Low damage etching method of low-k material with a neutral beam for interlayer dielectric of semiconductor device

Seung Hyun Kang, Jong Kyu Kim, Sung Ho Lee, Jin Woo Kim, and Geun Young Yeom

Citation: Journal of Vacuum Science & Technology A: Vacuum, Surfaces, and Films **33**, 021309 (2015);
View online: https://doi.org/10.1116/1.4905736
View Table of Contents: http://avs.scitation.org/toc/jva/33/2
Published by the American Vacuum Society

Low damage etching method of low-k material with a neutral beam for interlayer dielectric of semiconductor device

Seung Hyun Kang
Department of Advanced Materials Science and Engineering, Sungkyunkwan University, Suwon, Gyeonggi-Do 440-746, South Korea

Jong Kyu Kim
Department of Advanced Materials Science and Engineering, Sungkyunkwan University, Suwon, Gyeonggi-Do 440-746, South Korea and Memory Division Semiconductor Business, Samsung Electronics, San No. 16 Banwol-Ri, Taean-Eup, Hwasung-City, Gyeonggi-Do 449-711, South Korea

Sung Ho Lee
Memory Division Semiconductor Business, Samsung Electronics, San No. 16 Banwol-Ri, Taean-Eup, Hwasung-City, Gyeonggi-Do 449-711, South Korea

Jin Woo Kim
School of Information and Communication Engineering, Sungkyunkwan University, Suwon, Gyeonggi-Do 440-746, South Korea

Geun Young Yeom[a)]
Department of Advanced Materials Science and Engineering, Sungkyunkwan University, Suwon, Gyeonggi-Do 440-746, South Korea and SKKU Advanced Institute of Nano Technology (SAINT), Sungkyunkwan University, Suwon, Gyeonggi-Do 440-746, South Korea

(Received 22 June 2014; accepted 29 December 2014; published 21 January 2015)

To reduce the cross-talk between nanoscale devices, low-k materials such as methyl silsesquioxane (MSQ), which is damaged easily during plasma etching, are introduced as an intermetallic dielectric material in addition to the use of copper as the conducting material for the reduction of parasitic resistance and capacitance. In this study, beam techniques such as neutral/ion beams were used in the etching of MSQ and the effect of these beam techniques on the reduction of the degradation of the MSQ were investigated. When MSQ was etched using the same CF_4 etch gas at the similar etch rate as that used for conventional MSQ etching using inductively coupled plasmas (ICPs), the neutral/ion beam etching showed lower F contents and lower penetration depth of F, indicating decreased degradation by fluorination of MSQ during etching using the beam techniques. Especially, the neutral beam etching technique showed the lowest F contamination and the lower penetration depth of F among the etch methods. When the dielectric constant was measured after the etching of the same depth, the MSQ etched with the neutral beam showed the lowest change of the dielectric constant, while that etched using the ICP showed the highest change of dielectric constant. The lower degradation, that is, the lower chemical modification of MSQ material with the beam technique is believed to be related to the decreased concentration of radical species in the processing chamber reacting with the MSQ surface, while the lowest degradation using the neutral beam is believed to be due to the lower reaction rate of the reactive neutral compared to reactive ions. [http://dx.doi.org/10.1116/1.4905736]

I. INTRODUCTION

As the critical dimension of the metal line of the integrated circuit (IC) devices for back-of-the-line (BEOL) process scales down to lower than 100 nm, the capacitance between the metal lines and the resistance of the metal line increase further, which increases not only the signal delay between adjacent metal lines, but also that between different interconnect levels.[1] For the optimization of higher packing density ICs, various studies have been carried out to decrease the resistance–capacitance time delay, one of which introduced intermetallic materials with lower dielectric constant.[2] Among the various low-k (k: dielectric constant) dielectric materials investigated, silicon-based low-k materials have been the most widely examined due to their superior dielectric properties, low moisture absorption, increased crack resistance, etc., in addition to the advantage in the further reduction of the dielectric constant by increasing the Si-C content in the material.[3–6]

For the application of the investigated low-k materials to the intermetallic dielectric materials, the low-k material needs to be easily patterned during the integration process without the degradation of the material. Currently, copper is used as the conducting metal for the minimization of resistance for the BEOL process and, due to the difficulty in the etching of copper, the patterning is achieved by a damascene process where a copper metal line is made by patterning the low-k materials, followed by electroplating the copper on the patterned low-k material and removing the

[a)]Author to whom correspondence should be addressed; electronic mail: gyyeom@skku.edu

excessive copper using chemical mechanical polishing.[7,8] One of the most important process issues in the application of low-k materials to the damascene process of next generation nanoscale semiconductor devices is the process induced damage of low-k materials. The surface degradation of low-k materials caused by the process induced damage during the plasma processing alters the material characteristics of the insulating materials; therefore, this tends to increase the leakage current between the adjacent interconnects and increase the k value of the etched dielectric materials.[9]

To prevent the plasma induced damage of the low-k materials during the plasma processing, various processing techniques were investigated. The possibility of the wet etching of low-k materials instead of plasma etching to prevent any plasma damage has been investigated.[10] The restoring of the damaged low-k materials after etching processes such as annealing has also been investigated to restore the material's characteristics. Especially, the reduction of plasma damage to reduce the reaction of low-k material with the plasma has been the most widely investigated.[11–15] For the plasma etching of low-k materials, fluorocarbon-based gas mixtures such as CF_4, C_4F_8, etc., are generally applied, and the reactive ions and radical species such as F generated by the plasma using fluorocarbon-based gas mixtures transform Si–CH_3 bonding to Si–F bonding, forming dangling bonds and forming a fluorinated surface layer composed of CF_x, which degrades the performance of the low-k material.[16–19] Therefore, to reduce the plasma damage, the passivation of the low-k material surface or the optimization of plasma conditions such as the decrease of the plasma density, the minimization of the active radical species, and the minimization of the ion bombardment have been studied;[13–15] however, further investigation is required for the application to the next generation semiconductor devices.

Previously, a neutral beam was used in the etching of various materials and, by eliminating the charge of the energetic ions bombarding the surface of the materials, the plasma damage could be reduced.[20,21] In this study, in the etching of low-k materials, beam etching techniques such as ion/neutral beams have also been applied and the effects of beam etching on the characteristics of etched low-k material such as the chemical binding states, contaminated layer thickness, dielectric constants, etc., have been investigated and compared with those obtained with conventional inductively coupled plasma (ICP) etching techniques.

II. EXPERIMENT

To investigate the characteristics of the surface and bulk of the low-k material during the plasma etching, 3200 Å thick methyl silsesquioxane (MSQ, dielectric constant $k = 2.7$, refractive index $n = 1.42$ at 632.8 nm) was deposited on a 300 mm p-type silicon surface using conventional plasma enhanced chemical vapor deposition.

As plasma etching techniques, neutral beam etching, ion beam etching, and conventional ICP etching have been used and the effects of etching techniques on the material characteristics of the low-k materials remaining after the etching have been investigated. Figures 1(a) and 1(b) show the schematic diagram of the ion beam etching system and the neutral beam etching system used in the experiment. As shown, the ion beam etching system was composed of an ICP-type plasma source and three grids made of graphite (first grid: accelerating grid controlling the energy of the beam; second grid: focusing grid controlling the flux of the beam and; third grid: ground grid). In the case of the neutral beam in front of the third grid, a parallel graphite reflector set (a low angle reflector: 5° tilted from the ion beam to neutralize the ions extracted from the ion beam) was located to obtain a neutral beam instead of an ion beam. The neutral beam etching configuration was obtained by tilting the source after installing the reflector set to irradiate the neutral beam vertical to the substrate. Further details of the neutral beam system can be found elsewhere.[22]

For the etching of MSQ, CF_4 gas was used as the etching gas for all of the etching methods and the etching parameters were controlled to obtain the same etch rate of ~500 Å/min. For the ion beam etching, 500 W of 13.56 MHz ICP power was applied to the ion beam source and +280 V was applied to the first grid and −500 V was applied to the second grid while the third grid was grounded. For the neutral beam etching, the same conditions as the ion beam etching were used, except for the higher first grid voltage of +700 V, to maintain the MSQ etch rate as the ion beam etching (the MSQ etch rate with the neutral beam was lower than that using the ion beam due to the scattering of the ion beam at the reflector at the same operating condition). In the case of ICP etching, to obtain the same MSQ etch rate, 30 W of 13.56 MHz ICP power was applied to the ICP antenna and −50 V of dc self-bias voltage was applied to the substrate by using a separate 13.56 MHz rf power.

The damage on the etched MSQ was investigated after the etching of 2200 Å of MSQ for all of the etching techniques. The chemical binding states of the remaining MSQ after etching using the above methods were observed by x-ray photoelectron spectroscopy (XPS, Thermo VG, MultiLab 200, Mg Kα source). The depth of the damaged layer on the remaining MSQ after the etching was also investigated using the XPS depth profiling technique. The MSQ was depth profiled using an Ar^+ ion source with 2 μA and 3 kV. The thickness of the degraded MSQ layer was also observed using a field emission scanning electron microscope (HITACHI S-4700) after the capping of the etched MSQ layer with copper and by etching the MSQ using an HF solution (8:1) for 20 s to remove the degraded MSQ layer. For the measurement of dielectric constant, 1000 Å thick aluminum was deposited on the etched MSQ, and the characteristics of the capacitance and voltage were measured at 1 MHz frequency using a capacitance–voltage measurement tool (C-V, Boonton 7200). To investigate the characteristics of the surface and bulk of the low-k material during the plasma etching, 3200 Å thick MSQ (dielectric constant $k = 2.7$, refractive index $n = 1.42$ at 632.8 nm) was deposited on a 300 mm p-type

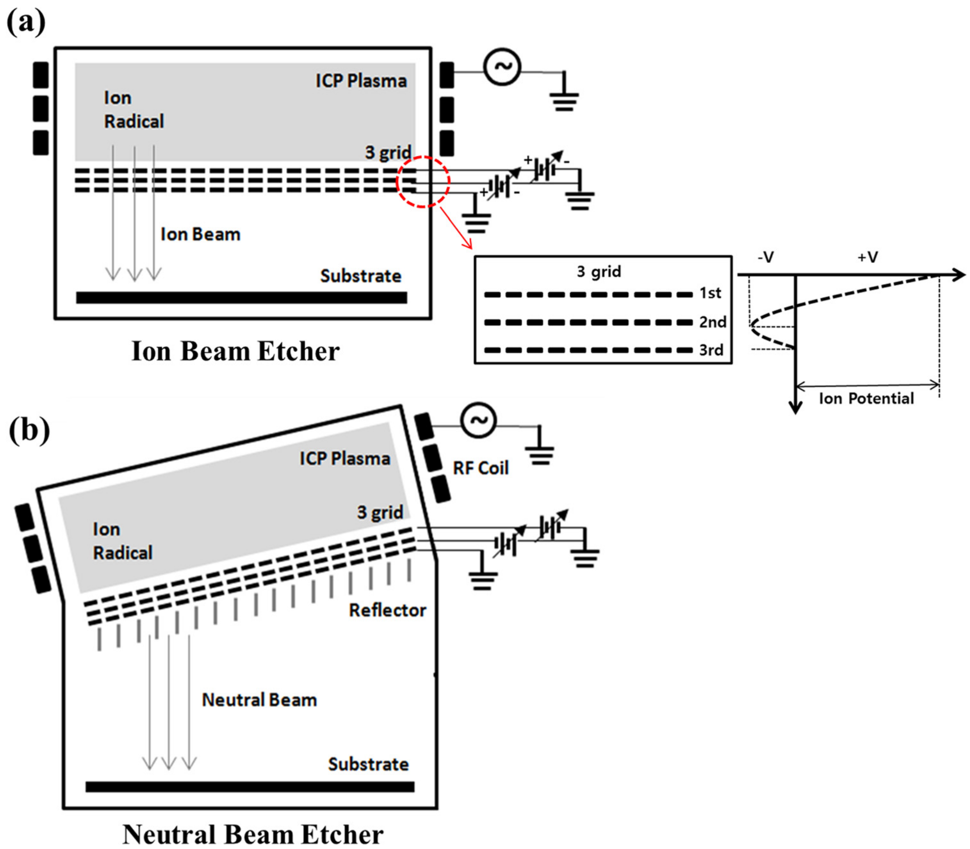

FIG. 1. (Color online) Schematic diagram of (a) the ion beam etching tool composed of a three-grid ICP ion source and (b) the neutral beam etching tool composed of a three-grid ICP ion source and a low angle reflector. In (a), the voltages to the grids and the voltage differences in the grids for the acceleration of the ions in the plasma are also shown.

silicon surface using a conventional plasma enhanced chemical vapor deposition.

III. RESULTS AND DISCUSSION

The surface of MSQ is generally damaged while etching with CF_4 plasmas. In this experiment, the electrical characteristics of 1000 Å thick MSQ layer remaining on the silicon wafer were investigated by etching the MSQ layer using the neutral beam, the ion beam, and the ICP. As described in Sec. II, the etching conditions have the same etch rate of ~500 Å/min with CF_4 and 2200 Å of MSQ that was etched for the measurement. After the etching, capacitors were fabricated by depositing 1000 Å thick aluminum on the etched MSQ. The dielectric constant of the remaining MSQ was calculated from the C-V measurement of the fabricated capacitors. The dielectric constant of the as-received MSQ was obtained with 3200 Å thick MSQ instead of 1000 Å thick MSQ. The results are shown in Figs. 2(a) and 2(b) for the measured dielectric constant of the MSQ and the percentage change of the dielectric constant, respectively; as shown in the figure, the dielectric constant of the as-received MSQ was 2.7 and, after the ICP etching, the dielectric constant was increased to 3.57, which is 32% higher than the dielectric constant of the as-received sample due to the degradation of the MSQ during the ICP etching. However, after the ion beam etching, the dielectric constant was decreased to 3.11 and, after the neutral beam etching, it was further decreased to 2.79, which are 15% and only 3% higher compared to that of as-received MSQ, respectively. Therefore, the MSQ etched using the neutral beam showed the lowest MSQ degradation while that etched using the ICP showed the highest MSQ degradation. To determine the reasons for the differences in the MSQ surfaces etched by the three etching methods, they were investigated using various techniques.

Using XPS, the change of chemical binding states on the etched MSQ surface as the indication of MSQ degradation and the depth of penetration of the etchant species were investigated. Figure 3 shows the XPS narrow scan spectra of (a) fluorine and (b) carbon of (1) the reference MSQ surface, (2) after the conventional ICP etching, (3) after the ion beam etching, and (4) after the neutral beam etching. The etching conditions are the same as those shown in Fig. 2. As shown in Fig. 3(a), after the ICP etching with −50 V of dc self-bias voltage, a peak at 685.8 eV appeared due to the fluorine contamination on the etched MSQ surface; also, as shown in Fig. 3(b), an increase of the carbon peak intensity near 284.8 eV was observed, possibly due to the formation of the carbon-rich layer.[23] When the MSQ was etched by the ion beam with 280 V of first grid voltage, even though the ion bombardment energy was higher than that of ICP etching while the etch depth of MSQ remained the same, the fluorine peak intensity on the etched MSQ was significantly lower by about 44% than that etched using the ICP. In the case of

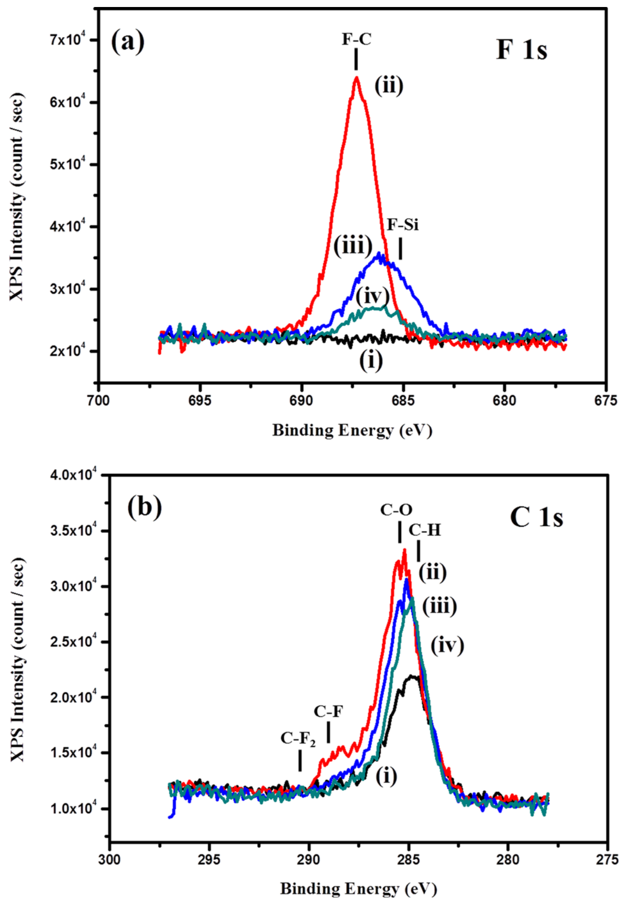

FIG. 2. (Color online) (a) Dielectric constant and (b) the percentage change of the dielectric constant of MSQ etched with ICP etching, with ion beam etching, and with neutral beam etching using CF_4. The MSQ was etched with CF_4 at the same etch rate. The thickness of the remaining MSQ was about 1000 Å.

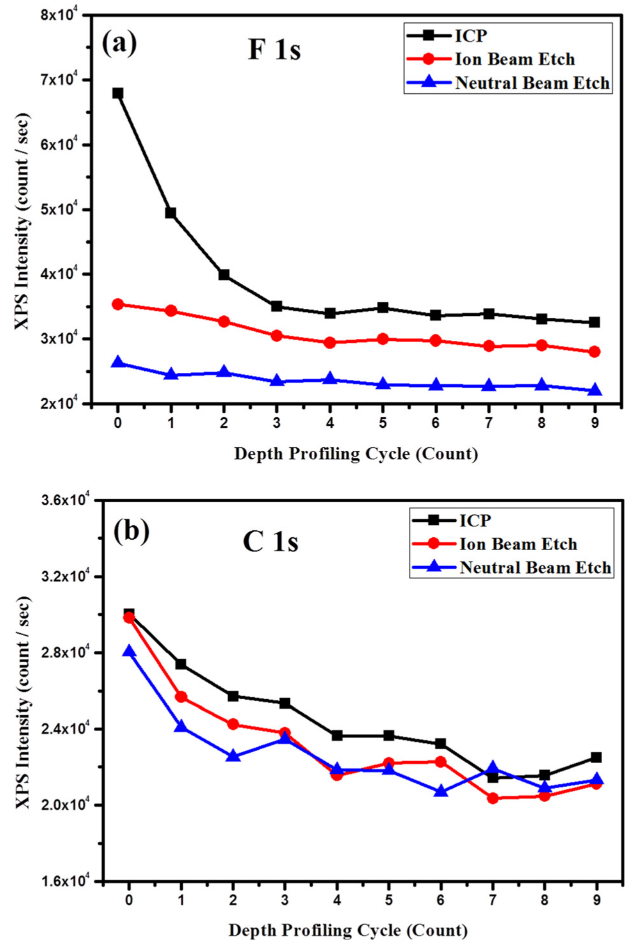

FIG. 3. (Color online) XPS narrow scan spectra of (a) fluorine and (b) carbon: (1) for the reference MSQ surface, (2) after the conventional ICP etching, (3) after the ion beam etching, and (4) after the neutral beam etching. The MSQ was etched with CF_4 at the same etch rate.

carbon peak intensity, the peak intensity was slightly decreased compared to that etched by the ICP. The decrease of fluorine and carbon peak intensities by using the ion beam instead of the ICP, even with the higher ion bombardment energy (~280 eV) of the ion beam etching compared to the ion energy (~50 eV) of the ICP etching, is believed to be related to the decreased density of radical species in the processing chamber during the etching in the ion beam system. During the ion beam etching, the processing chamber pressure is $\sim 1 \times 10^{-4}$ Torr, while the pressure is about 10 mTorr during the ICP etching; therefore, the density of the radical species is much lower for the ion beam etching than for the ICP etching.

When the MSQ was etched using the neutral beam, the fluorine peak intensity was decreased further to about 24% of the ICP etched MSQ and the carbon peak intensity also decreased slightly compared to that of ion beam etching. For the neutral beam etching, the higher energy (~700 eV) of the first grid compared to that (~280 eV) of the ion beam etching was required possibly due to the decreased beam flux to the substrate by the scattering of the ions at the reflecting plate, even though the same etch configuration as the ion beam etching was used, except for the installation of the reflecting plate. The decreased fluorine peak intensity and carbon peak intensity on the etched MSQ surface by using the neutral beam instead of the ion beam, even with the higher bombardment energy, are believed to be related to the differences in the reactivity of reactive ions such as F^+, $CF_x^{\ +}$, and reactive energetic neutrals such as F and CF_x.

To investigate the thickness of the degraded surface layer on the etched MSQ after etching using the ICP, the ion beam, and the neutral beam, the fluorine depth of penetration was measured using XPS depth profiling. Figures 4(a) and 4(b) show the intensities of the F 1s peak intensity and C 1s peak intensity, respectively, measured as a function of XPS depth profiling time for all of the etching techniques. The MSQ etching conditions are the same as those shown in Fig. 2. As shown in the figure, the MSQ etched using ICP not only showed the highest fluorine XPS peak intensity at the surface of the etched MSQ, but also showed the deepest penetration of fluorine into the MSQ. Among the MSQ etched using the three techniques, the MSQ etched with the neutral beam showed the shallowest penetration depth of fluorine in addition to the lowest XPS peak intensity of fluorine. In the case of carbon shown in Fig. 4(b), even though the results are not as clear as fluorine, similar trends can be observed. As mentioned earlier, the degradation of the MSQ

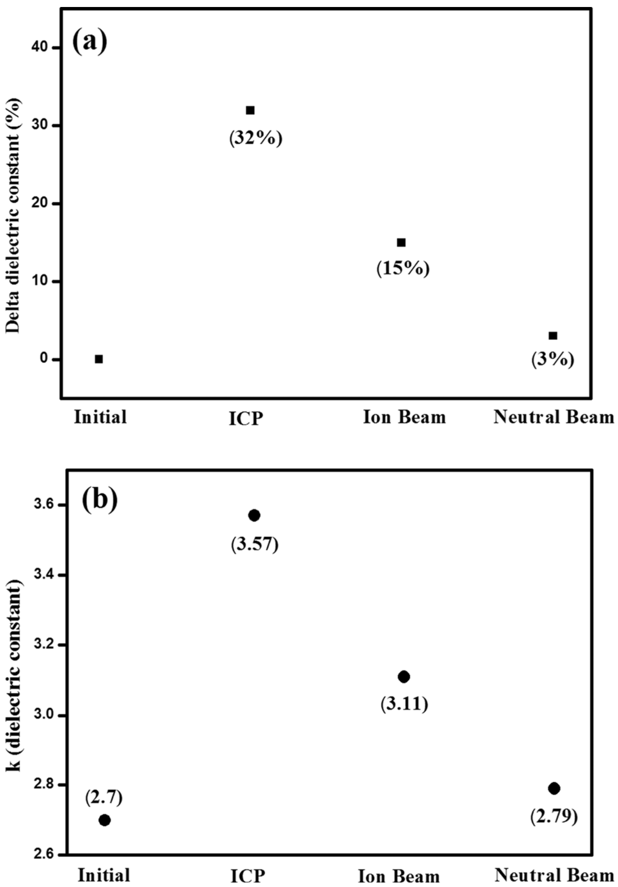

FIG. 4. XPS depth profiles of (a) fluorine and (b) carbon after the conventional ICP etching, after the ion beam etching, and after the neutral beam etching using CF_4.

surface during the etching appears to be more affected by the chemical reaction between the MSQ and reactive species than the physical reaction caused by the energetic particle bombardment. When the MSQ is etched by the ICP, due to the higher concentration of dissociated reactive radical species in the processing chamber compared to the ion beam etching or the neutral beam etching, the MSQ surface etched by the ICP was degraded the most significantly, even though the ion bombardment energy was the lowest at the same etch rate. In addition, due to the porosity of the MSQ (0%–9%), the reactive radical species are easily diffused into the material; therefore, the depth of the damaged layer was also the deepest. The thinner degraded layer observed for the MSQ etched with the neutral beam compared to that with the ion beam appears to be related to the differences of the reactivity of reactive ions and reactive neutrals as mentioned earlier.

To visualize the modified layer formed on the MSQ surface after the etching of MSQ, copper was deposited on the etched MSQ surface as a capping layer and the side of the MSQ located between the copper capping layer and the silicon wafer was etched using a HF solution ($HF:H_2O = 5:1$) for 30 s to observe the thickness of the degraded MSQ layer. When the MSQ is attacked by the plasma, the methyl group in the MSQ is broken and the hydrophobic MSQ surface changes to the hydrophilic surface in addition to the change of the material characteristics. The degraded MSQ layer tends to be easily etched by the HF solution; therefore, after the etching of MSQ of about 2200 Å, the damage on the remaining MSQ with the thickness of about 1000 Å was observed by SEM and the results are shown in Fig. 5. As a reference, the side of the as-received (undamaged) MSQ layer between the copper capping layer and silicon wafer was also observed by SEM after processing with the same HF solution. As shown in the figure, when the MSQ was not exposed to the plasma, no change of MSQ layer was observed after the processing with the HF solution. However, for the MSQ etched with the ICP, the degraded layer on the top of the etched MSQ could be observed. In the case of the MSQ etched with the ion beam, a thinner degraded layer could be observed, possibly due to the removal of the radicals in the processing chamber, while the thinnest degraded layer was observed for the MSQ etched using the neutral beam.

Based on the results obtained in the previous data, the mechanism of the MSQ surface degradation during etching using the ICP, the ion beam, and the neutral beam with CF_4 were schematically summarized in Fig. 6. In the case of the ICP etching, due to the high concentration of radical species such as CF_x and F in the processing chamber, even though the energy of the bombarding ions is low, the radical species were diffused into the MSQ and reacted; therefore, a thick degraded layer, that is, a thick chemically modified layer by

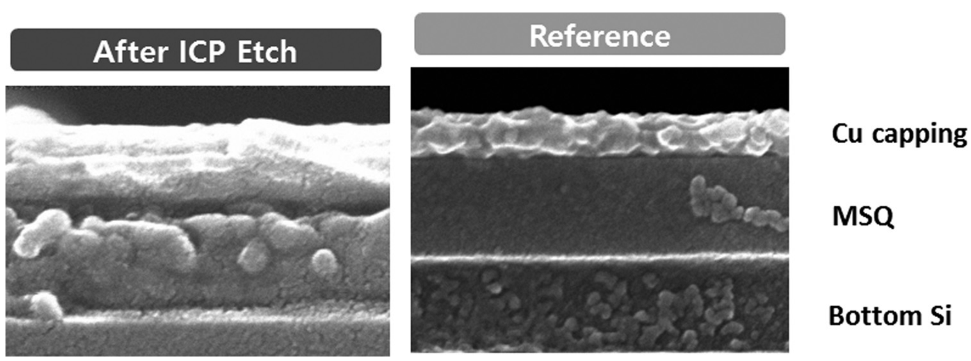

FIG. 5. SEM images of the MSQ etched using conventional ICP etching, using the ion beam etching, and using the neutral beam etching with CF_4. Copper was deposited on the etched MSQ surface as a capping layer and the side of the MSQ located between the copper capping layer and the silicon wafer was etched using an HF solution ($HF:H_2O = 5:1$) for 30 s to observe the thickness of the degraded MSQ layer.

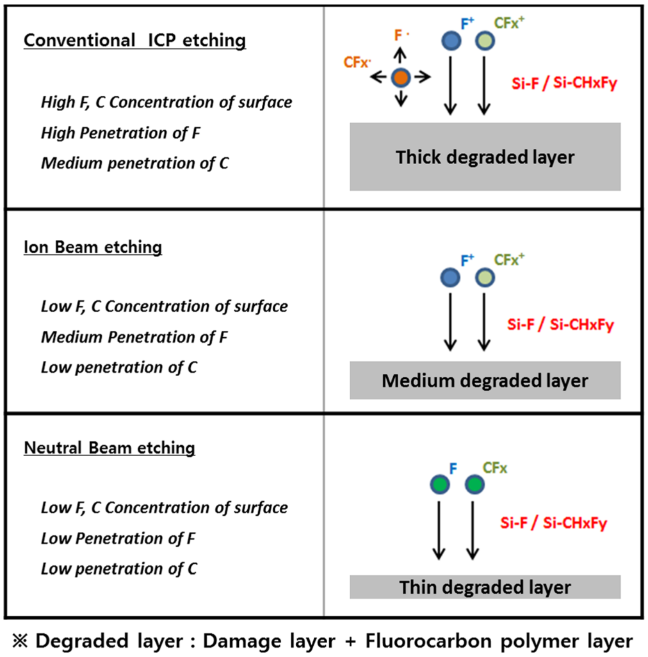

FIG. 6. (Color online) Schematic drawing mechanisms of MSQ surface degradation during the etching using the ICP, the ion beam, and the neutral beam with CF_4.

the fluorination of the MSQ was observed. However, in the case of the ion beam etching, due to the low concentration of the radical species in the processing chamber by using a remote ion source, even though the ion bombardment energy is higher than that of the ICP etching, a thinner degraded layer was observed. When the neutral beam etching was used, even though the energy of the beam bombarding the MSQ is much higher than the ion beam etching while other conditions are the same, due to the lower reactivity of neutrals compared to the reactive ions, the thinnest degraded layer was observed.

IV. CONCLUSIONS

In this study, MSQ was used, which is widely investigated as a low-k material for intermetallic dielectric. In addition, the degree of degradation on the MSQ during the etching with CF_4 using the neutral beam was investigated and the results were compared with those etched with the ion beam and the conventional ICP. The MSQ samples were etched at the same etch rates; therefore, for the ICP etching, the MSQ was exposed to a low ion bombardment energy with a high concentration of reactive radical species, while for the ion beam/neutral beam etching, the MSQ was exposed to a high particle bombardment energy with low reactive radical species. For the neutral beam etching, reactive neutrals instead of reactive ions were used. The thickness of the degraded layer and the degree of degradation by the fluorination of the MSQ was the highest for the ICP etching, while those for the neutral beam etching were the lowest. The degradation on the MSQ was more related to the concentration of the reactive radical species in the processing chamber than the energy of the bombarding species. In addition, the degradation of MSQ was also partially related to the reactivity of the bombarding species. By using neutral beam etching instead of the conventional ICP etching, significant improvement of the damage to MSQ could be observed.

ACKNOWLEDGMENTS

This research was supported by the Nano Material Technology Development Program through the National Research Foundation of Korea (NRF) funded by the Ministry of Education, Science and Technology (No. 2012M3A7B4035323) and was supported by the Industrial Strategic Technology Development Program (No. 10041681, Development of fundamental technology for 10 nm process semiconductor and 10 G size large area process with high plasma density and VHF condition), funded by the Ministry of Knowledge Economy (MKE, Korea).

[1]M. R. Baklanov, J. F. D. Marnefeef, D. Shairyan, A. M. Urbanowicz, H. Shi, T. V. Rakhimova, H. Huang, and P. S. Ho, J. Appl. Phys. **113**, 041101 (2013).
[2]T. E. F. M. Standaert, P. J. Matsuo, S. D. Allen, G. S. Oehrlein, and T. J. Dalton, J. Vac. Sci. Technol., A **17**, 741 (1999).
[3]T. Furusawa, D. Ryuzaki, R. Yoneyama, Y. Homma, and K. Hinode, Electrochem. Solid-State Lett. **4**, G31 (2001).
[4]A. T. Kohl, R. Mimna, R. Shick, L. Rhodes, Z. L. Wang, and P. A. Kohl, Electrochem. Solid-State Lett. **3**, 77 (1999).
[5]T. Ramos, K. Roderick, A. Maskara, and D. M. Smith, Mater. Res. Soc. Symp. Proc. **443**, 91 (1997).
[6]D. Fuard, O. Joubert, L. Vallier, M. Assous, P. Berruyer, and R. Blanc, J. Vac. Sci. Technol., B **19**, 2223 (2001).
[7]K. Hamioud *et al.*, Microelectron. Eng. **87**, 316 (2010).
[8]S. W. Chung, S. Y. Kim, J. H. Shin, J. K. Kim, and J. W. Park, Jpn. J. Appl. Phys. **39**, 5809 (2000).
[9]N. Lifshitz, W. Y. C. Lai, and G. Smolingsky, IEEE Electron Device Lett. **10**, 562 (1989).
[10]M. Claes, Q. T. Le, E. Kesters, M. Lux, A. Urionabarrenetxea, G. Vereecke, P. Mertens, R. Carleer, and P. Adriaensens, ECS Trans. **11**, 177 (2007).
[11]S. Ito, Y. Homma, E. Sasaki, S. Uchimura, and H. Morshima, J. Electrochem. Soc. **137**, 1212 (1990).
[12]R. E. Thomas, M. J. Mantini, R. A. Rudder, D. P. Malta, S. V. Hattangady, and R. J. Makunas, J. Vac. Sci. Technol., A **10**, 817 (1992).
[13]Y. H. Wang, D. Gui, R. Kumar, and P. D. Foo, Electrochem. Solid-State Lett. **6**, F1 (2003).
[14]N. Posseme, T. Chevolleau, T. David, M. Darnon, O. Louveau, and O. Joubert, J. Vac. Sci. Technol., B **25**, 1928 (2007).
[15]M. G. Albrecht and C. Blanchetter, J. Electrochem. Soc. **145**, 4019 (1998).
[16]M. R. Baklanov, S. Vanhaelemeersch, H. Bender, and K. Maex, J. Vac. Sci. Technol., B **17**, 372 (1999).
[17]M. Lam and A. Ashish, Solid State Technol. **42**, 71 (1999).
[18]Y. Iba, S. Ozaki, M. Sasaki, Y. Kobayashi, T. Kirimura, and Y. Nakata, Microelectron. Eng. **87**, 451 (2010).
[19]P. Lazzeri, X. Hua, G. S. Ohlelin, M. Barrozi, E. Iacob, and M. Anderle, J. Vac. Sci. Technol., B **23**, 1491 (2005).
[20]F. Shimokawa, J. Vac. Sci. Technol., A **10**, 1352 (1992).
[21]D. H. Lee, J. W. Bae, S. D. Park, and G. Y. Yeom, Thin Solid Films **398**, 647 (2001).
[22]B. J. Park *et al.*, J. Phys. D: Appl. Phys. **41**, 024005 (2008).
[23]J. K. Kim, S. H. Kang, S. H. Lee, and G. Y. Yeom, J. Nanosci. Nanotechnol. **14**, 9411 (2014).