Low temperature remote plasma cleaning of the fluorocarbon and polymerized residues formed during contact hole dry etching

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We investigated the remote oxygen and hydrogen plasma cleaning to remove reactive ion etching (RIE) induced fluorocarbon and polymerized residues formed during the dry etching of the contact hole. After the RIE process, RIE induced fluorinated surface and/or fluorocarbon formation with a very homogeneous spatial distribution at several tens of Å depth from the surface was observed. The photoresist films before and after the RIE process showed a similar ashing behavior. Ashing rate generally increased with increasing the process temperature and plasma power. X-ray photoelectron spectroscopy and Auger electron spectroscopy analysis showed that the carbon and fluorine associated contamination can be effectively removed by oxygen plasma but it left a small amount of carbon residue and sacrificial silicon oxide. Hydrogen plasma cleaning was necessarily required to remove the residual carbon contaminants formed on the silicon surface after oxygen plasma ashing. Two step cleaning, oxygen plasma ashing with an intentionally left very thin photoresist layer and subsequent hydrogen plasma cleaning, is a very effective cleaning process to remove residual carbon and polymer without forming a SiO₂ layer. This article presents the systematic evaluation of the remote oxygen and hydrogen plasma cleaning of RIE induced polymer residues. © 2002 American Vacuum Society. [DOI: 10.1116/1.1495904]

I. INTRODUCTION

As the feature size of the device becomes smaller, dry etching processes are commonly used to form small diameter contact or interconnection via holes. At the submicron level in modern semiconductor processing, isotropic characteristics of wet etching have the limitation of the control over the process. Therefore, contact holes via structures in devices are opened by the reactive ion etching (RIE) process using fluorocarbon gases due to their high anisotropic and selective silicon etching characteristics. However, the RIE process generally induced surface modifications such as nonvolatile fluorocarbon residues on the exposed surface.¹⁻⁴ Furthermore, these residues react with photoresist and form a polymerized surface layer.⁵ Consequently, these residues result in high contact resistance and defects at the metal–silicon interface which cause a high leakage current.⁶⁻⁹ For these reasons, RIE induced fluorocarbon residues and/or a polymerized surface layer must be removed prior to metal contact. However, these residues are reported to be nonvolatile, and also chemically and thermally stable.¹² Moreover, it is very difficult to remove such residues completely in high-aspect ratio structures especially with submicron diameter contact hole size.¹⁰,¹¹

The objective of post-RIE cleaning is to remove polymerized surface residues, impurities, and defects formed near the surface region and/or at greater depth. The current method of post-RIE cleaning is based on the ex situ wet strip process which includes an oxidizing step using ultraviolet/ozone or oxygen plasma followed by dipping in sulfuric acid (H₂SO₄) and hydrofluoric acid based chemicals. In previous reports, oxidizing is the most effective method to remove fluorocarbon residues.¹²,¹³ This oxidizing step with a wet chemical process typically completes the cleaning process to avoid leaving residues behind. However, as the feature size of the contact holes gets smaller, the wet strip process is reported not to remove organic residues completely.¹⁰,¹⁴ In addition, large quantities of these wet chemicals increase the process cost and cause significant environmental problems.¹⁵

Very extensive studies have been carried out on dry cleaning of post-RIE induced residues using plasma.¹²,¹⁶⁻¹⁸ Electron cyclotron resonance or radio frequency (rf) plasma was expected to remove post-RIE induced polymer residues effectively due to its activated state and anisotropic characteristics.¹⁷⁻¹⁹ However, previous studies showed some disadvantages of post-RIE dry cleaning using plasma such as plasma damage, incomplete removal of residues, and resist
popping.\textsuperscript{20} For these reasons, the minimization of plasma induced damage is required for dry cleaning using plasma.

In this study, the characteristics of RIE induced polymer residues formed on photoresist and silicon surfaces were evaluated. Also, we investigated the remote oxygen plasma ashing characteristics of photoresist and hydrogen plasma cleaning properties of residual photoresist and polymer. Remote plasma was used to minimize plasma damage by keeping the substrate distant from the discharge region.\textsuperscript{21} Oxygen plasma was expected to remove photoresist effectively since it generates reactive oxygen radicals which react with photoresist with a minimum of ion bombardment, resulting in a true chemical reaction and removing the RIE induced polymer effectively. Hydrogen plasma was subsequently employed to remove the strongly bonded chemical species, such as residual Si–O and Si–C, after the oxygen plasma exposure without causing much damage due to the light mass of the hydrogen.\textsuperscript{19}

II. EXPERIMENT

Two types of specimens, with and without pattern, were prepared to investigate the remote oxygen and hydrogen plasma cleaning efficiency of photoresist and RIE induced residues. For the samples without pattern, the positive photoresist with a thickness of about 7000 Å was spin coated on chemically cleaned boron doped p-type (100) silicon substrates with a resistivity of 8.5–11.5 Ω cm. Then, these photoresist coated silicon substrates were etched by RIE using a gas mixture containing CHF\textsubscript{3}, C\textsubscript{4}F\textsubscript{8}, O\textsubscript{2}, CO, and Ar to produce the RIE-related polymerized residues. The RIE process pressure and plasma power were 35 mTorr and 1500 W, respectively. The thickness of the photoresist remaining after the RIE process was about 5000 Å. For the samples with pattern, the silicon oxide films with a thickness of about 14500 Å were deposited on the same type of silicon substrates by the plasma enhanced chemical vapor deposition method and these oxide films were patterned under the same RIE process conditions. The aspect ratio of the pattern was about 4–7. Unlike the features of the contact hole, the pattern had open trench regions which made it possible to analyze the bottom of the pattern qualitatively using Auger electron spectroscopy (AES).

The remote rf plasma cleaning and surface analysis systems were connected by an ultra-high vacuum transfer system for the in situ analysis without vacuum disruption. The base pressure of the remote rf plasma cleaning system was approximately $1 \times 10^{-7}$ Torr and the process pressure was fixed at around 200–400 mTorr for oxygen plasma and 80 mTorr for hydrogen plasma discharge. The distance between samples and the center of plasma was fixed at 30 cm.

Samples were systematically cleaned by a two step cleaning process with oxygen and hydrogen plasma under various processing conditions. First, the oxygen plasma ashing process was conducted on samples. The substrate temperature was varied from 75 to 225 °C. All samples were maintained at each process temperature for 10 min before ashing and cleaning. The oxygen gas flow rate was fixed at 20 sccm and plasma power was varied from 50 to 300 W. The effect of oxygen plasma exposure time was investigated by varying the exposure times from 30 to 90 s to optimize the ashing conditions. After the step of oxygen plasma ashing, the hydrogen plasma cleaning was carried out subsequent to cleaning the oxidized substrate surface. The plasma power and substrate temperature were fixed at 200 W and 500 °C, respectively. The hydrogen gas flow rate and the processing pressure were 50 sccm and 80 mTorr, respectively. The process time of hydrogen plasma cleaning was varied from 10 to 20 min.

A scanning electron microscope (SEM) and an atomic force microscope (AFM) were utilized to investigate the morphological changes during the cleaning process. The ashing rate was determined by NanoSpec measurements before and after oxygen plasma exposure. For the samples without pattern, the chemical composition changes and their bonding structure were characterized by the in situ X-ray photoelectron spectroscopy (XPS) and AES analysis. For the samples with pattern, ex situ AES analyses were performed to analyze the top and bottom regions of the pattern using a spot analyzing technique.

III. RESULTS AND DISCUSSION

Three sections of results are described in this article. In Sec. III A, RIE induced polymer formation and surface characteristics after the RIE process are discussed. In Sec. III B, it contains the comparison of the ashing rate of samples before and after the RIE process and the removal efficiency of RIE induced fluorocarbon residue with oxygen plasma. In Sec. III C, we will discuss the removal efficiency of the residual carbon and the sacrificial oxide of subsequent hydrogen plasma cleaning for samples after oxygen plasma ashing.

A. RIE induced polymer formation and surface characteristics

Figures 1 and 2 show the AES and XPS spectra of the photoresist film before and after the RIE process, respec-
tively. The AES spectra showed peaks related with carbon and oxygen on the sample before the RIE process, while the sample after the RIE process using a gas mixture of CHF$_3$, C$_4$F$_8$, O$_2$, CO, and Ar showed a clear fluorine peak. Consistent with the AES analysis, XPS spectra showed a shifted C 1s peak with multiplets due to the bonding with fluorine after the RIE process as shown in Figs. 2(a) and 2(b). The deconvolution of C 1s spectra indicated that the multiplets are associated with C–CF$_x$ ($x$ = 1,2,3), C–F and C–F$_2$ types of bonding. These AES and XPS spectra are clear evidence of the RIE induced fluorinated surface and/or fluorocarbon formation. Similar results have been obtained in previous studies. In previous research, XPS analysis of polyimides exposed to plasma with a high fluorine concentration showed an increased fluorine coverage with increasing fluorine concentration in the feed composition. The passivation can occur by either direct fluorination of the surface or by polymerization of fluorocarbons from the gas phase. The AES depth profile also revealed that the fluorine was distributed at about 30 Å in depth from the surface as shown in the inset of Fig. 1. Also, a very homogeneous spatial distribution of fluorine with a relatively consistent depth profile was also observed.

Figure 3(a) shows the AES spectrum taken at the bottom of the trench structure patterned by the RIE process. AES peaks related with silicon, carbon, oxygen, and fluorine were observed. The carbon and fluorine peaks indicate that RIE induced CF$_4$ polymer film formation at the bottom and that the high intensity of the carbon peak implies carbon rich CF$_4$ polymer formation due to the incorporation with photoresist. The presence of the silicon peak indicates that the thickness of the surface residues may be less than several tens of Angstroms due to the escaping depth of a characteristic Auger electron, or that sputtered Si and O from SiO$_2$ might incor-
porate into the fluorocarbon residue layer. The oxygen peak is probably associated with the interfacial SiO₂ layer. One possible explanation for this is the oxygen in air diffused through the CF₃ polymer film to the Si substrate and reacted with the silicon substrate to form SiO₂. The other possibility is the incomplete removal of SiO₂ or contamination from the RIE chamber during the etching process. In either case, the SiO₂ layer would be partially or completely covered by the CF₃ residue film. Figures 3 ~ and 3 ~ show the SEM images in the plane and cross section views of the pattern after the RIE process, respectively. For the cross section view, the chemical treatment of buffered hydrofluoric acid was carried out to identify the presence of polymer film on the pattern. As shown in Fig. 3 ~, the top region was less etched than the bottom region. The lower etching rate near the top region is indirect evidence of the RIE induced polymer formation on the top region. This RIE induced polymer acted as the inhibitor of the etching. Previous reports suggested that the CF radicals (CF*) or F atoms react with hydrocarbon in photoresist to form the incorporated polymer near the top and sidewall of pattern during the actual RIE process to open contact holes.

B. Photoresist and fluorocarbon film removal using remote oxygen plasma

Figures 4(a) and 4(b) show the effect of sample temperature and rf plasma power on the ashing rates of the photoresist films before and after RIE process, respectively. Except the variable conditions, the fixed standard processing conditions of the sample temperature, oxygen gas flow rate, rf plasma power, and plasma exposure time in this experiment were 175 °C, 20 sccm, 200 W, and 1 min; respectively. Both of the photoresist films before and after the RIE process show similar ashing behavior. The ashing rate generally increased with increasing processing temperature. However, the increase of the ashing rate was slowed down at the temperatures between about 100 and 150 °C. This indicated that the removal kinetics or activation energy has been changed at around 100 °C. One possible reason for this is the photoresist surface modification at elevated temperature which caused this ashing rate change. As the temperatures increased higher than 150 °C, the photoresist ashing was accelerated again. Also, a more significantly increased ashing rate was observed with the photoresist as coated while the photoresist after the RIE process showed a relatively constant ashing rate as a function of rf plasma power. At the standard condition, the processing temperature was fixed at 175 °C and this temperature is considered to be somewhat insufficient for the full reaction of oxygen with the RIE induced fluorocarbon. The increased ashing rate at elevated temperatures indirectly indicates that the photoresist ashing is a thermally activated process. Actually, the ashing rate is often characterized by an Arrhenius expression and, thus, provides the effective activation energy. For the pure oxygen plasma, the reported activation energy is constant at 0.5 eV/atom. However, the calculated activation energy of this experiment is about 0.3 eV/atom. This difference is probably due to the plasma assisted photoresist ashing that is related not only to the thermal activation process but also the supply of active species. Commonly, the density of reactive oxygen radicals in the oxygen plasma significantly affects the ashing rate. Figure 4(b) shows that the increased rf plasma power raised the ashing rate. Thus, the higher ashing rate with increased rf plasma power is considered to be due to the increased active oxygen radicals.

Figure 5(a) shows the AFM and SEM images of samples processed with rf oxygen plasma powers of 100 and 300 W, respectively. These samples were RIE processed before oxygen plasma ashing. As shown in both AFM and SEM images, a very inhomogeneous ashing characteristic with a wavelet shape of residual photoresist was observed. The root mean square (rms) surface roughness decreased from 582 to 8.95 Å with increasing plasma power from 100 to 300 W due to the increased ashing efficiency with increasing plasma power. Two distinct regions were observed in both AFM and SEM images after the ashing process, well-ashed and poorly ashed regions. The AES survey spectra of these two distinct regions shown in Fig. 5(b) revealed the oxygen richness in the well-
ashed region and carbon richness in poorly ashed regions. The oxygen richness in well-ashed regions is considered to be due to the reactive oxygen atoms reacting with the silicon substrate to form SiO₂. The AES silicon peak around a kinetic energy of 1614 eV confirmed the characteristic of SiO₂ bonding.

XPS spectra of the samples ashed with rf oxygen plasma powers of 100 and 300 W are shown in Figs. 6(a) and 6(b), respectively. The sample ashed with 100 W rf plasma power showed C 1s multi-peaks associated with C–C, C–O, and C–F bondings. In comparison with the C 1s peak shown in Fig. 2(b), C–CFₓ and C–Fₓ types of bonding in the CFₓ residue film were significantly reduced while the C–O bonding was increased due to the oxygen plasma exposure. The C–O bonding was also observed in O 1s spectra as shown in the inset of Fig. 6(a). For the sample ashed with 300 W of rf
plasma power, C–O bonding and C–F\(_x\) bonding were diminished. The O 1\(s\) peak shown in the inset of Fig. 6~(b)~ also showed significantly decreased C–O bonding and increased O–O bonding. The amount of increased reactive oxygen radicals significantly increased ashing efficiency.

For the sample with pattern after oxygen plasma ashing under standard condition, the AES spectra taken at the top and bottom of the pattern showed no carbon and fluorine related peaks as shown in Fig. 7. The above results indicate that the oxygen plasma is very effective to remove C–H based photoresist and carbon rich CF\(_x\) polymer films even with a high aspect ratio structure. As discussed in the previous section, the reactive oxygen radicals produced by remote plasma are proposed to react rapidly to produce volatile byproducts such as CO, CO\(_2\), H\(_2\)O, and CH. The oxygen radicals are considered to go through the bottom of the trench structure before neutralization and ash the carbon rich CF\(_x\) polymer films. This result also implies that the plasma damage can be reduced by minimizing the ion bombardment using remote plasma. However, in spite of the efficiency of polymer removal using remote oxygen plasma, oxygen radicals reacted with the surface silicon atom and formed a SiO\(_2\) layer. The silicon peak around the kinetic energy of 1614 eV confirmed the formation of a SiO\(_2\) layer. Prior to metal deposition, this thin SiO\(_2\) must be removed to decrease contact resistance.

**C. Remote hydrogen plasma cleaning of residual polymer and sacrificial silicon oxide**

Figure 8 shows the C 1\(s\) XPS spectra of the oxygen plasma ashed and subsequently hydrogen plasma cleaned samples. For the oxygen plasma ashing, the sample was ashed under standard conditions for 30 s. For hydrogen plasma cleaning, the sample was cleaned at 500 °C for 10 or 20 min. A very thin photoresist layer was intentionally left during oxygen plasma ashing to investigate the hydrogen plasma cleaning effects on the residues containing carbon. As shown in Fig. 8, the carbon residue was almost completely eliminated below the detection limit of XPS after plasma ashing under standard condition, the AES spectra taken at the top and bottom of the pattern showed no carbon and fluorine related peaks as shown in Fig. 7. The above results indicate that the oxygen plasma is very effective to remove C–H based photoresist and carbon rich CF\(_x\) polymer films even with a high aspect ratio structure. As discussed in the previous section, the reactive oxygen radicals produced by remote plasma are proposed to react rapidly to produce volatile byproducts such as CO, CO\(_2\), H\(_2\)O, and CH. The oxygen radicals are considered to go through the bottom of the trench structure before neutralization and ash the carbon rich CF\(_x\) polymer films. This result also implies that the plasma damage can be reduced by minimizing the ion bombardment using remote plasma. However, in spite of the efficiency of polymer removal using remote oxygen plasma, oxygen radicals reacted with the surface silicon atom and formed a SiO\(_2\) layer. The silicon peak around the kinetic energy of 1614 eV confirmed the formation of a SiO\(_2\) layer. Prior to metal deposition, this thin SiO\(_2\) must be removed to decrease contact resistance.

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hydrogen plasma cleaning. As a result, the hydrogen plasma cleaning was required to remove the residual carbon contaminants on the silicon surface after oxygen plasma cleaning.

Figure 9 shows the Si 2p XPS spectra of the samples after hydrogen plasma cleaning at 500 °C for 10 and 20 min. The oxygen plasma ashing condition before hydrogen plasma cleaning was the same as samples discussed in Fig. 8. The intensity ratio of peaks related with SiO2 of Si 2p XPS spectra was decreased and pure Si 2p spectra was increased by increasing the hydrogen plasma cleaning time as shown in Fig. 9. This indicates that the longer hydrogen plasma cleaning reduced more oxygen species. The previous study showed that remote hydrogen plasma cleaning was insufficient to remove SiO2 due to the bridge bonding that involves two Si atoms and the Si–O bond of energy about 3.73 eV.21 From the above results, we consider that a very thin photoresist layer, which was intentionally left during oxygen plasma ashing, minimized the formation of SiO2. This two step cleaning, oxygen plasma ashing with an intentionally left very thin photoresist layer and subsequent hydrogen plasma cleaning, is the one possible solution for the effective dry cleaning process to remove residual carbon and polymer without forming SiO2 layer.

IV. CONCLUSIONS

In this study, photoresist and RIE induced polymer residues removal with oxygen and hydrogen remote plasma was systematically evaluated. After the RIE process, AES and XPS spectra showed clear evidence of the RIE induced fluorinated surface and/or fluorocarbon formation with a very homogeneous spatial distribution and relatively consistent depth profile. The photoresist films before and after the RIE process showed a similar ashing behavior with a generally increased ashing rate while increasing the processing temperature. However, the increase in the ashing rate was slowed down at the temperature between about 100 and 150 °C and this indicated that the removal kinetics or activation energy changed at the temperatures around 100 °C. The higher ashing rate with increased rf plasma power was also observed. This implies that the plasma assisted photoresist ashing is related to, not only the thermal activation process, but also the supply of active species. AES silicon peak around the kinetic energy of 1614 eV confirmed the formation of SiO2 during oxygen plasma ashing. Hydrogen plasma cleaning was necessarily required to remove the residual carbon contaminants on the silicon surface after oxygen plasma cleaning. Also, two step cleaning, oxygen plasma ashing with an intentionally left very thin photoresist layer and subsequent hydrogen plasma cleaning, is a very effective cleaning process to remove residual carbon and polymer without forming a SiO2 layer.
