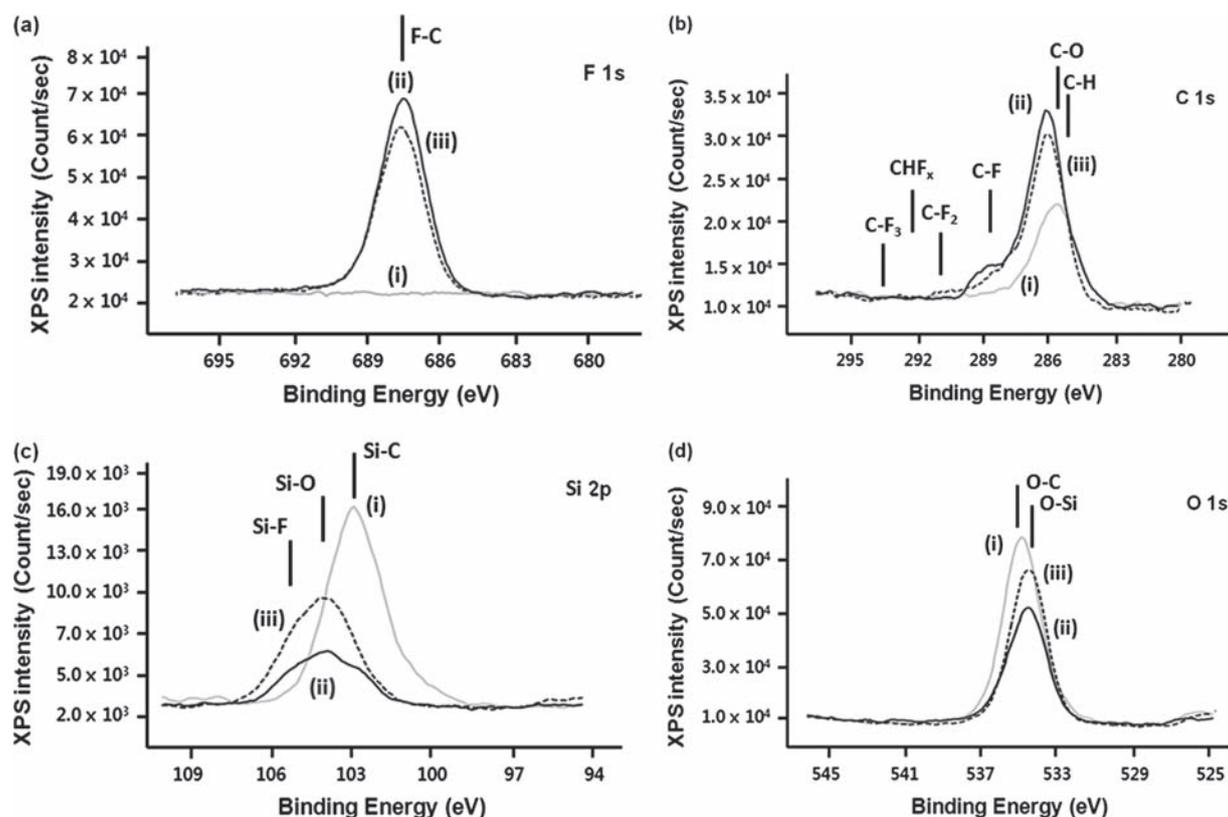
Figure 3. XPS narrow scan spectra of (a) fluorine, (b) carbon, (c) silicon, and (d) oxygen (i) for the reference MSQ surface, (ii) after a conventional ICP plasma treatment (−600 V dc-self biasing), (iii) and after a low bias (−50 V dc-self biasing) ICP plasma treatment.

carbon related bonding peaks such as C–HF$_2$ (290.7 eV), C–H$_2$F (288.5 eV), etc. could be also observed by the reaction of fluorine-based ions and radicals. Also, as shown in Figure 3(c), the formation of Si–F bonding peak (104.9 eV) while decreasing Si–O bonding peak (103.3 eV) and Si–C bonding peak (102.2 eV) from the MSQ could be also observed and, from the O 1s narrow scan data in Figure 3(d), the decrease of O–C bonding peak (533.3 eV) are also observed after the ICP etching. The formation of Si–F bonding from Si–O bonding in the MSQ is believed to be due to the thermodynamically more stable Si–F bond energy (11.3 eV) compared to the Si–O bond energy (8.3 eV) after the breaking the Si–O bonds by the ion bombardment.

Figure 3 also shows the effect of ion energy on the degradation of MSQ surface during the ICP etching by comparing (ii) −600 V of dc bias voltage and (iii) −50 V of dc bias voltage. As shown in the figures, even though the ion bombardment energy is about 12 times different, the differences in the bonding peak intensities of F 1s, C 1s, and O 1s are only slightly different (13∼18%) except for that (∼51%) of Si 2p. The more significant change of Si 2p bonding peak intensity compared to the change of the bonding peak intensities of F 1s, C 1s, and O 1s related to C–F (687.8 eV), C–HF$_2$ (290.7 eV), C–H$_2$F (288.5 eV) and O–C (534.2 eV) with increasing the ion bombardment energy appears to be related to the higher

bond energies of Si–O bond (8.3 eV) requiring higher thermodynamic energy in breaking the bond compared to C–H bond (3.5 eV). Therefore, the change of ion bombardment energy during the ICP etching generally affected the change of bonds related to silicon by the formation of Si–F bonds from Si–O bonds without significantly changing the bonds related to F 1s, C 1s, and O 1s.

When reactive ion etching or neutral beam etching is used instead of the ICP etching, due to the low radical density in the process chamber, the effect of radical species in the degradation of MSQ surface during the plasma etching using CF$_4$/Ar can be eliminated due to the low chamber pressure of 1.2 mTorr. Figure 4 shows the chemical bonding states of (a) F 1s, (b) C 1s, (c) Si 2p, and (d) O 1s
(i) after the ICP etching with −50 V of dc bias voltage in Figure 3,
(ii) after the reactive ion etching using CF$_4$/Ar, and
(iii) after the neutral beam etching using CF$_4$/Ar with the process conditions explained in the experimental section.

For all the three methods, the etch rate was kept the same at ∼500 Å/min and the etch depth was maintained the same at 1000 Å. As shown in Figures 4(a) and (b), by using the beam etching such as reactive ion beam etching or neutral beam etching instead of an ICP etching, no significant change in the C 1s bonding peak intensity is shown while showing significant decrease in F 1s peak
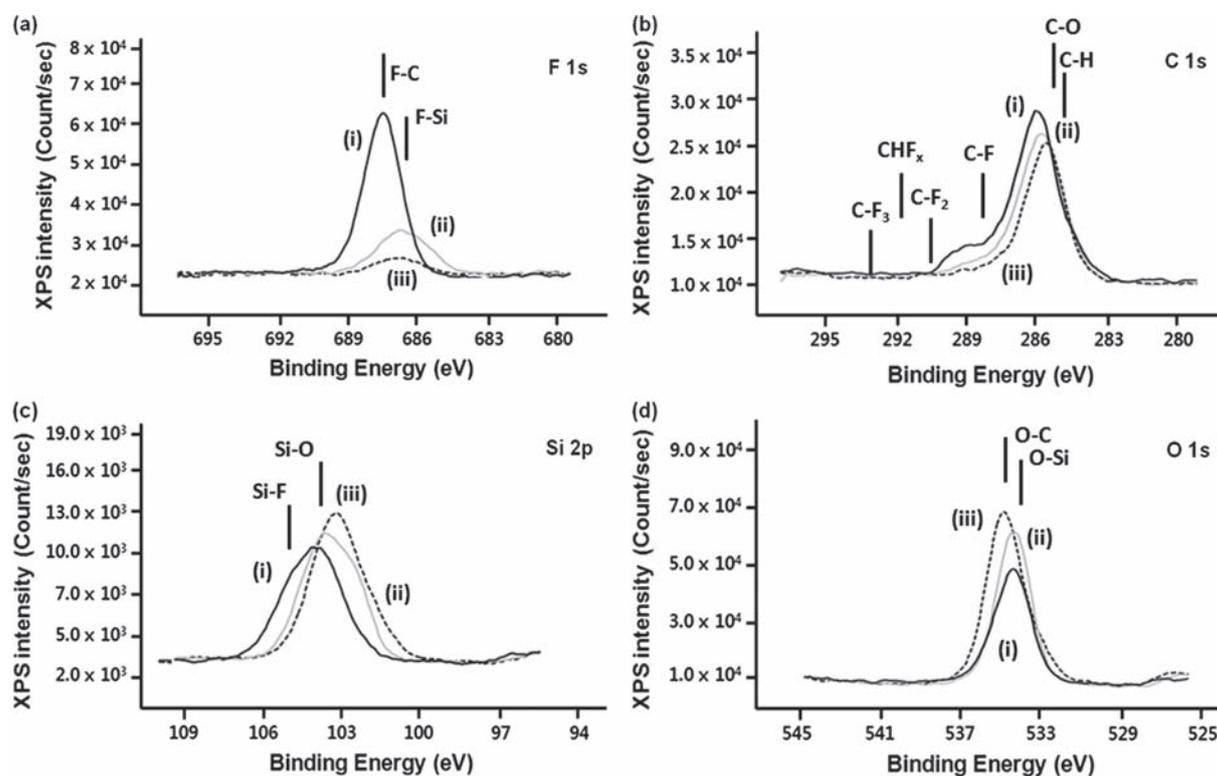
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Figure 4. XPS narrow scan spectra of (a) fluorine, (b) carbon, (c) silicon, and (d) oxygen (i) after a low bias ICP plasma treatment, (ii) after the reactive ion etching, and (iii) after the neutral beam etching.

intensity in addition to changing F bonding peak from C–F bonding (687.8 eV) to Si–F bonding (685.8 eV). Also, as shown in Figures 4(c) and (d), the use of beam etch techniques instead of the ICP etching slightly changed the Si 2p peaks from the degraded Si–F bonding (104.9 eV) to Si–O (133.3 eV) and Si–C (102.2 eV) bonding and increased O 1s peak intensity slightly indicating the relative increase of undamaged O–Si–CH$_3$ bonds in the MSQ. Therefore, it is believed that fluorine-based radical species in the plasma react with carbon in the Si-CH$_3$ functional group and tends to form Si-CH$_x$F$_y$ functional group ($X = (2, 1, 0)$, $Y = (1, 2, 3)$) without significantly reacting with Si–C and Si–O bondings consisting of MSQ backbone. The formation of Si-CH$_x$F$_y$ on the MSQ surface by the fluorine-based radical species can significantly degrade the low-*k* material characteristics of MSQ.

   Figure 4 also shows the effect of charged particle in the etching of MSQ. By comparing the surface characteristics of MSQ etched by the neutral beam etching and reactive ion etching, the effect of charged particle in the reactivity of MSQ surface can be identified. The same etch conditions were used for both the reactive ion etching and the neutral beam etching and, to maintain the same etch rates for both etching methods, the energy of the beam, that is, the 1st grid voltage was varied. For the reactive ion beam etching, 1st grid voltage was +280 V while for the neutral beam etching, 1st grid voltage was +700 V (it required a higher energy due to a lower etch rate for

the neutral beam etching). As shown in Figures 4(a) and (b), the use of neutral beam instead of reactive ion beam decreased the intensity of F 1s bonding peak to about 43% of F 1s peak etched by the reactive ion etching while not changing the C 1s peak intensity indicating the decrease of Si–CH$_x$F$_y$. Also, as shown in Figures 4(c) and (c) the further increase of Si–O and Si–C while decreasing Si–F caused by the decreased broken O–Si–CH$_3$ MSQ structure could be observed. In fact, during the neutral beam etching, much higher beam energy ($\sim$700 eV) of bombarding particle energy was used compared to the ion energy ($\sim$280 eV) for the reactive ion etching. Therefore, the MSQ surface etched by the neutral beam is bombarded by the higher energy compared to the MSQ surface etched by the reactive ion beam, however, as shown in the figure, the MSQ surface was damaged less for the neutral beam etching. It is known that the ions have more than 4$\sim$5 times higher thermodynamic energy compared to the neutrals due to the ionization energy in the ions. Therefore, ions tend to have higher reactivity with MSQ surface compared to neutrals. Therefore, the lower Si–CH$_x$F$_y$ bonding peaks and smaller broken O–Si–CH$_3$ bonds observed for the etching by reactive ion etching compared to the neutral beam etching appears to be the related to the higher reactivity of reactive ions compared to neutrals even though the bombardment energy is higher for the neutrals.

   The results observed by the XPS analysis of the MSQ surface etched by the three methods are summarized and

	Reference	After High ICP	After Low ICP	After Ion Beam	After Neutral Beam
Main Etchant	-	Energy Radical Ion	Radical Ion	Ion	High Energy Neutral
Reaction		Si-F reaction C-F reaction	Si-F reaction ↓↓ C-F reaction	Si-F reaction C-F reaction ↓↓	Si-F reaction ↓ C-F reaction ↓
Surface Bonding	Si-O Si-CH₃	Si-O ↓ Si-CH₃ ↓ Si-F ↑ Si-CHF₂ ↑ Si-CH₂F ↑ Si-CF₃ ↑	Si-O ↑ Si-CH₃ ↑ Si-F ↓ Si-CHF₂ Si-CH₂F Si-CF₃	Si-O Si-CH₃ Si-F Si-CHF₂ ↓ Si-CH₂F ↓ Si-CF₃ ↓	Si-O ↑ Si-CH₃ ↑ Si-F ↓ Si-CHF₂ ↓ Si-CH₂F ↓ Si-CF₃ ↓
F Intensity	0%	100%	82%	29%	10%
% ability In F intensity		100	Energy ~18%	Radical ~53%	Ion ~19%

Figure 5. Summary of the surface reaction mechanism of a low-*k* material for conventional ICP etching, ion beam etching, and neutral beam etching using fluorine-based gas.

the results are shown in Figure 5. As shown in the figure, as the factors affecting the damage to the low-*k* materials during the fluorine-based plasma etching can be divided into bombardment energy, reactive radical density, and charge of the ions. Among these, reactive fluorine-based radicals changed Si–CH₃ bonds to Si-CH$_x$F$_y$ and it degraded the bulk low-*k* properties. The particle bombardment energy broke the Si–C and Si–O bond of the MSQ backbone and formed Si–F bonds in the MSQ during the plasma etching, but it did not affect the formation of Si–CH$_x$F$_y$ in the MSQ surface significantly. By removing the charge of the ions during the bombardment, the MSQ properties were further improved by decreasing breaking the Si–O bonds and Si–C bonds of MSQ structure in addition to the slightly decreased degradation of Si–CH₃ to Si–CH$_x$F$_y$. When F intensity which is related to the damage on the MSQ surface is estimated, the bombardment energy, reactive radical density, and charge of the ions were responsible for ∼18%, ∼53%, ∼19% of the F intensity in the MSQ. Eventually, by using the neutral beam etching, the F intensity on the MSQ surface was decreased to 10% of a conventional ICP etching.

4. CONCLUSIONS

In this study, the effect of factors in the plasma responsible for the damage of a low-*k* material MSQ during the plasma etching using CF₄/Ar has been investigated. As the factors of the plasma responsible for the damage of the MSQ surface, three factors such as the bombardment energy, reactive radical density, and charge of the ions were used and, by using various etching methods such as ICP etching, reactive ion etching, neutral beam etching, the effect of those three factors on the degradation of MSQ surface was studied by using XPS. The XPS results showed that the ion bombardment during the plasma etching of MSQ

affects the breaking of MSQ bone structure such as the Si–O bonds and Si–C bonds mostly, while the reactive fluorine-based radicals in the plasma affect the change of Si–CH₃ bonds to Si–CH$_x$F$_y$. The charge of the ions during the ion bombardment also affected the degradation of MSQ possibly due to the higher thermodynamic energy possessed by the ion. Therefore, by using the neutral beam etching instead of a conventional ICP etching, the degradation on the MSQ surface estimated by the F intensity remaining on the MSQ surface could be decreased to 10%.

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