Surface roughening of silicon, thermal silicon dioxide, and low-k dielectric coral films in argon plasma

Yunpeng Yin and Herbert H. Sawin

Department of Chemical Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139

(Received 4 June 2007; accepted 13 November 2007; published 2 January 2008)

The surface roughness evolutions of single crystal silicon, thermal silicon dioxide (SiO₂), and low dielectric constant film coral in argon plasma have been measured by atomic force microscopy as a function of ion bombardment energy, ion impingement angle, and etching time in an inductively coupled plasma beam chamber, in which the plasma chemistry, ion energy, ion flux, and ion incident angle can be adjusted independently. The sputtering yield (or etching rate) scales linearly with the square root of ion energy at normal impingement angle; additionally, the angular dependence of the etching yield of all films in argon plasma followed the typical sputtering yield curve, with a maximum around 60°–70° off-normal angle. All films stayed smooth after etching at normal angle but typically became rougher at grazing angles. In particular, at grazing angles the rms roughness level of all films increased if more material was removed; additionally, the striation structure formed at grazing angles can be either parallel or transverse to the beam impingement direction, which depends on the off-normal angle. More interestingly, the sputtering caused roughness evolution at different off-normal angles can be qualitatively explained by the corresponding angular dependent etching yield curve. In addition, the roughening at grazing angles is a strong function of the type of surface; specifically, coral suffers greater roughening compared to thermal silicon dioxide. © 2008 American Vacuum Society. [DOI: 10.1116/1.2821747]

I. INTRODUCTION

The sidewall roughening developed during plasma etching process becomes crucial as the feature sizes have been continuously scaling down in order to maximize the transistor density. A trivial impact in the past has now become a significant contributor to the off-state leakage budget and short-channel effect control for sub-100 nm gate length devices. As shown in the literature, top line-edge roughness (LER) plays a very important role for the sidewall roughening of oxide patterning during etching in fluorocarbon chemistries. It was found that the resist sidewall roughness after development but before plasma etching was isotropic; during the antireflective coating (ARC) layer opening in plasma etching process, the photoresist layer became striated and the top edge of the photoreisst layer was facetted; the striation structure became much more significant and propagated down after etching of the subsequent SiO₂ layer.

The surface roughening of different films, such as dielectric oxide material, may occur during plasma etching in addition to the top LER effects on sidewall roughness evolution. Consequently, it is crucial to fully understand the mechanisms of the inherent surface roughening before we can optimize the plasma etching conditions to minimize the surface roughness level after etching. The following questions should be answered before we can propose a plausible mechanism for surface roughening during plasma etching process: What is the impact of ion bombardment on surface topography evolution? Is the roughening related to the etching chemistry? Will film properties influence the roughness evolution?

Some modeling effects aiming to understand the feature profile evolution and sidewall roughening in plasma etching have already been addressed in the literature. Among them, Kawai et al. have developed a three-dimensional (3D) simulator to simulate the plasma-surface interactions at nanoscale using Monte Carlo simulation. Specifically, a cellular representation of the substrate surface is used. In this 3D simulator, the sidewall roughening as well as inherent roughening of different films can be simulated. However, there are very limited experimental results on roughness evolution during plasma etching in literature which can be used to test the fidelity of the 3D simulator.

In this article, we addressed the surface roughening of three different initially smooth films (single crystal silicon, thermal SiO₂, and low-k dielectric coral) during etching in Ar plasma beam. The objective is to have a better understanding of the impact of ion sputtering on surface roughening evolution and provide an experimental database for the 3D profile simulation. In the literature, many researchers have already characterized the surface morphology evolution of silicon and SiO₂ films during pure Ar ion sputtering. What they found is that Ar sputtering might roughen the substrates depending on the ion energy level, ion bombardment angle, and some other factors. Unfortunately, most of the work focused on high incident ion energy level typically larger than 1000 eV despite that ion energies around several hundred eV are normally used in industrial plasma-based processes. Our focus in this article is on the surface roughness produced by...
ions less than 500 eV. Additionally, rather than using Kaufman-type ion beam sources to produce Ar ions, our Ar plasma beam is extracted from an inductively coupled plasma source through a grounded orifice. By this means, the plasma beam has a better representation of the plasmas used in industrial processes.

II. EXPERIMENT

The etching rate and surface roughness are measured using an inductively coupled plasma beam scattering apparatus which has been described previously. The plasma is formed in the upper chamber using inductive coupling to power the discharge. The chamber contains an insulating liner (ceramic or quartz) so that the plasma can be biased to create the desired ion bombardment energy. The plasma beam is generated using a grounded grid between the plasma chamber and the lower chamber that is evacuated by a cryogenic pump which maintains a sufficiently low pressure ($10^{-5} - 10^{-4}$ Torr under typical operating conditions) that gas phase collisions can be ignored in the lower chamber. The ion beam is charge compensated by tungsten filament electron emission that keeps the space charge of the ion beam from expanding the beam and maintains the surface potential of insulating samples at ground potential. The neutrals also expand through the grid producing a neutral flux at the sample. By manipulating the discharge pressure, plasma power, etc., the ion and neutral fluxes to the sample can be varied and measured by the mass spectrometer and a self-designed ion flux analyzer.

The sample stage can be rotated about its axis to change the beam impingement angle to the substrate surface. Sidewall roughening during plasma etching is investigated by etching blank films at glancing angles. One of the advantages of this method is that it is much more convenient to characterize the surface roughness on blank samples using atomic force microscopy (AFM) technique.

The surface etching and roughening are measured by determining the amount of material removed for a given exposure time and the roughness of the surface using an ex situ AFM characterization. Standard tapping-mode etched silicon probe tips were used in AFM to image the surfaces. Root-mean-squared (rms) roughness of each image was calculated after correction of any residual line-to-line offsets. All images were $1 \times 1 \mu m$, 256 line scans, with 256 pixels/line scan. The films thicknesses before and after plasma etching are measured by ellipsometer or profilometer. One should notice that the etching yield of single crystal silicon is assumed to be approximately the same as polysilicon because we lack the ability to characterize directly the thickness of single crystal silicon removed after etching. Encouragingly, this assumption has physical basis since a thin layer of amorphous layer will be formed on the surface of a substrate due to the ion bombardment. Therefore, the etching kinetics of polysilicon and single crystal silicon should be similar to each other. A variable angle spectroscopic ellipsometer (J.A. Woollam M-2000) was used to determine the etching rate of polysilicon and SiO$_2$. A profilometer (Tencor P-10) was used to measure the pre and postetch coral film thicknesses.

III. RESULTS AND DISCUSSION

A. Ar sputtering kinetics

The sputtering yields in argon plasma beam scale linearly with the square root of the ion bombardment energy and are consistent with data in the literature, which verifies that our ion flux measurement at normal angle and the etching rates characterized by ellipsometer/profilometer are reasonable. Figures 1 and 2 give the sputtering yields of polysilicon, coral, and SiO$_2$ as a function of square root of ion energy. The sputtering threshold energies of these films are all about 50 eV. The sputtering yield of coral, however, is higher than SiO$_2$ for the same ion energy level. This might be due to the different inherent film properties of different films. One possible reason is that plasma enhanced chemical vapor deposition (PECVD) low-$k$ dielectric coral is less dense compared with thermal SiO$_2$.

It is crucial to have adequate and comprehensive experimental database in order to develop a detailed model of plasma-surface interaction which can capture fine details happened during real plasma patterning conditions, such as the microtrenching and sidewall bowing effects. One of the most important experimental parameters required is the relative etching yield as a function of ion bombardment angle. A better understanding of sidewall scattering effects is not possible without a solid quantification of the angular dependence of the etching yield. Figures 3 and 4 show the normalized etching yield as a function of off-normal angle for polysilicon, SiO$_2$, and coral. Note that all of the etching yields are normalized to the corresponding yields at normal angle for each material. Obviously, the etching yield of all films in argon plasma followed the typical sputtering yield curve, with a maximum around 60°–70° off-normal angle. This suggests that our angular measurements of the ion flux are reliable. More specifically, the oxide and coral have the maximum yield shifted about 5°–10° toward more grazing angles compared to polysilicon. Additionally, the relative
shape of the angular etching yield curve is almost independent of the ion energies in the scope of less than 500 eV, which can be seen in Fig. 3.

B. Spatial frequency of roughening

It is extremely promising that we can investigate real sidewall roughening based on the etching of blank films at grazing angles in current plasma beam chamber since the characterization of roughening on real sidewall using AFM is complicated. One of the biggest concerns, however, is that if the beam measurements of roughening on blank films are of the same dimension as is encountered on real sidewalls. The spatial frequency of sidewall roughening was measured by cleaving patterned samples and using AFM analysis. Specifically, the roughening, in general, decreases in amplitude with depth and is correlated as it emanates from the mask. In Fig. 5(b), the dashed line demonstrates the cross section analysis of the oxide surface, 150 nm from ARC/oxide interface (line c in Fig. 4 of Ref. 2). In particular, the spatial frequency of the striation structure is about tens of nanometers.

Figure 5(a) gives one example of the surface topography of initially planar thermal SiO2 film after etching in Ar plasma at 75° off-normal angle using 310 eV ion energies, and the corresponding cross section analysis of this etched surface is shown as the solid line in Fig. 5(b). The dashed line shown in Fig. 5(b) is the cross section analysis of SiO2 layer on the feature sidewall after plasma patterning. The AFM image of this real feature sidewall is shown in Fig. 6. Based on this observation we can conclude that the spatial frequencies of the roughness captured by our plasma beam study and by real sidewall roughening characterization are comparable to each other, and both have a characteristic length around tens of nanometers. We have to admit that the specific characteristic length of surface roughening captured in our beam experiments varies with the film type. For instance, coral film has different roughening propensity with thermal SiO2 film because coral is a methyl/ethyl doped oxide. However, this variation of the roughening characteristic length with film type is within a magnitude. In summary, our plasma beam chamber is capable to replicate the roughness on real sidewall during plasma patterning by etching planar films at grazing angles using plasma beams.
The low-\textit{k} dielectric coral film prepared by PECVD method is supplied by Novellus. Specifically, the dielectric constant \textit{k} of this coral film is around 2.85. The unetched films were characterized using AFM and the images are shown in Fig. 7. The vertical scales of all films are 10 nm. The rms roughness level is about 0.2 nm for single crystal silicon and thermal SiO\textsubscript{2}, while 0.9 nm for coral film. In addition, the surfaces of all preetched films are isotropic without any specific orientation.

Figure 8 shows the AFM images after sputtering in Ar plasma at normal angle using 310 eV ions. Compared to the surface before etching, the rms roughness level of single crystal silicon and SiO\textsubscript{2} remains almost the same after sputtering. Coral, on the other hand, becomes smoother after sputtering and the rms roughness is 0.5 nm. These different roughness evolution trends are believed to be due to different initial surface roughnesses, which will be discussed further later on. Additionally, all of the surfaces remain isotropic after sputtering at normal angle.

The AFM images of these three films after sputtering in Ar plasma at 60° off-normal angle using 310 eV ions are shown Fig. 9. Obviously, the roughness evolution of each film is totally different from what it is at normal ion incidence angle. Most importantly, all of these three films get roughened and form striation structure at 60° off-normal angle. Specifically, the silicon and oxide samples show spatial waves transverse to the beam, while coral forms waves that are parallel with the beam.

Similarly, all of these films are also roughened and form striation structure on the surface after sputtering in Ar plasma at 75° off-normal angle using 310 eV ions, which can be seen from Fig. 10. One significant difference, however, is the direction of the striation structure for a given beam impingement direction. Specifically, all surfaces form spatial waves that are aligned with the ion beam at 75°, while the striation can be parallel or transverse to the beam at 60°.

Another intriguing thing is that coral shows higher roughening potential compared to SiO\textsubscript{2} for a given ion fluence reaching the surface at both 60° and 75° off-normal angles. This can be observed by comparing (b) and (c) in Fig. 9 or Fig. 10. For instance, after both receiving 3.5 × 10\textsuperscript{17} ions/cm\textsuperscript{2} at 75° off-normal angle, the rms roughness levels for SiO\textsubscript{2} and coral are 1.5 and 8.6 nm, respectively. One part of the reason why coral has higher roughening propensity is due to the faster etching rate of coral than SiO\textsubscript{2}. Unfortunately, it is very straightforward to see from Fig. 11 that the etching rate difference solely cannot fully explain the higher roughening capability of coral. For instance, for the same amount of film removed at 75° off-normal angle, coral has much higher rms roughness level compared to SiO\textsubscript{2}. One possibility is that coral material has some density inhomogeneities in the film since it is prepared by PECVD method, while SiO\textsubscript{2} film is prepared by thermal oxidation method and the density variation is trivial.
The surface roughness of each film after sputtering at grazing angles (60° or 75°) increases with the amount of material etched, unlike the roughening trends at normal ion incidence angle that does not change with exposure after reaching its steady state. The results are summarized in Figs. 11 and 12. As shown in Fig. 12, the roughness of single crystal and SiO₂ is almost independent of the material etched at normal angle; at grazing angles, however, the roughness increases when more material is removed. More specifically, all of these three films have higher roughening potential at 75° than at 60° off-normal angle for a given amount of material removed. In particular, the results of coral and single crystal silicon are more obvious than SiO₂.

At more grazing 82° off-normal angle, single crystal silicon and SiO₂ remain smooth but coral roughens despite a much smaller amount of material being removed compared to the situation at less grazing angles such as 75°. The AFM images of these etched films are given in Fig. 13. Moreover, for coral, the spatial frequency of the striation increases and the streak length becomes much longer compared to the previous results at 60° or 75° off-normal angle.

The surface roughness of each film after sputtering at grazing angles (60° or 75°) increases with the amount of material etched, unlike the roughening trends at normal ion incidence angle that does not change with exposure after reaching its steady state. The results are summarized in Figs. 11 and 12. As shown in Fig. 12, the roughness of single crystal and SiO₂ is almost independent of the material etched at normal angle; at grazing angles, however, the roughness increases when more material is removed. More specifically, all of these three films have higher roughening potential at 75° than at 60° off-normal angle for a given amount of material removed. In particular, the results of coral and single crystal silicon are more obvious than SiO₂.

At more grazing 82° off-normal angle, single crystal silicon and SiO₂ remain smooth but coral roughens despite a much smaller amount of material being removed compared to the situation at less grazing angles such as 75°. The AFM images of these etched films are given in Fig. 13. Moreover, for coral, the spatial frequency of the striation increases and the streak length becomes much longer compared to the previous results at 60° or 75° off-normal angle.

Fig. 7. The AFM images of undetached (a) single crystal silicon, (b) SiO₂, and (c) low-κ dielectric coral films. The vertical scale of all films is 10 nm and all of the images represent $1 \times 1 \mu m^2$ of the real sample surface. The rms roughness of single crystal silicon, SiO₂, and coral films are 0.2, 0.2, and 1.0 nm, respectively.

Fig. 8. The surface topography of (a) single crystal silicon, (b) SiO₂, and (c) coral after sputtering in Ar plasma at normal angle using 310 eV ions. The vertical scale is 15 nm for all AFM images. (a) The dosage is $2 \times 10^{18}$ ions/cm² and the rms roughness is 0.3 nm after 160 nm film etched; (b) the dosage is $1.5 \times 10^{18}$ ions/cm² and the rms roughness is 0.1 nm after 115 nm film etched; (c) the dosage is $1.5 \times 10^{18}$ ions/cm² and the rms roughness is 0.5 nm after 288 nm film etched.
D. Discussion

It is crucial to have a deep understanding of how ions impact the substrates in Ar plasma in order to understand the mechanism of roughness evolution data shown in the previous section. For a typical ion sputtering process, Abrams and Graves\textsuperscript{30} and Helmer and Graves\textsuperscript{31} studied the way that the ions interact with the substrate surface based on molecular dynamics simulation. They found that the scattering probability of normal incidence ions is very low and the fraction of reflected ion energy is small even if an ion is scattered away from the surface; on the contrary, the reflection probabilities were larger than 90\% for incident angles larger than 75\° from the surface normal. Additionally, we know that the etching yield peaks around 60°–75° off-normal angle $\theta_{\text{peak}}$ for a typical sputtering process because the energy transfer efficiency at this range is optimal. As a result, we can assume that the ion scattering probability is almost zero when the ion incident angle is less than $\theta_{\text{peak}}$, while the ion scattering probability becomes high if the ion incident angle is larger.
than $\theta_{\text{peak}}$. This assumption is shown schematically in Fig. 14. One has to notice that the ion scattering probability depends strongly on the relative masses of the projectile and the target atoms. In the experiments related to this article, the mass of ions $\text{Ar}^+$ is heavier than the masses of the target materials, therefore, resulting in low ion scattering. On the other hand, the ion scattering probability would be more significant when the ions are lighter. For instance, a helium ion would show larger backscattering even at normal incidence.

At normal ion incidence angle, the ion scattering effects are trivial and the surface smoothing phenomena shown in Fig. 8 (especially for coral) can be explained qualitatively by the sputtering yield curve. Figure 15 demonstrates two possible scenarios: initially smooth surface and surface with initial large features. For surfaces with initially large features, the surface will be relatively smoother after etching because of the larger etching yield at faceting angles. Specifically, the small features, if exist, typically have facet angles around or

![Graph showing RMS roughness vs. thickness etched for SiO$_2$ and coral](image)

Fig. 11. The surface roughnesses of (solid line) SiO$_2$ and (dashed line) coral after sputtering in argon plasma at various angles as a function of the thickness of material removed. SiO$_2$: (■) 60° and (□) 75°. Coral: (♦) 60° and (○) 75°.

![Imagery showing surface morphology](image)

Fig. 12. The surface roughnesses of (solid line) single crystal silicon and (dashed line) SiO$_2$ after sputtering in argon plasma at various angles as a function of the thickness of material removed. Single crystal silicon: (×) 0°; (♦) 60° and (○) 75°. SiO$_2$: (+) 0°; (■) 60° and (□) 75°.

![Surface topography images for silicon and SiO$_2$](image)

Fig. 13. The surface topography of (a) single crystal silicon, (b) SiO$_2$, and (c) coral after sputtering in Ar plasma at 82° off-normal angle using 310 eV ions. The vertical scales of these AFM images are (a) 10 nm, (b) 10 nm, and (c) 50 nm. In all cases, the ion fluence reaching the surface is $1.5 \times 10^{17}$ ions/cm$^2$. (a) The rms roughness is 0.1 nm after around 34 nm film etched; (b) the rms roughness is 0.2 nm after 16 nm film etched; (c) the rms roughness is 3.6 nm after 38 nm film etched.

less than 10° during the sputtering process. This can be observed in the cross section analysis results given in Fig. 5(b). It is worth noting that the cross section analysis is not in scale and the vertical scale is much less than the horizontal scale. For films with initially smooth features, on the other hand, the surface will be roughened to a low level because of the stochastic roughening due to the uniformity of the plasma beam at atomistic scale.

At normal ion incidence angle, the surface roughness evolution of polysilicon film prepared by low pressure chemical
vapor deposition method further confirms our previous analysis. The surfaces before and after sputtering as well as the corresponding cross section analyses are shown in Fig. 16. In particular, the rms roughness level of this unetched polysilicon film is about 3.6 nm, which is much higher than unetched single crystal silicon (0.2 nm). Due to relatively higher etching yield at facet angles, the surface after sputtering becomes much smoother and the rms roughness level is 1.3 nm after receiving $1.25 \times 10^{18}$ ions/cm$^2$. Consistently, according to the cross section analyses, those features on the unetched surface (shown as the solid line) are removed after sputtering (shown as dashed line).

In previous studies$^{11-19}$ it has been observed that off-normal incidence ion bombardment, typically ion energies at keV range, often roughens the surface and produces striation parallel or transverse to the beam direction. In particular, Bradley and Harper$^{11}$ developed a theoretical model where they believe that the striation formation is caused by a surface instability caused by the competition between roughening (curvature dependent sputtering) and smoothing (surface diffusion) processes. Moreover, the resulting striation direction depends on the incidence angle of ions. Specifically, the striation structure is perpendicular to the component of the ion beam in the surface plane when incidence angles are less than a critical off-normal angle $\theta_c$ [Fig. 17(a)], while the striation is parallel to the beam direction for incidence angles close to grazing.

---

Fig. 14. The prediction of the ion scattering probability as a function of off-normal angle based on the measurement of the angular dependence of the etching yield. The scattering probability is relative low when the off-normal angle is smaller than the peak angle, and we can assume that all of the ion energy is transferred to the substrate; while the scattering probability is high when the off-normal angle is larger than the peak angle, and we can assume that all of the ion energy is scattered away.

Fig. 15. The prediction of surface roughness evolution during sputtering in Ar plasma at normal incidence angle. The arrows represent the ions bombarding the surface. (a) With initially large features, the surface will be relatively smoother after etching because of the larger etching yield at factoring angles; (b) with initially smooth features, the surface will be roughened to a low level because of the stochastic roughening due to the uniformity of the plasma beam at microscale.

Fig. 16. With initially large features, the surface will be smoothed out after Ar sputtering at normal ion incidence angle. (a) Unetched polysilicon surface with a rms roughness level of 3.6 nm and the vertical scale of the image is 40 nm. (b) Etched polysilicon surface after Ar sputtering at normal angle using 310 eV ions and the ion fluence received is $1.25 \times 10^{18}$ ions/cm$^2$; the rms roughness level is 1.3 nm and the vertical of the image is 10 nm. (c) The cross section analysis of the (solid line) unetched and the (dashed line) etched surfaces.
As has been addressed by Bradley and Harper, however, the model they proposed did not account for the ion scattering effects. Consequently, the theory is not valid for ion incidence angles larger than \( \theta_{\text{peak}} \) where the sputtering yield peaks due to the significant ion scattering effects. Additionally, the predictions of Bradley and Harper model concerning the changes in the striation orientation apply only to materials in which the critical angle \( \theta_c \) is less than \( \theta_{\text{peak}} \).

Bradley and Harper model can be used to partially explain the roughness evolution at 60° off-normal angle. As mentioned previously in Fig. 9, the striation is transverse to the ion beam direction for single crystal silicon and SiO\(_2\), while parallel to the ion beam for coral. In addition, the maximal sputtering yield happens around 60°–70° off-normal angle for all of the films. Therefore, the ion scattering effects are not very significant at 60° off-normal angle, and Bradley and Harper model is suitable to explain the striation formation. The difference of surface striation direction between coral and SiO\(_2\)/single crystal silicon is not clear, but it might be caused by the corresponding different film properties.

At more grazing angles, however, Bradley and Harper model is not applicable anymore. We believe that the striation structure formation is mainly caused by the ion scattering effects. With these grazing angles (75° and 82°), scattering of ions is dominant. In particular, the scattered ions might be bounced around the surface along the beam direction and cause ion channeling effects, which is shown schematically in Fig. 17(b). Consequently, striation structure parallel to the beam impingement direction forms due to this ion channeling effects. Additionally, the ion scattering effects are more significant at 82° than at 75° off-normal angle. As an impact, the striation length is more elongated and the spatial frequency of the waves increases at more grazing angles, which has already been shown in Fig. 13(c).

One last thing we have to admit is that we still do not fully understand why coral and SiO\(_2\) display very different roughness evolution trends in many cases shown previously although they demonstrate similar etching kinetics. Intriguingly, coral often has more roughening capability at grazing angles. For instance, SiO\(_2\) remain smooth while coral roughens after sputtering at 82° off-normal angle. One possibility might be due to the inherent film property difference between coral and SiO\(_2\). Specifically, coral is prepared using PECVD method and there are some doped methyl or ethyl groups in the substrate. These doped groups introduce inherent inhomogeneity to coral film; therefore, the roughening trend of coral film might be different compared to thermal SiO\(_2\)/single crystal silicon.

**IV. CONCLUSIONS**

We have successfully demonstrated that the inductively plasma beam chamber can be used to quantify surface roughening of different films. Specifically, the beam measurements of roughening are of the same dimension as is encountered on sidewalls. Moreover, the sputtering caused surface roughening can be explained by the angular dependence of the etching yield curve. At normal ion incidence angles, surfaces with initial large features are smoothed out due to the relative higher etching yield at facet angles, while initially smooth surface will be roughened to a low level due to stochastic roughening. At intermediate off-normal angles (60° in this article), the roughness evolution can be partially explained by Bradley and Harper model where the roughening and striation formation are caused by the surface instability due to the competition between curvature dependent sputtering caused roughening and surface diffusion caused smoothing. At high grazing angles (75° and 82° in this article), the striation development on the etched surface is mainly due to the ion scattering caused ion channeling effects. Additionally, coral often displays higher roughening potential in many cases compared to SiO\(_2\) but the mechanism has not been fully understood yet.
Angular etching yields of polysilicon and dielectric materials in Cl$_2$/Ar and fluorocarbon plasmas

Yunpeng Yin and Herbert H. Sawin

Department of Chemical Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139

(Received 4 June 2007; accepted 13 November 2007; published 2 January 2008)

The angular etching yields of polysilicon in Cl$_2$/Ar plasmas, and dielectric materials (thermal silicon dioxide and low-$k$ dielectric coral) in fluorocarbon plasmas, have been characterized in an inductively coupled plasma beam apparatus. The effects of ion energy, feed gas composition, and plasma source pressure are studied. The experimental results showed that these etching parameters had a significant impact on the resulting angular etching yield curve. In particular, the angular etching yield curve was more sputteringlike at low plasma source pressure and/or low effective gas percentage (Cl$_2$ and C$_4$F$_8$), with a peak around 60°–70° off-normal ion incident angle. In contrast, ion-enhanced-etching-like angular curves, which dropped gradually with off-normal angle, were formed at high plasma source pressure and/or high effective gas percentage. Further analysis indicated that the effective neutral-to-ion flux ratio reaching the surface was the primary factor influencing the angular etching yield curve. More specifically, the angular etching yield curve had physical sputtering characteristics at low neutral-to-ion flux ratios; while etching process was really dominated by ion-enhanced etching at high ratios and the angular curve was ion-enhanced-etching-like. The polymer deposition effects are also discussed in this article. © 2008 American Vacuum Society. [DOI: 10.1116/1.2821750]

I. INTRODUCTION

It is more and more challenging to keep the fidelity of pattern transfer during plasma etching as the key feature size keeps shrinking below 100 nm regimes. One of the major difficulties is due to the feature sidewall roughening introduced by plasma etching. A heavy load of research interests have been focused on understanding the origin and mechanism of sidewall roughening since it is crucial to minimize the sidewall roughness in order to improve the device performance.\textsuperscript{1–14} Many researchers found that this top LER played an important role for pattern transfer during plasma etching.\textsuperscript{3,5,6,8,11,14} In particular, Goldfarb et al. reported that this top LER was an important role for the sidewall roughening of oxide patterning in fluorocarbon chemistries.\textsuperscript{5}

Different profile feature modeling tools have also been developed to understand the key effects causing the artifacts during feature patterning, such as sidewall bowing, microtrenching, undercut, notching, and sidewall roughening.\textsuperscript{15–20} However, a complete set of experimental database is necessary in order to make these modeling tools meaningful. Among them the angular etching yields are one of the most important parameters need to be collected.

It has been demonstrated that a minor change of the angular etching yield curves had a significant impact on the feature profile evolution.\textsuperscript{16,21} For instance, the feature profile during polysilicon gate etch is influenced by the etching chemistries, which alters the angular etching yield curves.\textsuperscript{4}

For pure Cl$_2$ plasmas, the etching yield remains constant with the off-normal ion bombardment angle up to 45°, while the etching yield starts dropping even with small off-normal angles in HBr plasmas. Lane et al.\textsuperscript{21} have experimentally showed that this slight difference of angular yields between HBr and Cl$_2$ resulted in very different etched feature profiles. In particular, microtrenches were formed at the bottom in Cl$_2$ chemistry, while the feature bottom remained flat in HBr plasmas. Using Monte Carlo simulation approach, Jin and Sawin\textsuperscript{16} also reported similar results on the feature profile evolution in plasma etching.

Previously, people have already observed that plasma etching parameters might change what the etching yields looked like. Mayer et al.\textsuperscript{22} found that the angular etching yields of polysilicon and SiO$_2$ could be manipulated by ion bombardment energy and plasma beam pressure. In particular, the etching yield curves could be physical-sputtering-like with a peak around 60°–70°, or ion-enhanced-etching-like where the etching yield dropped off gradually with ion bombardment off-normal angle. Similar results have also been reported by Barklund and Blom,\textsuperscript{23,24} during the etching of silicon nitride in fluorocarbon plasmas, in which they found that the angular etching yield curve was manipulated by changing the plasma pressure. More specifically, the angular etching yield curve was sputteringlike at low plasma pressure level, while ion-enhanced-etching-like at high plasma pressure levels.

In the literature,\textsuperscript{25,26} different researchers have tried to understand why the angular etching yields changed with etching parameters, such as the plasma pressure. Kwon et al.\textsuperscript{26} proposed an ion-enhanced polymer deposition mechanism to explain the evolution of angular etching yields.
during the etching of SiO$_2$ in fluorocarbon plasmas. However, this proposed polymer deposition effect could not explain why the angular etching yields sometimes peaked around 65° off-normal angles, which has already been reported in the literature$^{23,24}$ and is also shown in this article.

In this article, the angular etching yields of polysilicon in Cl$_2$/Ar plasmas, and dielectric materials in fluorocarbon plasmas, are experimentally quantified using an inductively coupled plasma beam apparatus. In the case of polysilicon etch in Cl$_2$/Ar plasmas, the impact of ion energy, Cl$_2$ percentage in the feed gas, and the plasma source pressure were studied. For the etching of dielectric films in fluorocarbon plasmas, we mainly focused on thermal SiO$_2$ etch in C$_4$F$_8$/Ar plasmas, where the effects of ion energy, C$_4$F$_8$ feed gas percentage, and plasma source pressure were investigated. In addition, the angular etching yields of low dielectric constant coral film in C$_4$F$_8$/Ar plasmas were also studied. Our objective was to have a clear understanding of the impact of etching parameters on the angular etching yields.

### II. EXPERIMENT

The etching rates and roughening were measured using an inductively coupled plasma beam scattering apparatus which has been described previously$^{27}$ and will be described briefly here. The plasma was formed in the upper chamber using inductive coupling to power the discharge. The chamber contained an insulating liner so that the plasma could be dc biased (0–500 V) to create the desired ion bombardment energy. The plasma beam was generated using a grounded grid between the plasma chamber and the lower chamber that was evacuated by a cryogenic pump to maintain a sufficient low pressure ($10^{-5}$–$10^{-4}$ torr under typical operating conditions) so that gas phase collisions could be ignored in the lower chamber. The ion beam was charge compensated by tungsten filament electron emission that kept the space charge of the ion beam from expanding the beam and maintained the surface potential of insulating samples at ground potential. The neutrals also expanded through the grid producing a neutral flux at the sample.

The flux of the plasma reaching the sample surfaces was measured using a line-of-sight mass spectrometer that could measure both the neutral and ion fluxes as a function of feed gases, flows, power, and pressure. The mass spectrometer chamber was pumped by a turbomolecular pump and the pressure level was lower than $10^{-4}$ torr under typical processing conditions. At such low pressures, the mean free path of molecules and ions is larger than the distance between the mass spectrometer head and the orifice where the plasma was sampled. The electron impact energy was no larger than 40 eV so that the dissociation of molecules inside the mass spectrometer chamber is minimized.

The sample stage could be rotated about its axis to change the beam impingement angle to the substrate surface. This sample stage was also water cooled so that the sample temperature could be controlled. By manipulating the discharge pressure, plasma power, etc., the ion and neutral fluxes to the sample can be varied and measured by the mass spectrometer. This allowed the surface kinetics to be characterized and modeled over reasonable variation of plasma fluxes.

This plasma beam chamber was integrated to a vacuum cluster system on which a load lock and other process chambers, including an x-ray photoelectron spectroscopy (XPS) chamber, were connected together under vacuum through a central sample transfer tube. Samples could be moved between chambers under vacuum. A detailed description of this integrated vacuum system has been reported previously.$^{28}$

The surface etching rates were measured by determining the amount of material removed for a given exposure time. The thickness of thermal oxides and polysilicon was measured using a variable angle spectroscopic ellipsometer (J.A. Woollam M-2000); while a Tencor P-10 profilometer was used to measure the pre- and postetch low-$k$ coral film thicknesses. After etching, samples were transferred for XPS characterization before exposure to air.

### III. ANGULAR ETCHING YIELDS OF POLYSILICON IN Cl$_2$/AR PLASMAS

The etching yields of polysilicon in chlorine chemistry have been measured previously using reactive ion beams$^{29-32}$ or real plasma beams$^{33}$ that consisted of Cl and Cl$_2$ neutrals and ions. In the present work, polysilicon was etched in Cl$_2$/Ar plasma beams. Ar gas was added to the plasma since Ar neutral did not contribute to the etching process so that the plasma composition could be modulated. The ion and neutral flux compositions in the plasma beam at different Cl$_2$/Ar gas mixing ratios are summarized in Table I. At a

<table>
<thead>
<tr>
<th>Plasma pressure (mtorr)</th>
<th>Ion flux (%)</th>
<th>Neutral flux (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Cl$^+$</td>
<td>Cl$_2^+$</td>
</tr>
<tr>
<td>7% Cl$_2$</td>
<td>39.6</td>
<td>8.2</td>
</tr>
<tr>
<td>10% Cl$_2$</td>
<td>50.7</td>
<td>8.4</td>
</tr>
<tr>
<td>20% Cl$_2$</td>
<td>61.1</td>
<td>10.4</td>
</tr>
<tr>
<td>25% Cl$_2$</td>
<td>69.3</td>
<td>13.9</td>
</tr>
<tr>
<td>50% Cl$_2$</td>
<td>69.7</td>
<td>20.5</td>
</tr>
<tr>
<td>60% Cl$_2$</td>
<td>68.9</td>
<td>25.7</td>
</tr>
<tr>
<td>67% Cl$_2$</td>
<td>54.4</td>
<td>41.4</td>
</tr>
</tbody>
</table>

TABLE I. Ion and neutral flux compositions in the Cl$_2$/Ar plasmas used in this study determined by mass spectrometry.
fixed rf power level, with the increase of Cl₂ percentage in the feed gas mixture, the fraction of effective neutrals including both Cl and Cl₂ increases. In addition, Cl/Cl₂ ratio also decreases with increasing Cl₂ percentage in the feed gas. In terms of ions in the plasma, both of the Cl⁺/Cl₂⁺ ratio and Ar⁺ fraction decrease when increasing the Cl₂ percentage in the feed gas. In particular, only about 5% of ions or less contribute to Ar ions if the percentage of Cl₂ is higher than 60%. This is because the energy for Ar ionization (15.6 eV) is higher than Cl ionization (13 eV). For this reason, at high Cl₂ percentages, Ar acts mainly as a dilution gas in the plasma.

Figure 1 shows the polysilicon etching yield at normal ion incident angle as a function of ion bombardment energy and Cl₂/Ar gas mixing ratios. Obviously, the etching yields scale linearly with the square root of ion energy under each gas mixing ratio, which is consistent with the literature. In addition, the etching yields at each ion energy level increase gradually with the Cl₂ percentage in the feed gas mixture. Further analysis indicates that the polysilicon etching yields in the present work follow the typical ion enhanced etching kinetics described previously: initially the etching yields increase linearly with the effective neutral-to-ion flux ratios, then a saturated etching regime is reached at high ratios. These observations are plotted in Fig. 2 at different ion energies. The method that the neutral-to-ion flux ratio was estimated has already been described in detail previously. It is important to notice that plasma composition influences silicon etching yield in Cl₂ plasma beams. Figure 3 compares the etching yields in the present work (67% Cl₂, plasma source pressure of 14 mtorr, and effective neutral-to-ion flux ratio of 130–160) and previous work in Cl₂ plasma beam reported by Vitale et al. in the saturated etching regime. For comparison, the saturated etching yield data from Cl⁺/Cl (Ref. 32) and Cl₂⁺/Cl₂ (Ref. 29) beam studies are also plotted in Fig. 3. Silicon etching yields in Cl⁺/Cl beams are higher than those in Cl₂⁺/Cl₂ beams at a given ion energy level. Since real Cl₂ plasma beams are a mixture of Cl and Cl₂ ions and neutrals, the etching yields are in the range between those two extreme cases. In addition, higher etching yields would be resulted in Cl₂ plasmas with higher Cl⁺/Cl₂ and/or Cl/Cl₂ ratios. In the work of Vitale et al., the ratios of Cl⁺/Cl₂ and Cl/Cl₂ were 0.43 and 0.11, respectively. In the present work, for the plasma beam of 67% Cl₂ at 14 mtorr, the ratios of Cl⁺/Cl₂ and Cl/Cl₂ were 1.31 and 0.29, respectively. Therefore, the etching yields in the present work are higher than those in the work of Vitale et al. at a given ion energy level, although the effective neutral-to-ion flux ratios are 130–160 in the 67% Cl₂ plasma beam at 14 mtorr, which has not completely fallen in the saturated etching regime.

Figure 4 reports the normalized angular etching yields of polysilicon under three different plasma conditions (both the Cl₂ feed gas percentage and the plasma source pressure) and two different ion energies (dc 150 V and dc 250 V, or equivalently, 160 and 260 eV). At low Cl₂ gas percentage (7%) and low plasma source pressure (5 mtorr), the angular.

**Fig. 1.** Etching yield of plasma-enhanced chemical vapor deposition (PECVD) polysilicon in Cl₂/Ar plasmas as a function of the square root of ion bombardment energy for different Cl₂ percentages at normal angle. For comparison, the sputtering rate of polysilicon was also shown in this figure.

**Fig. 2.** Etching yield of PECVD polysilicon in Cl₂/Ar plasmas as a function of the effective neutral-to-ion flux ratio and ion bombardment energies at normal ion incidence angle.

**Fig. 3.** Variation of polysilicon etching yields in chlorine plasmas with plasma composition. Cl⁺/Cl data are from Chang and Sawin (Ref. 32), and Cl₂⁺/Cl₂ data are taken from Balooch et al. (Ref. 29). The data points are experimental results, and the lines are linear fit to our data.
yields at both ion energy levels exhibit sputtering characteristics, with a peak around 60° off-normal angle. In contrast, the angular yields at high Cl\textsubscript{2} gas percentage (67%) and high plasma source pressure (14 mtorr) demonstrate ion-enhanced-etching-like curves. For comparison, the angular yields in the saturated etching regime from previous studies are also plotted. Clearly, the angular yields at high Cl\textsubscript{2} percentage and plasma pressure, which lead to high neutral-to-ion flux ratio and push the etching kinetics to the saturated regime, are consistent with the data reported earlier.

**IV. ANGULAR ETCHING YIELDS OF THERMAL SiO\textsubscript{2} IN C\textsubscript{4}F\textsubscript{8}/Ar PLASMAS**

The etching yields of thermal silicon dioxide as a function of ion energy for various C\textsubscript{4}F\textsubscript{8}/Ar feed gas ratios and plasma source pressures are shown in Fig. 5. For comparison, SiO\textsubscript{2} sputtering yields in pure Ar plasmas are also plotted in this figure. The etching yields increase with ion bombardment energy for all conditions, which is consistent with the previous data in the literature. Moreover, the etching behavior is influenced by the C\textsubscript{4}F\textsubscript{8} percentage and/or the plasma pressure in the feed gas mixture. At low beam source pressure level (10 mtorr) and low C\textsubscript{4}F\textsubscript{8} percentage (10%), the etching is dominated by net etching over the ion energy range investigated in this work, while net deposition happens at low ion bombardment energies with high plasma source pressure and/or C\textsubscript{4}F\textsubscript{8} percentages. Here, net deposition at low ion energies occurs due to two different reasons. First, the plasma becomes more electronegative with more C\textsubscript{4}F\textsubscript{8} addition to the feed gas mixture for a given rf power, therefore, the electron density decreases partially due to the electron attachments, which consequently makes the ion density lower. At the same time, effective neutral concentration becomes higher since more C\textsubscript{4}F\textsubscript{8} is added in the plasma mixture. Second, the electron temperature decreases with the increase of the plasma pressure. For this reason, the ionization efficiency is less at higher plasma source pressures, and consequently the ion density decreases. Due to these two reasons, at high plasma source pressure and/or C\textsubscript{4}F\textsubscript{8} percentages, the ion flux reaching the surface is less while neutral flux becomes higher. Consequently, net deposition happens at low ion bombardment energies.

The corresponding normalized angular etching yields under these plasma conditions in Fig. 5 are characterized at several ion energy levels, as shown in Fig. 6. Most importantly, the shape of the angular etching yields is influenced by the etching parameters. At low plasma source pressure (4 mtorr) and low C\textsubscript{4}F\textsubscript{8} percentage (10%), the resulting angular etching yield curve is sputtering-like. On the other hand, the measured etching yields demonstrate ion-enhanced-etching characteristics at high plasma source pressure (13 mtorr) and high C\textsubscript{4}F\textsubscript{8} percentage (15%). In addition, ion bombardment energy might also affect the angular etching yields. Specifically, higher ion bombardment energy seems
to result in angular etching yields with more sputtering characteristics. For instance, during the etching in 10% C4F8 at 10 mtorr, the etching yield curve at dc bias 420 V is more sputteringlike compared to that at dc bias 250 V.

Figures 7–9 show the influence of ion incidence off-normal angle on the surface elemental composition of etched thermal silicon dioxide under those plasma conditions (plasma pressure and C4F8 percentage) described in Fig. 5 at dc bias 350 V. In particular, Fig. 7 reports the results at low plasma pressure (4 mtorr) and C4F8 percentage (10%), while Fig. 9 shows the elemental compositions for high plasma pressure (13 mtorr) and C4F8 percentage (15%). The elemental fraction of each species was calculated based upon its XPS spectra and corrected to its corresponding XPS sensitivity factors. By comparison of these three figures, one can see that the surface carbon and fluorocarbon fractions roughly increase while silicon and oxygen decrease by increasing the plasma source pressure and C4F8 percentage. This is because at high pressure and/or high C4F8 percentages, there are more sticky reactive neutrals available but with less ion flux reaching the surface. As a result, local fluorocarbon deposition becomes more significant. In addition, roughly speaking, the fraction of each species does not change much with the ion bombardment off-normal angle, and there is no obvious evidence to show that ion-enhanced polymer deposition effects are important at least in the range explored in this work. Additionally, the carbon and fluorine fractions at 75° off-normal angle after etching in the plasma beam at high pressure and C4F8 percentage are slightly lower than at lower off-normal angles. This might be because that the ion penetration depth becomes smaller at grazing angles at a given ion energy; therefore, the XPS signal intensities are attenuated more by the bulk SiO2 in the substrate than at lower off-normal angles.

At an approximately fixed plasma pressure (4–6 mtorr), the effects of C4F8 percentage (10%, 20%, and 33%) in the feed gas on the plasma composition were studied. The plasma neutral and ion compositions analyzed by mass spectrometry are shown in Figs. 10 and 11, respectively. The ionization efficiency, quadrupole transmission efficiency, and electron multiplier gain of various species have been considered when calculating the concentrations based upon their peak intensities. These sensitivity factors are adopted from previous studies. The mass range (amu) of the mass spectrometer was calibrated from 5 to 140.

In plasma neutrals, with the increase of C4F8 percentage in the gas mixture, the intensities of most of C and F related species such as C, CF, CF2, and CF3 increase, while the intensity of Ar decreases. In plasma ions, the situation is a little complicated. The intensity of Ar ion decreases with the increase of C4F8 percentage, which is consistent with our previous analysis since the plasma becomes more negative with more C4F8 addition. For C and F related ion species,
their intensities increase first, and then drop off. Actually, the same phenomenon was also observed for 10% C₄F₈/Ar plasmas with various plasma source pressures (5, 9, and 15 mtorr) and the results are not shown in this article. A possible explanation is related to the method of maintaining the inductively coupled plasma. The plasma is inductively coupled and the mass spectrometer locates on the sidewall of the beam source and is closer to the top. When the beam source pressure is pretty low, the high density region is larger and we are sampling the plasma from this denser region. When increasing the beam source pressure, the volume of this denser region is smaller, which means the ion density in this denser region might become higher since the rf used to produce the plasma is constant. If the mass spectrometer is sampling the plasma from the denser region in this scenario, the signal intensity would be higher. When increasing the beam source pressure further, the denser region shrinks further. Finally, it is possible to sample the plasma from outside of the denser region, and then the signal intensity would drop off. Since we only care about the fractions of each ion species reaching the sample surfaces and the absolute ion flux bombarding the sample surface can be quantified by an ion flux analyzer, this modulation of plasma ion composition with plasma source pressure has no significant negative impact on the current research.

The etching yields at normal ion incident angle are shown in Fig. 12 as a function of the square root of ion energy at these three different C₄F₈ percentages (10%, 20%, and 33%). Similarly, with the increase of C₄F₈ percentage, the etching yields at high ion energies (e.g., dc bias 350 V) increase while decrease and even fall into the net deposition regime at a very low ion energy level (dc bias 50 V) when the C₄F₈ percentage is high (20% and 33%). The corresponding normalized angular etching yields at dc bias 350 V for these three C₄F₈ percentages are summarized in Fig. 13. Consistently, at low C₄F₈ percentage (10%) the angular etching yields.
V. IMPACT OF O₂ ADDITION ON SIO₂ ANGULAR ETCHING YIELDS

The fluorocarbon thin film formed during the dielectric materials etching in fluorocarbon plasmas has an obvious influence on the etching kinetics and surface roughening evolution. Experimentally, people have shown that the thickness of this fluorocarbon thin film can be altered by changing the etching parameters, such as the ion bombardment energy, etching time, and more importantly the etching chemistry. Oxygen addition to the plasma will change the plasma composition, both the neutrals and ions; there-

Fig. 14. Impact of O₂ addition on the etching yields of thermal silicon oxide in 20% C₄F₈/Ar plasmas at different ion energy levels at normal angle. The plasma source pressures are 10 and 13 mtorr before and after O₂ addition, respectively. For comparison, the sputtering rate of thermal silicon dioxide in argon plasma was also shown in this figure.

curve is physical-sputtering-like; at high C₄F₈ percentage (33%) ion-enhanced-etching-like angular yield curve is formed. The angular etching yield curve at 20% C₄F₈ percentage is between these two extremes.

Fig. 15. Impact of O₂ addition on the angular etching yields of thermal silicon oxide in 20% C₄F₈/Ar plasmas. The plasma source pressures are 10 and 13 mtorr before and after O₂ addition, respectively. All of the etching yields were normalized to the corresponding etching yields at normal angle.

Fig. 16. Surface carbon (C₁s) XPS spectra of etched SiO₂ films. The etching parameters are (a) 0° off-normal angle, and (b) 75° off-normal angle in 20% C₄F₈/Ar plasmas at 10 mtorr; (c) 0° off-normal angle, and (d) 75° off-normal angle in 20% C₄F₈/20% O₂/Ar plasmas at 12 mtorr. In all cases, the ion fluence reaching the surface is 2.0 × 10¹⁷ ions/cm².
Therefore, the plasma polymer deposition capability is manipulated. In particular, more O₂ addition makes the plasma less polymerizing.

In the net etching regime in the present work, the effect of oxygen addition to the plasma on the angular etching yield evolution was studied. Figure 14 indicates the impact of oxygen addition on the etching yields at normal ion incident angle for 20% C₄F₈/Ar plasmas. It can be seen that oxygen addition has no obvious effect on the etching yields at high ion energies (e.g., dc bias 350 V). In contrast, the etching behavior is quite different at low ion energy levels. In particular, at dc bias 50 V, the etching is in the net deposition regime before oxygen addition, while it is in the net etching regime after oxygen addition. These experimental observations are consistent with the plasma composition analysis with oxygen addition. Since oxygen addition makes the plasma less polymerizing, the polymer formed on the surface even at a very low ion energy level (dc bias 50 V) is very thin and the etching process is still in the net etching regime. On the other hand, at high ion energies the polymer layer formed can also be relatively thin even without oxygen addition because of the high ion bombardment energy; therefore, the etching kinetics is not influenced significantly by the oxygen addition.

Figure 15 shows the resulting angular etching yield curves at dc bias 350 V before and after oxygen addition. Intriguingly, oxygen addition has no obvious impact on the angular etching yields under this specific situation. In both cases, the angular etching yield curves have similar trends. In particular, the etching yields almost keep constant up to 60° off-normal angles, and then drop off with the off-normal angle.

The surface carbon (C1s) XPS spectra at 0° and 75° off-normal angles of SiO₂ surfaces are shown in Fig. 16 after etching in 20% C₄F₈/Ar plasmas with and without oxygen addition. Various peaks including C–Si, C–C, and CFₓ (x =1,2,3) are found on the etching surfaces without oxygen addition; while mainly C–Si peak is detected after oxygen addition to the plasma. We believe that the carbon (C1s) XPS signal is a reflection of the content of fluorocarbon deposition on the substrate surface. Consistently, the fluorocarbon content on the etched surface is higher in plasmas without oxygen addition at both normal and 75° off-normal angles. On the contrary, O₂ addition leads to an etching kinetics with lower fluorocarbon content on the etched surface because of less polymerizing capability after O₂ addition. Based upon the angular etching yield curves in Fig. 15 and the XPS analysis results above, it is concluded that the polymer deposition effects on the angular etching yield evolution are not obvious under this specific scenario.

In order to have a better understanding of the polymer deposition effects, thermal SiO₂ was etched in plasmas with relatively higher polymer deposition capability: 15% C₄F₈/Ar plasmas before and after oxygen addition at plasma pressure of 18–20 mtorr. Figure 17 reports the etching yields at normal ion incident angle and Fig. 18 shows the resulting normalized etching yield curves at dc bias 350 V. Figure 19 summarizes the surface carbon (C1s) XPS spectra at 0° and 75° off-normal angles of SiO₂ surfaces after etching in 15% C₄F₈/Ar plasmas with and without oxygen addition. Similarly, oxygen addition to the plasma leads to less polymer deposition; therefore, weaker C1s signals in the XPS analysis for both 0° and 75° off-normal angles.

Consistently, in 15% C₄F₈/Ar plasmas at 18–20 mtorr, oxygen addition has more significant impact on the etching kinetics at low ion bombardment energies, where oxygen addition helps us to push the etching kinetics from net deposition to net etching. At a high ion energy level (dc 350 V), the etching yields at normal angle are slightly different. At this high energy level (dc 350 V), however, oxygen addition has an obvious impact on the angular etching yields. In particular, the angular etching yields decrease more quickly without oxygen addition. We believe that this angular etching...
yield difference is mainly caused by the difference of fluorocarbon deposition layer thickness. Further discussion of polymer deposition effects on angular etching yield curves will be performed in Sec. VIII.

VI. ANGULAR ETCHING YIELDS OF LOW-K CORAL MATERIAL IN FLUOROCARBON PLASMAS

Low-k dielectric materials etching in plasmas, especially in fluorocarbon plasmas, has attracted the interests of many researchers since low-k material is promising to lower signal delay between copper interconnects. However, the angular etching kinetics of low-k materials has seldom been addressed in the literature although it is one of the most important parameters that must be experimentally characterized. In this section, the angular etching yield of low-k dielectric coral material was studied in C4F8/Ar plasmas.

Figure 20 shows the etching yields of coral material at normal ion incident angle for two different plasma conditions: low plasma pressure (4 mtorr) and C4F8 percentage (10%), and high plasma pressure (21 mtorr) and C4F8 percentage (15%). Ion bombardment energy has obvious effects on the etching behavior, as has already been addressed for oxide etching in C4F8/Ar plasmas. The etching kinetics transits from net deposition regime to net etching with the increase of ion energy. In addition, the threshold energy needed to have net etching is higher than that for SiO2 etching. This might be related to the difference between coral and thermal silicon dioxide since there are doped ethyl groups in coral film. These ethyl groups in the preetched coral film might enhance the local fluorocarbon deposition in fluorocarbon plasmas; therefore, net deposition might happen at relatively high ion bombardment energy compared to SiO2 etching.

In fluorocarbon plasmas, the angular etching yields of coral demonstrate similar trends with SiO2 materials etching discussed previously in this article. Figure 21 shows the normalized angular etching yield curves of coral in C4F8/Ar plasmas described in Fig. 20 at dc bias 350 V. At low plasma pressure (4 mtorr) and C4F8 percentage (10%), the resulting angular etching yield curve is physical-sputtering-like. On the other hand, ion-enhanced-etching-like angular etching yield curve is resulted at high plasma pressure (21 mtorr) and C4F8 percentage (15%).
VII. IMPACT OF NEUTRAL-TO-ION FLUX RATIO

So far, it has been demonstrated in our experiments that etching parameters have an obvious impact on the evolution of angular etching yields. In particular, it seems that physical-sputtering-like angular curves are formed at low plasma source pressure and/or low effective reactive gas percentage (Cl₂ or fluorocarbon gas), while ion-enhanced-etching-like angular etching kinetics is resulted with high plasma source pressure and/or high effective reactive gas percentages. In addition, plasma source pressure and effective reactive gas percentage essentially affect the effective neutral-to-ion flux ratio, which is a key factor to determine the etching behavior. At low plasma pressure and/or reactive gas percentage, low neutral-to-ion flux ratio is resulted, where the etching process is limited by the reactive neutrals on the etching surface. In contrast, high plasma pressure and/or reactive gas percentage lead to high neutral-to-ion flux ratio, where enough reactive neutrals are available on the sample surface and the etching reaction is generally ion flux limited.

It has already been demonstrated that there are two etching regimes with changing the effective neutral-to-ion flux ratios for silicon etching in Cl₂/Ar chemistries, which has already been shown in Fig. 2. They were defined as nonsaturated and saturated etching regimes, respectively. In the nonsaturated etching regime, the neutral-to-ion flux ratio is very low and the etching yield increases almost linearly with increasing the neutral-to-ion flux ratio. At the saturated etching regime (high flux ratios), the etching yield only increases moderately with increasing flux ratio. Similar trends are also found from silicon dioxide etching in C₄F₈/Ar plasmas. Figure 22 summarizes SiO₂ etching yield variation with the effective neutral-to-ion flux ratio at different ion bombardment energies. Consistently, at low flux ratios nonsaturated etching kinetics is resulted, while high flux ratios push the etching to saturated etching regime.

 Intriguingly, it is found that physical-sputtering-like angular etching yield curves are resulted at the nonsaturated etching regime (low effective neutral-to-ion flux ratios). On the other hand, the angular etching kinetics is ion-enhanced-etching-like at the saturated etching regime (high neutral-to-ion flux ratios). Actually, these experimental observations are reasonable. In the nonsaturated regime, the etching surface is limited by reactive neutrals, and therefore, ion-enhanced etching is not dominating the etching kinetics and physical sputtering kinetics is important. Consequently, the overall angular kinetics has physical sputtering behavior, with a peak around 60°–70° off-normal angle. In the saturated etching regime, the etching surface is highly saturated with reactive neutrals, and ion-enhanced etching is much more important compared to physical sputtering kinetics. As a result, the resulted angular etching yield curves are ion-enhanced-etching-like.

The argument mentioned above is supported by the etching yield date at normal ion incident angle, which has been shown multiple times in previous sections. An example is the thermal SiO₂ etching yields at different C₄F₈ percentages shown in Fig. 12. At very low neutral-to-ion flux ratio (10% C₄F₈, 4 mtorr), the etching yield at a given ion energy is only doubled compared to the pure physical sputtering yield. Roughly speaking, this means the ion-enhanced-etching component is comparable to the physical sputtering component. Since the ion-enhanced etching is not dominating, the resulting angular etching yield curve has physical sputtering characteristics. On the other hand, at high neutral-to-ion flux ratio (33% C₄F₈, 6 mtorr), the overall etching yield is much higher than the pure sputtering yield at dc bias 350 V, which means that the physical sputtering kinetics is trivial in the overall etching kinetics. Therefore, ion-enhanced-etching-like angular etching yields are formed in this high neutral-to-ion flux ratio.

In order to have a further understanding of the impact of neutral-to-ion flux ratio on the angular etching kinetics, XPS analysis of etched polysilicon surface in Cl₂/Ar plasmas was performed at different ion bombardment angles and different plasma conditions. Figure 23 illustrates the signal intensity variation as the XPS takeoff angle is changed on an etched
polysilicon surface. The XPS signals at different takeoff angles in this figure have been corrected to the lens collection factors. The Cl(2p) signal intensity does not change obviously with the takeoff angle, which suggests that chlorine is mainly confined to the top surface with a layer thickness less than the integrated depth over which Si signal is collected. On the other hand, the Si(2p) signal intensity increases significantly when the takeoff angle increases from 30° to 80° because the XPS can sample deeper into the substrate at higher takeoff angles. Similar observations have also been reported by Chang and Sawin.28

The amount of chlorine incorporated into the substrate surface is strongly influenced by the processing conditions, such as the ion bombardment off-normal angle, ion energy, and neutral-to-ion flux ratio. Figure 24 shows the Cl(2p) photoemission intensity as a function of ion bombardment off-normal angle at different neutral-to-ion flux ratios and ion energies. Interestingly, the evolution of Cl(2p) intensity with off-normal angle at low flux ratio (7% Cl2, 5 mtorr) is quite different from that at high flux ratios (67% Cl2, 14 mtorr). At low flux ratios (7% Cl2, 5 mtorr), the Cl(2p) signal intensity is maximized at normal ion bombardment angle and then decreases obviously with increasing the off-normal angle. On the other hand, the Cl(2p) signal intensity remains relatively constant at different off-normal angles at high flux ratios (67% Cl2, 14 mtorr).

A possible explanation is related to the ion incorporation efficiency at different ion bombardment off-normal angles and the neutral-to-ion flux ratio. At low neutral-to-ion flux ratio (7% Cl2, 5 mtorr), the surface reaction is limited by the reactive neutrals on the surface, and reactive neutral adsorption has a trivial contribution to the surface chlorine concentration. Therefore, reactive ion incorporation mainly contributes to the chlorine on the top surface detected by XPS. Since the ion incorporation efficiency becomes lower at high off-normal angles compared to that at near normal angles,50,51 the overall amount of Cl(2p) photoemission intensity decreases as we increase the ion bombardment off-normal angle. At high neutral-to-flux ratio (67% Cl2, 14 mtorr), the etching is mainly limited by ions bombarding the surface. As a result, reactive neutral adsorption on the surface is more important and reactive ion incorporation becomes relatively trivial. Since the reactive neutral adsorption has a weaker dependence on the ion incident off-normal angle compared to ion incorporation, the overall Si(2p) photoemission intensity remains relatively constant at different ion bombardment off-normal angles.

VIII. POLYMER DEPOSITION EFFECTS

The angular etching yield curves in our current research always remain in the net etching regime even at grazing ion
bombardment off-normal angles. This is because polymer deposition becomes very significant on the mesh between the plasma source chamber and the processing chamber when the plasma becomes very polymerizing. Consequently, positive charge is accumulated on this polymer insulating layer since we use dc bias method to accelerate the ions across the plasma sheath. This positive charge on polymer insulating layer repels the ions coming from the plasma bulk and causes ion flux instabilities reaching the etching surface. As a result, the etching process is not stable and the resulting etching kinetics is not believable.

In the literature, however, many researchers have reported that net deposition happened when etching dielectric materials in fluorocarbon plasmas at grazing angles. For instance, Chae et al. reported the angular dependence of oxide etching yield with C4F8 and C4F8/O2 plasmas. When pure C4F8 plasma was used, the angular etching yield decreased quickly with increasing the off-normal ion incident angle, and the etching was in the net deposition regime when the off-normal angle is beyond 50°. On the other hand, with 60% C4F8/O2, the plasma was less polymerizing and the angular etching yield over the experimental range remained in the net etching regime.

People have argued that the fluorocarbon thin film formed on the etching surface of dielectric materials in fluorocarbon plasmas has a significant impact on the etching kinetics and surface roughness development. In particular, this fluorocarbon thin film was believed to play a key role on the resulting angular etching yield curve. Barklund and Blom proposed that the difference of polymer deposition rate at different ion bombardment off-normal angles was the main reason of forming physical-sputtering-like angular etching yield curve. Kwon et al. however, suggested an ion-induced position deposition mechanism to explain the variation of the angular etching yields under different processing conditions in fluorocarbon plasmas.

For the future work, it is critical to specify the polymer deposition effects on the angular etching yield curves. In the current work, where the etching is always in the net etching regime, however, polymer deposition effects are not the primary reason for the angular etching yield development. In particular, the thickness of the fluorocarbon polymer layer remained relatively thin since the plasma is not extremely polymerizing. In addition, the surface elemental composition analysis with ion bombardment off-normal angle shown in Figs. 7–9 indicates that fluorocarbon deposition rate is not influenced obviously by the off-normal angle although the thickness of the thin fluorocarbon layer, which is not necessarily continuous, varies with the plasma conditions. Therefore, the ion-enhanced polymer deposition effects proposed by Kwon et al., if they exist, are not important in the present work since the polymer thickness depends weakly on the ion bombardment off-normal angle.

**IX. CONCLUSIONS**

It has been demonstrated in an inductively coupled plasma beam reactor that the angular etching yields can be manipulated by changing the plasma processing conditions, such as the plasma source pressure, reactive feed gas percentage, and ion bombardment energy. The angular etching yield curve was more sputter-angling at low plasma source pressure and/or low effective gas percentage (C1 and C2), with a peak around 60°–70° off-normal ion incident angle. In contrast, ion-enhanced-etching-like angular curves, which dropped gradually with off-normal angle, were formed at high plasma source pressure and/or high effective gas percentage. These observations have a meaningful impact on the processing side of the integrated circuits. In particular, the surface roughening in plasma processing can be altered by manipulating the angular etching yield curves, which has been addressed in detail elsewhere. Further analysis indicated that the effective neutral-to-ion flux ratio reaching the surface was the primary factor to influence the angular etching yield curve. At low flux ratios, the etching process was limited by the reactive neutrals on the etching surface. Therefore, the overall etching process had physical sputtering characteristics since the ion-enhanced etching was not dominantly important. For this reason, the overall angular etching yield curve had physical sputtering characteristics at low flux ratios. At high flux ratios, enough neutrals were available on the etching surface and the overall etching process was limited by ion flux. Therefore, the overall etching process was really dominated by ion-enhanced etching and the resulting angular etching yield curve was ion-enhanced-etching-like. Although polymer deposition effects might have an obvious impact on the angular etching yield curves, it is not the primary factor over the experimental range explored in the present work since the fluorocarbon plasmas involved in this work were not very polymerizing.


Impact of etching kinetics on the roughening of thermal SiO$_2$ and low-$k$ dielectric coral films in fluorocarbon plasmas

Yunpeng Yin$^a$ and Herbert H. Sawin
Department of Chemical Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139
(Received 23 February 2007; accepted 21 May 2007; published 20 June 2007)

The impact of etching kinetics and etching chemistries on surface roughening was investigated by etching thermal silicon dioxide and low-$k$ dielectric coral materials in C$_4$F$_8$/Ar plasma beams in an inductive coupled plasma beam reactor. The etching kinetics, especially the angular etching yield curves, were measured by changing the plasma pressure and the feed gas composition which influence the effective neutral-to-ion flux ratio during etching. At low neutral-to-ion flux ratios, the angular etching yield curves are sputteringlike, with a peak around 60°–70° off-normal angles; the surface at grazing ion incidence angles becomes roughened due to ion scattering related ion-channeling effects. At high neutral-to-ion flux ratios, ion enhanced etching dominates and surface roughening at grazing angles is mainly caused by the local fluorocarbon deposition induced micromasking mechanism. Interestingly, the etched surfaces at grazing angles remain smooth for both films at intermediate neutral-to-ion flux ratio regime. Furthermore, the oxygen addition broadens the region over which the etching without roughening can be performed. © 2007 American Vacuum Society. [DOI: 10.1116/1.2748797]

I. INTRODUCTION

As the feature sizes have been continuously scaling down in order to maximize the transistor density, the interconnect signal delay becomes increasingly important. With copper as a common metallization material, lowering signal delay by signal delay becomes increasingly important. With copper as a common metallization material, lowering signal delay by replacing SiO$_2$ with low-$k$ dielectric can be a very promising choice. However, the application of these materials is often hampered by the lack of process compatibility with damascene process as scaling feature sizes continues. One of the major difficulties is related to the sidewall roughening produced in plasma etching process during the formation of vias and trenches for the fabrication of multilevel interconnects.5,6

The etching kinetics of SiO$_2$ and SiO$_2$-like low dielectric materials in fluorocarbon plasmas has been investigated extensively partially because of their ability to etch certain films selectively with respect to other films.7–12 From roughening perspective, however, many experimental observations have been reported and the mechanism causing surface roughening during plasma etching process is still vague.

As shown in the literature,6,13,14 top line-edge roughness (LER) played a very important role for the sidewall roughening of feature patterning in various etching chemistries. The top LER is defined as the roughness on the photoresist sidewall, and it is primarily formed during the development process of photoresist layer. In particular, Goldfarb et al.6 found that the resist sidewall roughness after development but before plasma etching was isotropic; during the antireflective coating layer opening in plasma etching process, the photoresist layer became striated and the top edge of the photoresist layer was faceted; the striation structure became much more significant and propagated down after etching of the subsequent SiO$_2$ layer.

The surface roughening of low-$k$ films may occur during etching in fluorocarbon plasmas in addition to the top LER effects on sidewall roughness evolution mentioned above. Consequently, it is crucial to fully understand the mechanisms of the inherent surface roughening before we can optimize the plasma etching conditions to minimize the surface roughness level after etching. The following questions should be answered before we can propose a plausible mechanism for surface roughening during plasma etching process. Is the roughening related to the etching chemistry and etching kinetics? Do film properties influence the roughness evolution?

In this article, the impact of etching chemistry and etching kinetics, especially the angular etching yield dependence, on surface roughening of thermal SiO$_2$ and low-$k$ dielectric coral materials has been investigated in C$_4$F$_8$/Ar plasmas. We found that the surface roughness evolution of these films is influenced by the etching conditions such as the etching chemistry and etching kinetics. It is shown in this article that the major cause of surface roughening at grazing impingement angles associated with LER is the angular dependence of the etching yield. At low neutral-to-ion flux ratios, the etching yield curve becomes physical with a peak in yield at about 65°. Under these conditions the surface is roughened because of the sputteringlike kinetics of the oxide etching. At high neutral-to-ion ratios, the greater polymerization potential (even without the formation of fluorocarbon deposition) can lead to roughening of the surface as well. Surfaces can be etched without roughening at intermediate ratios and/or with the addition of oxygen to the discharge. More interest-

$^a$Electronic mail: yinyp@mit.edu
ingly, the oxygen addition broadens the region over which etching without roughening can be performed.

II. EXPERIMENTS

The etching process was performed in an inductively coupled plasma beam scattering apparatus which has been described previously and is shown in Fig. 1. The plasma is formed in the upper chamber using inductive coupling to power the discharge. The chamber contains an insulating liner so that the plasma can be biased to create desired ion bombardment energy. The plasma beam is generated using a grounded grid between the plasma chamber and the lower chamber that is evacuated by a cryogenic pump which maintains a sufficiently low background pressure \(10^{-5} - 10^{-4}\) Torr under typical operating conditions. Gas phase collisions can be ignored in the lower chamber. The ion beam is charge compensated by tungsten filament electron emission that keeps the space charge of the ion beam from expanding the beam and maintains the surface potential of insulating samples at ground potential. The neutrals also expand through the grid producing a neutral flux at the sample. By manipulating the discharge pressure, plasma power, etc., the ion and neutral fluxes to sample can be varied and measured by the line-of-sight mass spectrometer. The sample stage can be rotated around its axis to change the beam impingement angle to the substrate surface. Sidewall roughening during plasma etching is investigated by etching blank films at glancing angles.

The surface etching rates are measured by determining the amount of material removed for a given exposure time. The thickness of thermal oxides was measured using a variable angle spectroscopic ellipsometer (J.A. Woollam M-2000); while a Tencor P-10 profilometer was used to measure the pre- and postetch low-\(k\) coral film thicknesses. The roughness of the surfaces was characterized using an \textit{ex situ} Digital Instruments 3100 atomic force microscope (AFM) in tapping mode. The sample can also be transferred \textit{in situ} for x-ray photoelectron spectroscopy (XPS) characterization.

The rms surface roughness levels of unetched thermal silicon dioxide and low-\(k\) coral materials are 0.2 and 1.0 nm, respectively. The XPS carbon (C1s) analysis suggests that there is no carbon on thermal SiO\(_2\) surface, while the carbon (C1s) peaks in coral material indicate that carbon exists as C=H and C–Si. The results discussed above are summarized in Fig. 2.

III. RESULTS AND DISCUSSION

A. Angular etching yields

Different researchers have demonstrated that the angular etching yields could be changed significantly with various etching chemistries and etching parameters. Here we also investigated the angular etching yields of thermal silicon dioxide and low-\(k\) coral films in C\(_4\)F\(_8\)/Ar plasmas as a function of plasma chemistry, plasma source pressure, and ion energy. The normalized etching yields of thermal silicon dioxide and coral are consistent with the trends in previous studies, which are shown in Figs. 3 and 4, respectively. In particular, at low neutral-to-ion flux ratios, the etching yield curves are sputtering-etching-like, with a peak around \(60^\circ - 70^\circ\) off-normal angles; while at high neutral-to-ion ratios the etching yield curves are ion-enhanced-etching-like. This transition of the etching yield curves from sputteringlike to ion-enhanced-etching-like has a significant impact on the surface roughening at grazing ion bombardments, as will be shown later on in this article. The possible explanation of the variation of the angular etching yields as a function of neutral-to-ion flux ratios is reported in another paper.

B. Surface roughening in pure sputtering kinetics

The sputtering caused surface roughening can be partially explained by the angular dependence of the etching yield...
At normal ion incidence angles, surfaces with initial large features are smoothed out due to the relative higher etching yield at large off-normal surface facet angles. At intermediate off-normal angles, the roughness evolution can be partially explained by Bradley and Harper’s model where the roughening and striation formation are caused by the surface instability due to the competition between curvature dependent sputtering caused roughening and surface diffusion caused smoothing. At high grazing angles (75° and 82° in this article), the striation development on the etched surface...
is mainly due to the ion scattering caused channeling effects. Specifically, the ion reflection probability increases with increasing the ion bombardment off-normal angle. These reflected ions travel along the ion beam impingement direction projected on the surface and form ion-channeling effects. Additionally, coral often displays higher roughening potential in many cases compared to SiO$_2$. One possible explanation might be due to the inherent film property differences between coral and SiO$_2$. In particular, coral is prepared using plasma-enhanced chemical vapor deposition method and there are some doped methyl or ethyl groups in the substrate, which might introduce some density variation to the film.

C. Roughening at grazing ion bombardment at different etching regimes

As mentioned earlier, the etching kinetics, especially the angular etching yields, have a significant impact on the
roughening of thermal SiO$_2$ and coral films at grazing angles in C$_4$F$_8$/Ar plasmas. Figures 5 and 6 show the variation of the surface roughness of SiO$_2$ and coral films with the plasma pressure and the C$_4$F$_8$/Ar volumetric ratios. In particular, from top to bottom in both cases, the neutral-to-ion flux ratio increases gradually with increasing plasma pressure and C$_4$F$_8$/Ar ratio. As can be seen from both films, the surfaces are roughened at low neutral-to-ion flux ratios (left-hand side), then become smooth at intermediate neutral-to-ion flux ratios, and are roughened again at high neutral-to-ion flux ratios (right-hand side). The corresponding surface carbon (C1s) XPS spectra under different etching conditions are also shown in Figs. 5 and 6. As reported previously in the literature, a thin layer of fluorocarbon layer, which is not necessarily continuous, was often formed during the etching of dielectric materials in fluorocarbon chemistries. We believe that the carbon (C1s) XPS signal is a reflection

Fig. 6. Surface AFM images and the corresponding surface carbon (C1s) XPS spectrums of low-k dielectric coral film after etching in C$_4$F$_8$/Ar plasmas under various plasma source pressures and C$_4$F$_8$/Ar volumetric ratios. The vertical scale of all films is 15 nm and all of the images represent 1 x 1 $\mu$m$^2$ of the real sample surface. The C$_4$F$_8$ percentage, beam source pressure level, and the ion fluence that reach the surface are (a) 10%, 4 mtorr, and 3.0 x 10$^{17}$ ions/cm$^2$; (b) 20%, 5 mtorr, and 3.0 x 10$^{17}$ ions/cm$^2$; (c) 20%, 8 mtorr, and 2.0 x 10$^{17}$ ions/cm$^2$; and (d) 20%, 15 mtorr, and 1.75 x 10$^{17}$ ions/cm$^2$, respectively. In all cases, the ions bombard the surface at 75° off-normal angle and the dc bias level is 350 V, and the ions reach the surface from the upright direction. The rms roughness and the film thickness etched are (a) rms 1.4 nm and 199 nm etched; (b) rms 0.57 nm and 211 nm etched; (c) rms 0.81 nm and 195 nm etched; and (d) rms 4.16 nm and 63 nm etched, respectively.
of the content of fluorocarbon deposition on the substrate surface. As demonstrated in both figures, the carbon (C1s) XPS signal becomes stronger with the increase of the neutral-to-ion flux ratios from left-hand side to right-hand side. This means that the local fluorocarbon deposition becomes more significant as the neutral-to-ion flux ratio increases. In addition, the carbon (C1s) peak around 280 eV for coral film corresponds to C–H signal, which also roughly becomes weaker when the neutral-to-ion flux ratio increases because the fluorocarbon content on the surface becomes stronger and C–H signal is attenuated.

The roughening of these two films at low neutral-to-ion flux ratios [Figs. 5(a) and 6(a)] is mainly due to ion-sputtering caused ion scattering effects rather than the local polymer deposition effects. The carbon (C1s) XPS spectrums at this low neutral-to-ion regime indicate that the carbon on the surface mainly exists in the form of C–Si, and no obvious CF$_x$ ($x=1,2,3$) related signal was detected. This suggests that local polymer deposition related effects are not important in terms of the surface roughness evolution. In contrast, as discussed earlier, the angular etching yield curves are sputteringlike in this low neutral-to-ion ratio regime. Therefore, the ion scattering caused ion-channeling effects along the ion bombardment direction become important. As a result, the surface becomes roughened and sometimes striations parallel to the beam impingement direction are formed, which can be clearly seen in Fig. 6(a).

On the other hand, the surface roughening of these two films at high neutral-to-ion ratios is mainly related to local fluorocarbon deposition induced micromasking effects that have been discussed in detail previously. As shown in Figs. 5(d) and 6(d), the surface carbon (C1s) XPS signals at this high neutral-to-ion ratio regime indicate that carbon on the surface mainly exists in the form of C–C and CF$_x$ ($x=1,2,3$) rather than C–Si. This makes sense because the surface can see more reactive fluorocarbon neutrals per ion bombardment; therefore, the surface fluorocarbon content is much higher than that at low neutral-to-ion ratios. As proposed in our previous studies of porous low-$k$ material roughening in fluorocarbon chemistries, this local fluorocarbon deposition introduces inhomogeneity on the substrate surface and leads to surface roughening. It is commonly observed that fluorocarbon rich surfaces are etched more slowly than oxide rich surfaces during exposure to the same plasma...
fluxes. Under the condition of high selectivity, it has been observed that polymer is deposited on the fluorocarbon surfaces while etching occurs on the oxide surfaces. Under these particular conditions, it is believed that the polymer rich regions grow while the oxide rich regions etch. This process continues with time, and the polymer rich regions form micromasks that induce roughening.

The evolution of the roughness with etching time of these two materials at high neutral-to-ion flux ratio regime is shown in Figs. 7 and 8. In general, the surface roughness level increases with increasing etching time for both films. For instance, the roughness level of coral increases from 1.42 to 4.16 nm when the ion fluence reaching the surface changed from $1.0 \times 10^{17}$ to $1.75 \times 10^{17}$ ions/cm$^2$. The typical dosage during an etching process is of order $10^{17} - 10^{18}$ ions/cm$^2$ on surface facets parallel to the macroscopic wafer surface and much less for facets nearly perpendicular to the macroscopic surface. Moreover, the surface carbon (C1s) XPS signal becomes stronger when the etching time increases. Specifically, C–Si signal becomes weaker while CF$_x$ ($x=1,2,3$) signal stronger. Consistently, the intensity of C–H peak in coral C1s spectrum decreases with etching time since more fluorocarbon deposition forms on the surface.

The results of roughness evolution with etching time at the high neutral-to-ion flux ratio regime discussed above are consistent with the proposed local-polymer-deposition induced micromasking mechanism. It is commonly observed that fluorocarbon rich surfaces are etched more slowly than oxide rich surfaces during exposure to the same plasma fluxes. Under the condition of high selectivity, it has been observed that polymer is deposited on the fluorocarbon surfaces while etching occurs on the dielectric surfaces. Consequently, fluorocarbon local deposition is more significant with the increase of etching time, which has already been confirmed by the C1s XPS spectrums shown in Figs. 7 and 8. Therefore, the inhomogeneity introduced by the fluorocarbon local deposition becomes more significant when the etching time is longer. As a result, the surface roughness level increases with etching time.

The surface roughness of both films after etching is minimized at intermediate neutral-to-ion flux ratios and the re-
results are shown in Figs. 5(b), 6(b), and 6(c). Consistently, the C1s XPS spectrums indicate that carbon on the surface is mainly bonded to Si to form C–Si. Again the C1s peak around 280 eV in coral film is due to the contribution of C–H bonds. Since the local fluorocarbon deposition on the surface is minimized, the inhomogeneity introduced to the surface is trivial. For this reason, the surfaces remain smooth after etching at this intermediate neutral-to-ion flux ratio regime.

**D. Effects of oxygen addition on roughening with grazing ion bombardment**

It is very intriguing that the etched surfaces remain smooth for both films at intermediate neutral-to-ion flux ratio regime. Furthermore, the oxygen addition broadens the region over which etching without roughening can be performed. The results shown in Figs. 9 and 10 display the roughening of these two films at different neutral-to-ion flux ratios with oxygen addition to the plasma. Obviously, the surface roughness level is comparable or lower than that before plasma etch. In particular, coral film becomes slightly smoother (rms roughness level of 0.4–0.6 nm) after etch, compared to the rms roughness level of 1.0 nm on unetched surface. Moreover, the C1s XPS analyses show that carbon on the surface is mainly C–Si for SiO2, and C–H and C–Si for coral; while CF\(_x\) (x=1, 2, 3) peaks are not obvious. This suggests that the plasma fluorocarbon deposition propensity is decreased by the oxygen addition. As a result, the surface fluorocarbon content is much lower compared to that without oxygen addition to the plasma. Therefore, the surface after etch remains smooth since the local polymer deposition induced micromasking is not important.

The impact of ion scattering caused channeling effects at intermediate and high neutral-to-ion flux regimes has not
been discussed so far. In fact, ion scattering is important in terms of roughness evolution when the angular etching yield curves are sputteringlike. However, this ion scattering effect becomes trivial when ion enhanced etching becomes more important during etching. Rasgon\textsuperscript{32} has demonstrated that during the etching of single-crystal silicon and polysilicon materials at grazing angles in HBr plasmas, where the plasma has almost no polymer deposition capability on the substrate surface and the angular etching yield curves are ion-enhanced-etching-like, surfaces remained smooth if there is no obvious initial roughness on the unetched films. The roughness evolution of thermal silicon dioxide and coral materials at intermediate neutral-to-ion flux ratios, where the ion enhanced etching becomes important and the local fluorocarbon deposition induced roughening is minimal, also suggests that the ion scattering effects are not important to develop surface roughness in ion enhanced etching kinetics.

IV. CONCLUSIONS

It was demonstrated that the etching kinetics has a significant impact on the surface roughening of thermal silicon dioxide and low-\(k\) dielectric coral films in \(C_4F_8/Ar\) plasmas. By manipulating the effective neutral-to-ion flux ratios through changing the etching parameters such as the plasma pressure and the \(C_4F_8\) percentage in the feed gas mixture, the etching kinetics can be physical-sputtering-like or ion-enhanced-etching-like. Specifically, at low neutral-to-ion flux ratios, the angular etching yield curves are sputteringlike with a peak around 60°–70° off-normal angle. At this low neutral-to-ion flux ratio regime, surfaces after etching are roughened due to the ion scattering effects. In contrast with the surface roughening at high neutral-to-ion flux ratios, where the etching kinetics is dominated by ion enhanced etching kinetics, local fluorocarbon deposition induced mi-
cromasking mechanism is the major reason of the surface roughening at grazing angles. Intriguingly, surfaces can be etched without roughening at grazing ion incidence at intermediate neutral-to-ion flux ratios and/or with the addition of oxygen to the discharge. The oxygen addition broadens the region over which etching without roughening can be performed.

ACKNOWLEDGMENT

The authors would like to thank Semiconductor Research Corporation for funding support.

Investigation of surface roughening of low-$k$ films during etching using fluorocarbon plasma beams

Yunpeng Yin, Stacy Rasgon, and Herbert H. Sawin

Department of Chemical Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139

(Received 27 March 2006; accepted 25 July 2006; published 25 September 2006)

The surface roughness evolution of solid organosilicate glass (OSG) and methylsilsesquioxane (MSQ) spin-on porous low-$k$ films after etching in $C_2F_6/Ar$ plasmas was characterized as a function of ion bombardment energy, ion fluence reaching the surface (or, equivalently, the etching time), ion impingement angle, and plasma polymerization propensity in a newly designed plasma beam system in which the plasma chemistry, ion energy, ion flux, and ion incident angle can be adjusted independently. A polymerization-induced micromasking mechanism was proposed to explain the surface roughening of these low-$k$ films. The porous structure in the substrate plays a critical role in the film roughening evolution. This effect can be understood using the concept of pore filling with polymeric deposits that etch more slowly under fluorocarbon plasma exposure. Upon exposure to etching, the polymer forms micromasks that induce roughening. Under the same etching conditions, the solid OSG film remains smooth during etching because only a fairly thin and uniform layer of polymer deposits on the surface of solid OSG substrates during the etching in $C_2F_6/Ar$ plasmas. Consequently, the inhomogeneity caused by the polymer deposition is not sufficient to induce micromasking in the absence of surface inhomogeneities. Additionally, the roughness level of the porous low-$k$ film etched in $C_2F_6/Ar$ plasma is primarily related to the film thickness removed, although it also increases with the ion bombardment energy; no similar trend was observed on nonporous OSG films under the same etching conditions. Striations formed when etching porous low-$k$ films at grazing angles. The striation formation is mainly due to shadowing effects, although conditions of net polymer deposition quenched the striation formation. © 2006 American Vacuum Society. [DOI: 10.1116/1.2338044]

I. INTRODUCTION

For the patterning of sub-100-nm features, a clear understanding of the origin and control of line-edge roughness (LER) is extremely desirable, both from a fundamental and a manufacturing perspective. Plasma etching processes often roughen the feature sidewalls, leading to the formation of anisotropic striations. It is this postetch sidewall roughness which ultimately affects device performance and yield.\(^1,2\)

When the device key dimensions shrink to the deep submicrometer regime, the interconnect resistance-capacitance ($RC$) delay can become dominant over intrinsic gate delay.\(^3,4\) Dielectric materials with low dielectric constants become advantageous in order to further reduce interconnect delay and enable higher device speeds. For instance, solid organosilicate glass (OSG) and methylsilsesquioxane (MSQ) spin-on porous low-$k$ films are attractive candidates.\(^4-6\) Specifically, the etching kinetics of various promising low-$k$ films in fluorocarbon plasmas and other etching chemistries have been reported.\(^7-12\) However, the integration of low-$k$ films as low-$k$ interlayer dielectrics presents new challenges from a roughening standpoint, particularly when using highly polymerizing fluorocarbon plasma chemistries typical of oxide etching. The first consequence of the sidewall roughening of low-$k$ film is the copper interconnect resistance increase related to the deposition of thicker conformal liner/barrier layers to avoid gaps that would allow the diffusion of Cu into the pores of the low-$k$ materials.\(^13,14\) Because of the sidewall roughness after plasma processing, a thicker layer of barrier layer has to be deposited in order to get good coverage. Consequently, the space for subsequent copper line filling is limited, which leads to the increase of the copper interconnect resistance. In addition, the postetching cleaning of low-$k$ film surfaces before the deposition of the liner layer becomes difficult due to the sidewall roughness, especially for the cleaning of porous low-$k$ films because of the retaining of fluorocarbons in the pores. Roughening can also lead to shadowing effects, although top LER (or equivalent templating effects) plays a very important role for the sidewall roughening of oxide patterning during etching in fluorocarbon chemistries. It was found that the resist sidewall roughness after development (but before plasma etching) was isotropic; during the antireflective coating layer opening in the plasma etching process, the photoresist layer became striated and the top edge of the photoresist layer was faceted. The striation structure became much more significant and propagated down after etching of the subsequent SiO$_2$ layer. The surface roughening of low-$k$ films may occur during etching in fluorocarbon plasmas, in addition to the templating effects on sidewall roughness evolution mentioned above. Consequently, it is crucial to fully understand the

\(^{4}\)Electronic mail: yinyp@mit.edu
mechanisms of the inherent surface roughening before we can optimize the plasma etching conditions to minimize the surface roughness level after etching.

In this article, the inherent roughening of low-k films during plasma etching was investigated in the fluorocarbon plasma chemistries. The roughening was characterized as a function of ion bombardment energy, ion fluence, ion impingement angle, and plasma polymerization propensity of C₂F₆/Ar plasma beams. Our objective is to explore the inherent roughening mechanism of low-k films during plasma etching.

II. EXPERIMENTS

A. Plasma beam reactor

Commercialized and home-designed plasma etchers have been extensively used to characterize the etching kinetics of low dielectric constant materials, as well as other films in various etching chemistries. Plasma etchers lack the flexibility to control the plasma chemistry, ion bombardment energy, and incident angle independently, which is needed in order to fully understand the origin and evolution of the surface roughness during plasma etching. Therefore, a new dedicated plasma beam apparatus with the abilities mentioned above has been designed to characterize the etching kinetics and roughening of semiconductor materials. The schematic of this newly designed beam chamber is shown in Fig. 1.

The beam source is located at the upper part of the main chamber, with the plasma powered by inductively coupling through a ceramic/quartz window located on the top of the chamber. A ceramic/quartz liner is used to isolate the plasma from the wall, which enables the plasma to be dc biased up to 500 V by using a metal electrode placed on the interior of the beam source. The plasma potential relative to ground is the sum of the dc bias applied to the metal electrode and the plasma self-biased potential, which is typically 5–20 eV with the plasma density sufficiently high that the power is primarily coupled inductively. The pressure in the beam source can be controlled by throttling the flow to a turbomolecular pump (Leybold TMP 361). The lower chamber is evacuated by a 4000 l/s cryogenic pump (CTI Cryogenics Cryo-torr 8), maintaining a base pressure of 10⁻⁸ torr and a pressure of ~1.0 × 10⁻⁴ torr during processing, thus ensuring an adequately long mean free path for beam scattering. The plasma beam is extracted from the beam source to the lower part of the main chamber through a gridded orifice, which is grounded. A tungsten filament (0.004 in. in diameter) emits low energy electrons into the emerging beam in order to minimize the beam spreading due to space charge and to prevent charging of insulated samples. The lower chamber holds a sample stage (for about 0.5 in. wafer chips), an ion energy analyzer (to characterize the ion bombardment energy of the ions in the beam), and an ion flux analyzer (to characterize the ion current/flux from the beam). All three items are mounted on linear motions, rotatable or z axis feedthroughs, and can be backed away from the chamber center when not in use.

The sample stage can be rotated about its axis to change the beam impingement angle to the substrate surface. Sidewall roughening during plasma etching is investigated by etching blank films at glancing angles. One of the advantages of this method is that it is much more convenient to characterize the surface roughness on blank samples using the atomic force microscopy (AFM) technique.

B. Ion energy analysis

A gridded “retarding field” energy analyzer was used to analyze the ion energy distribution levels in the plasma beam chamber system. A detailed schematic of the design has been shown elsewhere. The assembly is mounted inside a grounded aluminum housing. The pressure inside the system is around 1.0 × 10⁻⁴ torr or less during operation so that the collisions of ions inside the system will not distort the measurements. Figure 2 gives typical I-V curves and ion energy distribution function (IEDF) measured by this ion energy analyzer. The averaged ion energy level scales very well with the dc bias voltage applied and the difference between these two reflects the plasma self-bias potential, which is about 5–20 eV in inductive coupling mode.

The low energy tail of the IEDFs shown in Fig. 2(b) may be related to the collisions of ions in the plasma sheath, since the sheath becomes more collisional as the sheath thickens with increasing dc bias voltage. For collisionless sheaths in low pressures, the Child-Langmuir sheath kinetics give the sheath thickness such that

\[
d = \sqrt{\frac{4\varepsilon_0 k T}{9e}} \left( \frac{2e^{v_0}}{m} \right)^{1 \frac{3}{2}} \frac{1}{j},
\]

where \(\varepsilon_0\) is the dielectric constant, \(e\) the elementary electric charge, \(m\) the ion mass, \(j\) the ion current density at the plasma-sheath boundary, and \(V\) the voltage drop across the sheath. \(V\) is equal to the summation of the dc bias level and the plasma self-bias potential at the center of the grounded orifice. For the collisional sheath in which the ions’ movement is mobility limited, the sheath thickness is given by

[Image of a newly designed beam chamber system. The beam source locates at the upper part of the main chamber and the plasma is inductively coupled. This beam system has the flexibility to control the plasma chemistry, ion bombardment energy, and incident angle independently.]
For Ar plasma at 10 mtorr with radio frequency source power level at 350 W, the ion current density \(j\) at the plasma-sheath boundary was estimated to be \(\sim 130 \mu A/cm^2\) and is a very weak function of dc bias voltage level. The mean free path \(\lambda_i\) is about 3.3 mm under these plasma running conditions. The plasma sheath is collisionless when the sheath thickness estimated by (1) is smaller than the mean free path (\(\sim 3.3 \text{ mm for Ar at 10 mtorr}\)); otherwise the plasma sheath is collisional and the thickness can be estimated by (2). The estimated plasma-sheath thickness is shown in Fig. 3 as a function of dc bias voltage level. The plasma sheath is collisionless when the dc bias is low enough and there are trivial ion collisions in the sheath region. This can explain why there is almost no low energy tail on the IEDF at the dc bias level of 100 V in Fig. 2(b). On the contrary, the plasma sheath is collisional when the dc bias level is high enough (dc bias level of 150 V or more), which leads to the significant low energy tails of the IEDFs at the corresponding dc bias levels.

### C. Plasma beam uniformity

Well controlled plasma beam uniformity is desired in order to achieve accurate etching kinetics on various substrates by \textit{ex situ} film thickness measurements. Over the entire range of our measurements, the variation of the normalized ion current across the sample is less than 20%. In this newly designed plasma beam chamber system, the uniformity of the plasma beam extracted from the grounded orifice is controlled by neutralizing the space charge using low energy electron emission from the tungsten filament. Figure 4 shows the contour plots of the normalized ion current collected by the ion flux analyzer at dc bias values of 100 and 350 V along the beam center for 10 mtorr Ar plasma with rf source power at 350 W. The plasma beam uniformity is poor when the space charge neutralization filament is turned off. Specifically, the beam uniformity is even worse at high dc bias. Consequently, a small misalignment during the film thickness characterization might result in a large error of the corresponding etching rate measurements when using this beam. However, the plasma beam uniformity is well controlled using the tungsten filament with a filament current \(1.4 \text{ A}\), as shown in Fig. 5. The variation of the ion current is less than 20% over the sample center diameter of 0.3 in. when the dc bias level is 100 V. The beam uniformity is enhanced by increasing the dc bias.

### D. Plasma composition analysis

A UTI 100C quadrupole line-of-sight mass spectrometer is used to analyze the ion and neutral compositions for \(\text{C}_2\text{F}_6/\text{Ar}\) plasmas addressed in this work. The ionization efficiency, the quadrupole transmission efficiency, and the electron multiplier gain of various ions have been explored previously\(^{27,30,31}\) and were adopted here for semiquantitative plasma composition analyses. An electron impact energy of 30 V was used to avoid fragmentation of neutrals in the ionizer. The ionizer grids were grounded when analyzing the plasma ion composition.

Figures 6 and 7 give the neutral and ion spectra of 10% \(\text{C}_2\text{F}_6/\text{Ar}\) and 20% \(\text{C}_2\text{F}_6/\text{Ar}\) plasmas with a total flow rate of 5 SCCM (SCCM denotes cubic centimeter per minute at STP) and a beam source pressure of 10 mtorr at 350 W radio frequency source power. The fluorocarbon species greatly
increased in the ion spectrum when increasing the flow rate percentage of C\textsubscript{2}F\textsubscript{6} from 10% to 20% in the mixed feed gas. Additionally, the amount of silicon related species (SiF\textsubscript{x}, \( x = 1, 2, 3 \)) and CO decreased in the ion spectrum, while there was no such trend observed in the neutral spectra. The silicon bearing species and CO were created by the plasma interaction with the quartz liner.

### E. Standard etching procedure and film characterization methods

Polymer was gradually deposited on the liner interior when the fluorocarbon plasma run, which gradually modified the chamber conditions. Consequently, the plasma composition in the gas phase was also influenced by the chamber history. A standard etching procedure was developed to minimize the historical effects. Before each sample etching experiment, the chamber was cleaned and warmed up in Ar/O\textsubscript{2} plasma for about 15 min, followed by 4 min of running with identical running conditions to the sample etching experiments.

An \textit{in situ} x-ray photoelectron spectroscopy (XPS) was used to characterize the near surface composition before and after plasma etching of the low-\textit{k} substrates. Both the XPS chamber and the plasma beam chamber were integrated with an ultrahigh vacuum transfer tube running at 10\textsuperscript{-8} torr, which enabled \textit{in vacuo} sample transfer between the process and analytic chambers. The schematic of the transfer tube system has been demonstrated elsewhere.\textsuperscript{32}

A Tencor P-10 profilometer was used to measure the pre- and postetch porous low-\textit{k} film thicknesses, since the polymerization in the porous structure could change the film composition, rendering ellipsometry unreliable. Surface roughness was measured using a Digital Instruments 3100 AFM in tapping mode. Standard tapping-mode etched silicon probe tips were used to image the surfaces. Root-mean-squared (rms) roughness of each image was calculated after correcting any residual line-to-line offsets. All images were 1 \times 1 \mu m\textsuperscript{2}, 256 line scans, with 256 pixels/line scan.
III. RESULTS AND DISCUSSION

A. Characterization of unetched films

Solid OSG and MSQ spin-on porous low-k films supplied by Texas Instruments Corporation were used in this work. Specifically, both the OSG and the porous low-k film were spun-on coated on single crystal silicon wafers. The dielectric constant of the solid OSG film was about 2.8. The porous low-k film had a solid phase composition similar to the OSG, with approximately 30% porosity and a dielectric constant of around 2.2.

The unetched OSG and porous low-k films were characterized using AFM. The images are shown in Fig. 8. The vertical scale of both films is 10 nm. The rms roughnesses of OSG and porous low-k films are 0.9 and 1.2 nm, respectively. Compared with the etched samples, which will be discussed later on, both the preetched films are very smooth, although the porous low-k film was slightly rougher than the solid OSG film. This might be due to the porous structure of the porous low-k film, although the radius of curvature of the AFM tip is actually likely too large to capture the pore structure in the images. In addition, the roughness of both preetched films is isotropic, with no specific orientation.

The near surface elemental compositions of these two low-k films were characterized by XPS and summarized in Fig. 9. The surface atom fractions are based upon the signal intensities of each element after correction of the corresponding XPS sensitivity factors:

- $S_{\text{Si}(2p)} = 0.817$
- $S_{\text{C}(1s)} = 1.00$
- $S_{\text{O}(1s)} = 2.93$
- $S_{\text{F}(1s)} = 4.43$

As shown in Fig. 9, no fluorine species was detected on both the low-k films by XPS before processing in fluorocarbon plasma beams. The XPS result indicates that the OSG and the porous low-k films have similar chemical composition, except that there is a bit more carbon in the OSG film.

B. Surface roughness evolution with etching time

The surface roughnesses of solid OSG and porous low-k films after processing in 20% C$_2$F$_6$/Ar plasma are shown in Figs. 10 and 11 as a function of ion fluence reaching the sample surface at the normal angle. The plasma etching conditions are as follows: total flow rate of 5 SCCM, beam source pressure of 10 mtorr, radio frequency source power of 350 W, and ion bombardment energy of 370 eV, which corresponds to dc bias voltage of 350 V. The porous low-k films became significantly roughened after etching and became even rougher with the increasing ion fluence. In particular,
the porous low-k film roughening increased, with the rms roughness value going from 3.2 to 9.0 nm, as shown in Fig. 10. In contrast, the solid OSG films remained smooth after processing under identical plasma etching conditions. The roughness of OSG appeared to approach a constant at rms value of 1.0 nm for both of the ion fluences of $2.0 \times 10^{17}$ and $5.0 \times 10^{17}$ ions/cm$^2$.

The XPS C(1s) signal before and after processing in 20% C$_2$F$_6$/Ar plasma for both solid OSG and porous low-k films is shown in Fig. 12. The C(1s) signal loses its symmetry after processing in fluorocarbon plasma. The high energy tail is caused by the CF, CF$_2$, and CF$_3$ peaks of the thin fluorocarbon films deposited on the surface of the substrates during processing in fluorocarbon plasmas. Similar XPS characterization results have been reported in the literature. The polymer layer deposited on the surface of OSG after processing is very thin according to the XPS C(1s) signal in Fig. 12(a). Additionally, the polymer film thickness does not vary greatly with the increase of etching time. The polymer thickness on the porous low-k film is also thin when the processing time is short (ion fluence level of $2.0 \times 10^{17}$ ions/cm$^2$). However, the polymer layer becomes thicker when the processing time is longer (corresponding to $5.0 \times 10^{17}$ ions/cm$^2$), which results in relatively stronger CF$_x$ ($x=1, 2, 3$) peak intensities at the high energy tail in C(1s) signal. This trend is believed to be related to the porous structure in porous low-k films, which retains fluorocarbon chain structures during etching in fluorocarbon plasmas. These polymer chains retained in the pores enable further polymer deposition and make the polymer layer thicker.

C. Effects of ion bombardment energy on surface roughening and etching kinetics

Figure 13 gives the etching rate and surface roughness of solid OSG and porous low-k films after etching in 20% C$_2$F$_6$/Ar plasma. The plasma running conditions are as follows: total flow rate of 5 SCCM, beam source pressure of 10 mtorr, and rf source power of 350 W. The etching rate of both films increases when the ion bombardment energy level is higher, as shown in Fig. 13(a). Additionally, the porous low-k film etches
faster than the solid OSG film because the porous structure in the film makes the substrate less dense. With the increase of the ion bombardment energy, the porous low-\(k\) film becomes rougher, while the roughness of the solid OSG film is almost constant and identical to the rms roughness value of 1.0 nm before etching, which can be seen in Fig. 13(b).

XPS analysis result suggests that the thickness of the fluorocarbon film is thicker at low ion bombardment energies for both the solid OSG and porous low-\(k\) films, which can be seen in Fig. 14. Additionally, the signal intensities of CF\(_x\) (\(x=1, 2, 3\)) at the high binding energy tail become weaker as the ion bombardment energy grows higher, which indicates that the fluorocarbon layer on the surface becomes thinner with the increase of the ion energies. Our observation is consistent with the results in the literature. Standaert \textit{et al.}\(^{20}\) argue that the etching rates of SiO\(_2\) in fluorocarbon plasma are significantly influenced by the thin fluorocarbon film deposited on the substrate film during plasma processing. More specifically, a higher etching rate is typically accompanied by thinner fluorocarbon film. Through the molecular dynamics simulation approach, Vegh \textit{et al.}\(^{35}\) also found that the etching yield of silicon in fluorocarbon and Ar plasmas is inversely related to the fluorocarbon film content on the substrate surface.

The XPS results also confirm that the porous structure in porous low-\(k\) films enhances the fluorocarbon polymer thin film deposition. For instance, the porous low-\(k\) substrate surface is covered by a relatively thick layer of fluorocarbon film when the dc bias level is 50 V; the XPS signal of other species, including O(1s) and Si(1s) (XPS spectrum not shown here), cannot be detected below this ion energy level since the polymer layer is thick. Consequently, net deposition occurs under this condition, as shown in Fig. 13(a). However, the fluorocarbon film is not thick enough to stop the etching process for the solid OSG film at the dc bias level of 50 V because of the absence of porous structure in the solid OSG film.

D. Impact of plasma polymerizing effects on surface roughening

The etching kinetics of solid OSG and porous low-\(k\) films is significantly influenced by the plasma polymerization ca-
pability. Figure 15 shows the etching rate and surface roughness of both films after processing as a function of C$_2$F$_6$ molar percentage in the feed gas. The plasma running conditions are a total gas flow rate of 5 SCCM, beam source pressure of 10 mtorr, rf source power of 350 W, ion fluence of 5.0 \times 10^{17} \text{ ions/cm}^2, and ion energy level of 370 eV (equivalent to dc bias of 350 V).

Consistently, net deposition is always accompanied by a fairly thick fluorocarbon film, which corresponds to strong CF$_x$ signal intensities at the high binding energy tail shown in Fig. 16.

The etching rate variation with C$_2$F$_6$ percentage in C$_2$F$_6$/Ar is partially related to the modulation of ion flux by the addition of Ar. Specifically, the direct ion penetration into the substrate surface is enhanced when the ion flux is high and the ion-bombardment-induced mixing mechanism contributes more to the etching. It was found in this work that the ion flux reaching the sample surface was enhanced by the addition of Ar. Pure C$_2$F$_6$ plasma under these plasma running conditions is not stable, which can be seen under visual observation in terms of luminosity difference. It is believed that negative ions are formed by electron attachment in fluorocarbon plasma, which can cause fluctuation of electron density and consequently leads to plasma instability. In contrast, Ar is electropositive and the addition of Ar to the fluorocarbon gas increases the electron density and energy of the plasma, thereby stabilizing the plasma, which consequently results in the increase of the ion density according to the ambipolar diffusion assumption. Therefore, the ion flux extracted from the grounded gridded orifice is also enhanced. This ion flux enhancement is not significant until the Ar percentage exceeds some threshold value related to the fraction required to increase the electron energy. Since the ionization energy for Ar atoms is about 15.68 eV, which is higher than those for fluorocarbons and the fluorocarbon dissociation products in most ionization processes, the addition of Ar does not initially change the electron energy. As a result, Ar

![Figure 15](image1)

![Figure 16](image2)
only acts as a dilution gas when the molar percentage of it is lower than the threshold value. With greater dilution, Ar is ionized as the electron energy increases. The modulation of ion flux in fluorocarbon plasmas by the addition of Ar has also been reported in the literature and is consistent with our observations.21,37

Another contribution to the etching rate variation is the impact of the C2F6 percentage on fluorocarbon neutral concentrations in the plasma. Generally speaking, fluorocarbon neutral concentrations become higher with the increase of C2F6 percentage, as already demonstrated in Fig. 6. Higher neutral concentration levels in the plasma phase typically enhance the adsorption of fluorocarbon neutrals on the substrate surface and tend to result in thicker fluorocarbon film on the film surface. This argument has already been proved by experiments and molecular dynamics simulation.20,35 Our etching rate measurement also supports this argument. For instance, the etching kinetics go from net etching to net deposition when the percentage of C2F6 increases from 20% to 40%.

The evolution of surface roughness of these two films with the percentage of C2F6 shows totally different trends. The solid OSG film surface after etching is independent of the C2F6 percentage and always remains smooth. In contrast, the roughening of porous low-k films can be divided into three regimes according to the polymerization capability of the plasma: net deposition regime, “clean” etching regime, and local polymer deposition regime. The surface remains smooth after etching in the net deposition regime. For instance, the rms roughness of the porous low-k film is about 1.0 nm after etching in 40% C2F6/Ar plasma. In the clean etching regime, the plasma polymerization effects are trivial and the surface after etching becomes moderately rougher. Etching of the porous low-k film in 10% C2F6/Ar plasma falls into this regime where the rms roughness after etching is 2.2 nm. In the local polymer deposition regime, the surface becomes much rougher after etching. The etching of the porous low-k film in 20% C2F6/Ar plasma (rms values goes up from 1.2 nm before etching to 9.0 nm) is an example of this regime.

E. Local polymer deposition induced micromasking roughening mechanism

The surface roughening of low-k films during etching in fluorocarbon plasmas can be explained by a polymerization-induced micromasking mechanism, which is shown schematically in Fig. 17. The porous structure in the substrate plays a critical role in the film roughening evolution. The pores at the near surface region in the substrate allow the deposition of fluorocarbon polymers within the protected recesses of the pores, which are shielded from ion bombardment. Consequently, local polymer-rich regions form on the surface. It is commonly observed that fluorocarbon-rich surfaces etch more slowly than oxide-rich surfaces during exposure to the same plasma fluxes. Under the condition of high selectivity, it has been observed that polymer is deposited on the fluorocarbon surfaces while etching occurs on the oxide surfaces. Under these particular conditions, it is believed that the polymer-rich regions grow while the OSG-rich regions etch. With time, the polymer-rich regions form micromasks that induce roughening.

The surface roughness evolution of the solid OSG film is very different from that of the porous low-k film because of the absence of a porous structure in the substrate. Only a very thin layer/amount of polymer forms on the surface of the solid OSG film in the net etching regime. The polymer deposition inhomogeneity is not significant to trigger the formation of polymer-rich and OSG-rich regions to roughen the surface.

This proposed polymer deposition induced micromasking roughening mechanism explains the experimental results. First, it demonstrates why the porous low-k film becomes rougher when the etching time is longer while the solid OSG film does not become rougher after etching in 20% C2F6/Ar plasma, as shown in Figs. 10 and 11. Since the etching kinetics in 20% C2F6/Ar plasma is in the local polymer deposition regime as mentioned in Sec. III D, the inhomogeneity caused by local polymer deposition becomes more significant when the etching time is longer and, consequently, the surface becomes rougher after etching. In contrast, the amount of polymer accumulated on the surface of the solid OSG film is small and does not change with etching time because of the absence of pores; the surface remains smooth after etching for different time scales. Second, this micromasking mechanism explains why the roughening of porous low-k films can be divided into three regimes according to the polymerization capability of the plasma. A fairly thick layer of polymer is deposited on the substrate surface when net deposition is prevalent on both films; the micromasking roughening mechanism is not in effect, the surface of both films remains smooth after etching, and the rms roughness values are almost identical to each other. Minor polymer deposits on the substrate surface in the clean etching regime; the micromasking mechanism, if it exists, is not very important. Interestingly, slightly more polymer is accumulated on the porous low-k film surface and the surface after etching becomes moderately rougher. Appropriate amounts of polymer are retained on the porous low-k film, which makes the micromasking mechanism very significant and leads to a much rougher surface after etching. Similarly, the totally different roughness evolution trend between solid OSG and porous low-k films is caused by the porous structure. Third, the roughening of both films as a function of ion bombardment
energies is also consistent with this micromasking mechanism. It has been mentioned in Fig. 13(b) that the roughness of the porous low-$k$ film scales with ion energy, while for the solid OSG film it does not. Interestingly, the roughness of the porous low-$k$ film after etching in the net etching regime is mainly related to the amount of film removed, as indicated in Fig. 18. This is because the polymer deposition induced inhomogeneity on the porous low-$k$ substrate is more significant after more material is removed according to the micromasking mechanism. This argument is again not applied to the solid OSG film because of the absence of porous structure in the substrate; consequently, the surface remains smooth no matter how much material is removed.

F. Surface roughening during etching at grazing angles

Surface kinetics of low-$k$ film etching at a grazing angle can be achieved by adjusting the angle between the ion impingement direction and surface normal, which is defined as off-normal angle. Figure 19 gives the surface topography evolution of OSG and porous low-$k$ films after etching at a grazing angle in $C_2F_6/Ar$ plasma chemistry. The ion dosage levels are measured at normal angle and corrected to the corresponding view factor at 75° off-normal angle. Most surprisingly, a striation structure parallel to the ion beam impingement direction emerges, which does not exist for the etching at normal angle. The striation structure on the porous low-$k$ film is more significant than that on the solid OSG film.

A possible explanation of the striation formation on the substrate during etching at glancing angle is related to the shadowing effects. As is well known, the substrate surface is not perfectly smooth; indeed, there are some microsize cones, pyramids, or ridges on the surface. These microstructures might show some shadowing effect at the initial stage of the etching, as shown in Fig. 20. Due to the very glancing angle formed by the beam ions, areas of the surface directly behind a protrusion receive no flux. Consequently, this portion of the surface could not be etched during etching and, therefore, some specific shadowing structure formed and will be propagated along the beam direction. Finally, the striation structure forms on the surface.

There is a good way to check if the proposed shadowing effect is reasonable or not. As has been mentioned previously, uniform polymerization will be prevalent when the dc bias level is low enough for the etching of the porous low-$k$ film at normal angle in $C_2F_6/Ar$ plasma chemistry. Net polymerization can also be achieved for the etching of the porous low-$k$ film in $C_2F_6/Ar$ chemistry at glancing angle (off-normal angle is 75°); the AFM image of the etching under this condition is shown in Fig. 21. Most importantly, the shadowing effect is not possible because of net polymerization. As an impact, the striation structure is quenched and isotropic roughness results. Additionally, the rms roughness of the substrate after etching becomes smoother compared to the preetched porous low-$k$ film.

Although polymerization can quench the striation structure, it is not crucial for the origin of the striation formation, at least under these conditions. Figure 22 gives the surface topography evolution of the porous low-$k$ film after sputtering in pure Ar chemistry with real ion fluence level of $1.5 \times 10^{17}$ ions/cm$^2$. As can be observed from the AFM images,
the striation structure is developed at glancing angle using only Ar sputtering, which does not have any polymerization capability. As a result, the polymerization effect is not the key factor for striation formation when etching at grazing angle. Additionally, this striation structure can also be formed on solid substrates such as polycrystalline Cu substrate after physical sputtering at grazing angles, as demonstrated in the literature.38

IV. CONCLUSIONS

A plasma beam chamber system has been used to characterize surface roughening of low-\(k\) films in fluorocarbon beams. A polymerization-induced micromasking mechanism was proposed to explain the surface roughening of porous low-\(k\) films. The porous structure in the substrate plays a critical role in the film roughening evolution. Pores at the near surface enhance the fluorocarbon thin film, which is not necessarily continuous. Polymeric deposition etches more slowly under fluorocarbon plasma exposure and forms micromasks that induce roughening. On the contrary, only a very thin layer/amount of polymer forms on the surface of the solid OSG film in the net etching regime under the plasma running condition in this work. Therefore, the polymer deposition induced inhomogeneity is not significant enough to roughen the surface. This local polymer deposition induced micromasking mechanism explains the surface roughness evolution of porous low-\(k\) and solid OSG films as a function of etching time, ion bombardment energies, and the plasma polymerization capabilities.

Etching at glancing angles in the fluorocarbon chemistries resulted in the striation formation on the films in the direction parallel to the beam impingement direction. Shadowing effects are the major reason for striation formation at glancing angle. Although the polymerization effect can quench out the striation structure, it is not crucial for the origin of the striation formation on the substrate.

ACKNOWLEDGMENT

The authors would like to thank Semiconductor Research Corporation (SRC) for funding support.

---