Role of the dense amorphous carbon layer in photoresist etching

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The development of new photoresists for semiconductor manufacturing applications requires an understanding of the material properties that control the material’s plasma etching behavior. Ion bombardment at ion energies of the order 100 s of eV is typical of plasma-based pattern-transfer processes and results in the formation of a dense amorphous carbon (DAC) layer on the surface of a photoresist, such as the PR193-type of photoresist that currently dominates the semiconductor industry. Prior studies have examined the physical properties of the DAC layer, but the correlation between these properties and the photoresist etching behavior had not been established. In this work, the authors studied the real-time evolution of a steady-state DAC layer as it is selectively depleted using an admixture of oxygen into an argon plasma. Observations of the depletion behavior for various DAC layer thicknesses motivate a new model of DAC layer depletion. This model also correlates the impact of the DAC layer thickness with the etch rate of the bulk photoresist. The authors find that up to a 40% depletion of the DAC layer thickness does not have a significant impact on the bulk photoresist etch rate. However, further depletion results in an exponential increase in the etch rate, which can be up to ten times greater at full depletion than for the fully formed DAC layer. Thus, with these trends the authors show that the photoresist etch rate is controlled by the thickness of the DAC layer. Furthermore, thickness loss of the DAC layer in an O2-containing plasma coincides with a chemical modification of the layer into an oxygen-rich surface overlayer with properties that are intermediate between those of the DAC layer and the bulk photoresist. Support for this interpretation was provided via x-ray photoelectron spectroscopy characterization. Atomic force microscopy was used to gauge the impact on surface roughness as the DAC layer is formed and depleted. The trends established in this work will provide a benchmark in our development of new photoresists, which will be suitable for pattern transfer processes that will ultimately be a part of enabling smaller semiconductor device feature sizes and pitches. Published by the AVS.

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I. INTRODUCTION

A plasma-exposed photoresist can undergo modification due to processes that include vacuum ultraviolet (VUV) irradiation and ion bombardment.1,2 These surface modifications are important for the understanding of the steady-state etching behavior in a plasma environment, because at high ion energies there is significant bond scissioning in the surface layers and depletion of oxygen, hydrogen, and volatile-product-forming species. These phenomena result in the formation of a dense amorphous carbon (DAC) layer with a thickness that is proportional to the ion penetration depth.1,3,4 Previous work involving deposited amorphous carbon films has characterized the physical properties of these films as having a density and etch resistance that are significantly greater than those of photoresist polymers.5,6 The properties of photoresist-derived DAC films are similar to those of deposited amorphous carbon films. The photoresist layer structure formed in a plasma environment consists of a DAC layer on top of a bulk photoresist layer. The DAC layer behaves as an energy-dissipating layer that is depleted of precursors of highly volatile species, and thus mediates the etching of the bulk. Similar behavior is observed for SiO2 overlayers on Si-containing photoresists and fluorocarbon overlayers on Si or Si3N4.7–9

The main objective of the work presented here is to examine the etch-mediating behavior of the DAC layer by describing the quantitative relationship between the thickness of the DAC layer and the corresponding etch rate of the bulk photoresist. By selectively controlling the thickness of
the developed DAC layer via oxygen addition to the plasma composition, we have identified the threshold DAC layer thickness required for maintaining a steady-state photoresist etch rate and have identified an exponentially increasing etch rate trend with decreasing DAC layer thickness below this threshold.

One of the secondary effects that we have observed by controlling the DAC layer thickness via oxygen injection is that thickness loss occurs concurrently with a chemical modification of the DAC layer. Based on evidence from x-ray photoelectron spectroscopy (XPS), depletion of the DAC layer coincides with the formation of an oxygen-rich overlayer on the DAC layer. The optical density of this overlayer is intermediate between those of the DAC layer and the bulk photoresist layer, which is consistent with amorphous carbon erosion mechanisms that have been explored for deposited films.10–12 These observations provide insights into the sensitivity of the DAC layer to processing conditions, as a stable DAC layer is required for maintaining a stable and reproducible photoresist etch rate.

For pattern-transfer applications, a well-controlled photoresist surface roughness is as critical for reproducibility as is the etch rate. Although VUV irradiation plays a lesser role in the etching of a photoresist relative to ion bombardment, a synergistic effect between VUV irradiation and ion bombardment leads to a buckling instability in UV-sensitive photore sist, resulting in the formation of surface roughening.13–16 Attaining critical feature sizes requires the minimization of surface, line edge, and line width roughness to preserve feature fidelity.17,18 Characterization of photoresist surfaces by atomic force microscopy (AFM) can be used to correlate the impact of the DAC layer thickness and structure on the observed surface roughness.

In this article, we evaluate the influence of the DAC layer thickness on etching behavior, photoresist structure, and surface roughening using an industry-standard PR193 photoresist. Experimental data collected using XPS, AFM, and ellipsometry provide the basis for an ellipsometric model that describes the evolution of the photoresist layer structure. Application of this model to time-dependent ellipsometric data allows for the real-time thickness tracking of each of the individual layers that compose the photoresist structure.

II. EXPERIMENTAL SETUP

The samples used in this work consisted of a 193 nm photoresist material produced by the Japan Synthetic Rubber Corporation that has been extensively characterized.3,19 In this work, we studied the photoresist in the form of a blanket film with a thickness of approximately 200 nm. The general formulation of 193 nm photoresists consists of a terpolymer structure with a polymethylmethacrylate (PMMA)-based backbone with leaving, lactone, and polar groups serving as the functionalized side groups.4

Plasma etching of the samples was conducted using an inductively coupled plasma reactor. The system consists of a spiral antenna on a quartz dielectric that is located 13 cm above a Si electrode with a 12.5 cm diameter. We operated the top antenna at an excitation frequency of 13.56 MHz. The substrate was biased at a radio frequency of 3.7 MHz. Additionally, the substrate temperature was maintained at 10°C using water-cooling on the substrate backside.

For the plasma processing of the samples, we kept the chamber at a pressure of 10 mTorr. An argon plasma with a 40 sccm flow rate was used as the carrier gas. We used a source power of 300 W. Immediately after plasma ignition, we applied a −100 V substrate bias to bombard the sample with high-energy (up to ~125 eV) ions. This steady-state configuration is representative of the conditions that are used for photoresist pattern transfer.6

The general processing diagram for the experiments is shown in Fig. 1. The three phases of the processing setup, prebias, phase I, and phase II, correspond to setting up the gas flow in the absence of plasma, observing the formation of the DAC layer, and observing the depletion of the DAC layer, respectively. The computer-controlled gas injection system introduced oxygen into the chamber for intervals of 2, 6, and 10 s to modify the DAC layer by varying amounts. The flow rate of the oxygen was set so that the differential pressure between the argon and oxygen flows would be minimized, ensuring a smooth flow of oxygen into the chamber during the oxygen pulsing.

Information regarding the thickness and refractive index of the photoresist structure was collected in real-time using in situ ellipsometry in the polarizer-rotating compensator-sample-analyzer configuration at a wavelength of 632.8 nm. We interpreted the raw data generated from ellipsometry, parameterized through the optical constants psi and delta, by an optical model that incorporates modification to the photoresist from VUV irradiation and ion bombardment.

Ellipsometry is a powerful tool for examining the evolution of the photoresist layer structure, as any deviations in the trajectory of the raw data correspond to a change in the thickness and/or the refractive index of one or more of the layers. Notably, under steady-state etching conditions, the initial
deviation in the trajectory [Fig. 2(a)], which is characteristic of phase I in our processing setup, corresponds to an impact on the photoresist structure. This deviation is due primarily to the formation of the DAC layer from the impact of high-energy ion bombardment. The high reproducibility of the data under different conditions indicates that the photoresist structure responds in a consistent manner to high-energy ion bombardment. Changes from the steady-state structure can be probed by transiently altering the plasma composition for a fixed duration. We implement this process by using a computer-controlled gas injection system to introduce oxygen into the plasma for various durations. The alteration of the steady-state plasma condition corresponds to phase II in our processing setup. The advantage of this approach is that we can control the degree of modification of the DAC layer. The impact of the oxygen pulse on the overall photoresist structure and the corresponding etch rates can be ascertained for both partial and complete modification of the DAC layer.

Postprocessing, we obtained information about the chemical structure and morphology of the samples with XPS and AFM. The XPS analysis was performed using a Vacuum Generators ESCA Mk II surface analysis chamber with a non-monochromatized Al Kα x-ray source (1486.6 eV). Spectra were obtained at emission angles of 20° and 90° in the constant-energy analyzer mode at a 20 eV pass energy. To preserve the surface condition postprocessing, we moved all samples to the analysis chamber using a vacuum transfer system. The AFM analysis was performed using an Asylum Research MFP3D instrument in the tapping mode configuration with a fixed scan size of 2 × 2 μm. We acquired surface roughness information from these scans by calculating the root mean square of the surface profile.

In addition to evaluating the sample properties, we also determined the composition of the plasma using optical emission spectroscopy (OES). The oxygen emission line near 844 nm was monitored relative to the argon emission line near 764 nm, as this ratio provides information on the fraction of dissociated oxygen that is present in the plasma. The fraction of dissociated oxygen can, in turn, be related to the ellipsometric etching data. The 844 nm oxygen emission line was chosen because emission at this wavelength corresponds to the formation of atomic oxygen, which is the main oxygen reactive species that interacts with the sample surface.20,21

III. RESULTS

Our interpretation of the structure and etching behavior of the photoresist system is based primarily on the fitting of the raw ellipsometric data to a model. In Sec. III, we discuss the experimental data that were used to develop and support the model, and in Sec. IV we discuss the behavior of the photoresist as interpreted by this model.

A. Ellipsometry

The psi-delta trajectories obtained via ellipsometry for the different oxygen pulse lengths used are shown in Fig. 2(b). We implemented a cyclic process, with the pulsing repeating every 40 s for each pulse length. This approach permits the effect of the modification from oxygen to be observed in a time-dependent manner and also allows us to verify the reproducibility of the modification. In the boxed area in Fig. 2(b), which corresponds to the data in Fig. 2(a), we focused on a comparison of the modification during the first pulse, as the initial state of the photoresist prior to the pulse shows excellent consistency among the three tested conditions. As we discuss below, we can use one model for the quantitative evaluation of the evolution of the layer structure and etch rate as the modification progresses for all the different samples tested.

B. XPS

The XPS scans shown in Fig. 3 provide information on the composition of the surface layer as it undergoes initial modification from high-energy ion bombardment, followed by the subsequent modification from oxygen interaction. We compared the sample before being subjected to the plasma.
During etching but before the oxygen pulse (before-pulse), and during the oxygen pulse (midpulse). Compared to the pristine sample, the before-pulse sample has more C–C bonding and less C–O bonding, which is consistent with the formation of a DAC layer on the surface. Similarly, the enhancement of C–O and C=O bonding in the midpulse sample confirms that the oxygen pulse modifies the DAC layer into one that is significantly more oxygen-rich. The C1s spectrum in Fig. 3(a) indicates that oxygen addition produces a shoulder on the main peak that is representative of oxidation of the DAC layer, as has been observed previously.\textsuperscript{22}

C. AFM

Figure 4 compares the amount of surface roughening observed in the pristine sample, under steady-state argon plasma etching, during the middle of the first oxygen pulse, and following each of the first three oxygen pulses. The key observation from these data is that the depletion of the DAC layer during the oxygen pulse does not have a significant impact on the magnitude of the surface roughness. This observation is consistent with current understanding. Stress leads to the formation of buckling instability and is released by surface roughening. When the DAC layer reforms after the pulse, the magnitude of surface roughness is enhanced relative to the midpulse and pre-first pulse conditions. A possible explanation for this behavior is that the loss of oxygen in polymer materials induces surface roughening as stresses form in the material. Increased surface roughness may result from the depletion of oxygen from the DAC layer after the oxygen pulse.\textsuperscript{24} As the DAC layer is etched and reformed over subsequent pulses, this mechanism is a likely contributing factor for the increasing surface roughness. Additionally, roughening models have suggested that the mitigation of surface roughness is dependent on the relative magnitudes of the lateral and vertical diffusion of species in the photoresist.\textsuperscript{6} Therefore, this interpretation suggests that the enhanced roughness observed after each pulse is a result of an enhanced magnitude of species diffusing vertically instead of laterally in the photoresist. Because the net amount of material etched increases continuously during the plasma exposure, the greater total amount of material removed when each subsequent pulse occurs is consistent with the production of greater surface roughness by the greater net movement of surface species that has occurred up to that point. The significance of these AFM results is that the oxygen-induced modification and depletion of the DAC layer during the pulse does not result in a noticeable change in the surface morphology; this has the implication that a plasma process that involves oxygen will primarily reduce the thickness of the DAC layer without causing an increase in the surface roughness. The introduction of oxygen in fact mediates any increase in surface roughness since the PR193 surface roughness increases only once the oxygen is removed from the chamber upon the completion of phase II of our process and an argon-dominant plasma regime is restored in phase I of the next cycle. The observed magnitude of the surface roughness provides information on the sensitivity of the surface morphology to changes in the photoresist structure as a result of plasma-induced modifications.

IV. ELLIPSOMETRIC MODELING

Based on our experimental data, we developed a multi-layer ellipsometric model that tracks the evolution of the DAC layer and the bulk photoresist layer during the plasma exposure. In Fig. 5(a), we visualize the model in psi-delta space to describe the significance of the directionality of the raw ellipsometric data. Our model distinguishes between the DAC layer and the bulk photoresist layer, because the XPS data and SEM cross sections in Fig. 5(b) indicate that the DAC layer is a separate entity from the bulk photoresist. In
Secs. IV A–IV C, we discuss the parameters of our ellipsometric model, analyze the modifications to the photoresist structure that occur as the plasma process outlined in Fig. 2 proceeds, and comment on the observed relationships that impact the etching behavior.

A. DAC layer evolution

1. Formation of the DAC layer

For a pristine, PR193-coated Si substrate, there are three separate layers: the Si substrate, a native SiO₂ layer, and the deposited bulk photoresist. Upon plasma exposure coupled with high-energy ion bombardment, a fraction of the bulk photoresist layer undergoes modification from VUV irradiation. The thickness of the affected layer depends on the VUV penetration depth. For PR193-type photoresists, this penetration depth is on the order of 200 nm. Ion bombardment preferentially removes hydrogen and oxygen from the first several nanometers on the surface of the bulk photoresist layer, thus forming a DAC layer. Based on simulations using the STOPPING RANGE OF ION IN MATTER (SRIM) software package, for an ion energy of 100 eV, the corresponding thickness of the DAC layer is approximately 2.8–3.6 nm for our conditions. This thickness has been confirmed experimentally in previous works. We assume that the DAC layer has a uniform refractive index over its entire thickness for the prepulse duration. As a result, the initially formed DAC layer is eventually converted into a thinner DAC layer with a greater refractive due to the decreased ion penetration depth. Generally, the agreement between the ion energy dependent DAC layer thickness measured ellipsometrically and that predicted by SRIM is excellent. This comparison, along with

Fig. 4. (Color online) AFM scans performed at various points in the plasma etching process. Stresses in the surface layer of the photoresist are released through the formation of roughness. Further pulsing results in additional cycles of DAC layer depletion and formation, increasing the surface roughness.

Fig. 5. (Color online) (a) Ellipsometric model used for describing the evolution of the DAC and bulk layers in the photoresist. The inset shows the significance of the directionality in the ellipsometric model. (b) SEM cross section of the photoresist structure after plasma processing. Reprinted with permission from Metzler et al., J. Vac. Sci. Technol., B 33, 051601 (2015). Copyright 2015, American Vacuum Society.
consideration of the effect of the changing ion penetration depth on the DAC layer properties and etching behavior, will be discussed in a future paper. Each layer incorporated in the ellipsometric models can be simulated over a range of thicknesses or refractive indices of the simulated layer itself and/or of other layers. For evaluating the properties of the DAC layer during plasma exposure, we simulated the thickness of the DAC layer over a range of DAC refractive indices at various thicknesses of the bulk layer. This combination of simulated parameters allows for the evaluation of the DAC layer properties as the bulk photoresist layer is etched away. As the bulk layer is being etched away, it is also modified by VUV irradiation, as the quaternary carbons that make up the PMMA backbone of PR193 photoresist are prone to bond scission upon VUV irradiation.\(^2\)\(^9\) We integrated the rate of modification from VUV exposure into the model for the bulk layer based on an experimental calibration in which no substrate bias was applied, thus minimizing ion bombardment. One consideration that we took into account for the DAC layer refractive index is that the ion-induced dehydrogenation of the photoresist surface results in the development of an amorphous carbon layer that absorbs light, and thus no longer behaves as a pure dielectric material. This phenomenon is modelled by introducing loss in the form of an extinction coefficient.\(^3\)\(^0\)\(^,\)\(^3\)\(^1\) A relationship for the magnitude of the extinction coefficient relative to the real component of the refractive index for amorphous carbon films was previously established by Schwarz-Selinger et al.\(^5\) More recent work by Metzler et al. used the work by Schwarz-Selinger, in conjunction with newer studies on amorphous carbon, to improve the accuracy of the extinction coefficient relationship for a wider range of refractive indices.\(^1\)\(^9\) We used these data to model the DAC layer extinction coefficient.

Figure 6 shows our model superimposed on the raw ellipsometric data. Based on these data, we proposed the following interpretation of the DAC layer behavior. In phase I of our process, upon initiation of substrate biasing, etching of the bulk layer proceeds. At the same time, there is a distinct change in the trajectory of the psi-delta data, corresponding to the growth of the DAC layer. Prior to the introduction of the oxygen pulse, the DAC layer attains a steady-state thickness of 3.6 nm. Combined with the information from the SEM cross-section in Fig. 5(b), the XPS data for the before pulse condition in Fig. 3, and the reproducibility of the ellipsometric data upon the initiation of high-energy ion bombardment, we have distinguished the formation of a distinct DAC layer that has a composition that is distinct from that of the bulk photoresist.

### 2. Depletion of the DAC layer

In phase II of our process, the introduction of the oxygen pulse rapidly depletes the DAC layer thickness. Figure 6 shows that the DAC layer is partially depleted by 2 and 6 s pulses and fully depleted by 10 s pulses. It is evident from the trajectory of the raw data that the addition of oxygen into the plasma selectively depletes the DAC layer, as has been observed previously.\(^3\)\(^2\) Based on our ellipsometric model, the raw data trajectory would seem to imply absence of bulk layer etching for a brief period. In reality, etching of the bulk layer must continue, as there is uninterrupted ion bombardment of the sample. Based on the XPS data, we interpret this behavior as being due to a modification of the DAC layer properties by the interaction with the oxygen species as the layer is depleted. We termed this modification oxygenation of the DAC layer. A close examination of the data trajectory during the depletion of the DAC layer shows that the trajectory tracks in the opposite direction of bulk layer etching, implying a net growth of the thickness of the composite layer. A more plausible explanation is that the oxygen modifies the DAC layer as it is depleted in such a way that the modified DAC layer has properties that are more comparable to those of the less dense bulk layer. Several experimental studies have found that the density of deposited amorphous carbon decreases in an oxygen plasma environment.\(^1\)\(^1\),\(^3\)\(^3\),\(^3\)\(^4\) Therefore, it is likely that the photoresist-derived DAC layer undergoes a similar modification. Not only is the thickness of the DAC layer reduced, but the refractive index of the oxygenated layer also decreases due to the incorporation of oxygen. As the refractive index is related to the density, this decrease suggests a decrease in density of the DAC layer as well. To model this modification, we developed a separate model to interpret the properties of the DAC layer during the oxygen pulse, as shown in Fig. 7(a). The model is based on the one for the formation of the DAC layer, but with the addition of a component to account for oxygen modification. We make two main assumptions for this model. First, the etching of the bulk photoresist layer initially proceeds at the same rate during the oxygen pulse as before the pulse. Second, the refractive index of the oxygenated DAC layer is between those of the unmodified layer and bulk photoresist layer. The first assumption is likely an underestimation of the actual etching rate during this period, given the fact that

![Fig. 6. (Color online) Overlay of the experimental data on the ellipsometric model used for describing the evolution of the DAC and bulk layers in the photoresist. (Inlay) Significance of the directionality in the ellipsometric model.](image)
an argon/oxygen plasma synergistically enhances the etching of an amorphous carbon surface through physical and chemical sputtering.35–38 For the timescales considered here, the modification of the DAC layer during the oxygen pulse is expected to be considerably greater than the modification of the bulk photoresist layer. The second assumption is supported by previous modeling work that included a soft layer in addition to the graphitic layer when describing modification to PMMA under ion bombardment.39 Additionally, oxygen modification of the DAC layer produces a highly graded layer. Because the optical parameters measured by ellipsometry are representative of the average properties in a graded layer, we assume that this layer has a refractive index that is less than that of the parent DAC layer but greater than that of the bulk photoresist.40 For simplicity, we also assume that the extinction coefficient of the oxygenated DAC layer is negligible. To ensure that the model is physically consistent, we also calculated a limit for the maximum potential oxygenated DAC layer thickness that can be achieved through a modification of the parent DAC layer. This limit is based on the concept of conservation of optical density, which is the product of the refractive index and thickness of the DAC layer. As Schwarz-Selinger et al. showed, the refractive index is proportional to the density of an amorphous carbon film.11 Thus, the conservation of optical density is consistent with a conservation of mass. As shown in Fig. 7(b), overlaying the model on the raw data, we observe that regardless of the oxygen pulse length, approximately the first nanometer of the depleted DAC layer is fully converted into a modified, oxygenated DAC layer with a thickness of approximately 1.6 nm. Further depletion of the DAC layer is also accompanied by a decrease in the oxygenated DAC layer thickness as the oxygenated DAC layer reaches steady state and then begins to be etched. Once the oxygen pulse begins to dissipate, we observe a sharp interruption in the DAC layer depletion, and an almost immediate reformation and increase in thickness of the layer. From the modeling work and experimental characterization, we have identified a modification mechanism for the DAC layer in the presence of plasma oxygen species that corresponds with the depletion of the layer.

B. Photoresist layer structure

We used the ellipsometric model to extract the time-dependent thickness of each of the dynamic layers in the photoresist structure for each of the various oxygen pulse lengths, as shown in Fig. 8. Due to the number of dynamic layers during the pulse, we manually fitted the thickness change of the bulk layer during this period to a smooth transition between the calculated thickness prior to and following the pulse. This procedure allowed for the thickness of the modified and unmodified DAC layers to be modeled explicitly. We identified three distinct behaviors that occur during the oxygen pulse. First, as oxygen is introduced into the chamber, the thickness of the oxygenated DAC layer develops concurrently with the depletion of the DAC layer. The partially hydrogenated photoresist-derived DAC layer depletes more slowly than nonhydrogenated, amorphous carbon films.41 Second, once the oxygen pulse is terminated, the oxygenated DAC layer begins to be etched away concurrently with a reformation of the DAC layer. Upon the resumption of an argon plasma-dominant ion bombardment regime, the oxygenated DAC layer is preferentially etched relative to the unmodified DAC layer, because the higher oxygen content has lower etching resistance.20,42 Third, the rate of thickness loss of the bulk layer is dependent on the thickness of the DAC layer. For a depletion of the DAC layer of approximately 1.6 nm [Fig. 8(a)], the bulk layer thickness loss rate remains unchanged. However, for the greater depletions of the DAC layer that occur with the 6 and 10 s pulse lengths [Figs. 8(b) and 8(c)], the thickness of the DAC layer is no longer sufficient to mediate the steady-state etching of the bulk layer, and thus, the bulk layer is removed at an increasing rate. This relationship between the DAC layer thickness and the bulk layer etch rate can be explained by the ion dose reaching the
bulk layer being mitigated by the thickness of the DAC layer, which leads to a reduced sputter yield of the bulk layer.\textsuperscript{43,44} Our key conclusion is that the initial thickness loss of the DAC layer occurs as a result of the oxygenation of the layer, which persists only for as long as oxygen is introduced into the system. Once the oxygen dissipates, the oxygenated DAC layer is rapidly depleted and the DAC layer begins to reform.

C. DAC layer/etch rate relationship

We determined the overall photoresist etch rate as a function DAC layer thickness from the time-dependent thickness evolution of the photoresist layer structure, which was the main objective of this study. We illustrate this relationship in Fig. 9 for the three tested pulse lengths. The key impacts of the DAC layer thickness on the photoresist etch rate become evident based on the duration of the oxygen pulse. For the 2 s pulse length, the depletion of the DAC layer by approximately 1.6 nm does not result in a significant increase in the overall etch rate. The DAC layer remains sufficiently thick that the introduction of oxygen enhances the photoresist etch rate by less than 10 nm/min. In this condition, there remains a sufficient graphitization of the surface of the photoresist to maintain the etch rate.\textsuperscript{45} At the longer pulse lengths, the effect of the thinning DAC layer on the photoresist etch rate becomes much more apparent. Below a DAC layer thickness of 2 nm, the etch rate increases inversely proportional to the DAC thickness. Below a DAC layer thickness of 1 nm, the trend for the etch rate is further enhanced, culminating in a maximum etch rate 260 nm/min upon full depletion of the DAC layer. As the DAC layer reforms after the pulse, the trajectory of the etch rate with increasing DAC layer thickness follows a similar trend to when it is being depleted. The increased or decreased rate of etch rate progression as the DAC layer is nearing depletion or is being formed initially, respectively, implies that the presence of the DAC layer plays a large role in controlling the

Fig. 8. (Color online) Modeled thicknesses of the layers composing the photoresist during oxygen pulses of (a) 2 s, (b) 6 s, and (c) 10 s. The outlined area indicates the period over which oxygen is being input into the system. Dashed line represents maximum thickness of oxygenated DAC layer if there is a complete conversion of the depleted DAC layer into an oxygenated layer. In (b) and (c), the thickness loss rate of the bulk layer increases rapidly due to the depletion of the DAC layer, resulting in a greater total bulk layer thickness loss over the pulse duration.

Fig. 9. (Color online) Relationship between the PR193 etch rate and the thickness of the DAC layer. Arrows indicate the direction of the trend during the depletion and reformation of the DAC layer.
magnitude of photoresist etching. Correlating the time dependence of the DAC layer thickness and etch rate, as shown in Fig. 10, provides information on the relative etch yield of the DAC layer compared to the unmodified bulk layer. Upon initiation of high-energy ion bombardment, the etch rate is elevated as the corresponding etch yield of the surface layers is enhanced due to the volatilization of oxygen and hydrogen in the polymer structure. As the DAC layer thickness approaches steady-state, the etch rate sharply decreases and attains a steady-state threshold as the etch yield of the DAC layer decreases not only due to the dehydrogenation and crosslinking which occurs in this layer, but also because the ion penetration depth in the modified layer is less than that in the unmodified bulk layer. At the surface of the DAC layer, dangling bonds predominate the structure. Upon the introduction of oxygen into the plasma, the etch yield of the DAC layer is enhanced by the oxygen reacting with the dangling bonds and forming a sputtering product. However, from the reduced penetration depth of ions in the DAC layer, up to a 1.6 nm depletion of this layer does not cause the etch rate of the total layer structure to increase appreciably. The ability of the remaining approximately 2 nm thick DAC layer to maintain an etch yield that is significantly lower than that of the bulk layer, and thus can to maintain the overall steady-state etch rate, is supported by findings from MD simulations and other experimental works.46,47

We corroborated the etching behavior of the photoresist by using OES to interpret the DAC layer etching behavior from the perspective of the plasma condition. Figures 11(a) and 11(b) depict the relationship between the ratio of monoatomic
oxygen to argon in the plasma versus the etch rate and DAC layer thickness, respectively. We believe that the increasing hysteresis with pulse time for both properties arises from the following mechanism. The initial presence of oxygen in the plasma primarily reduces the thickness of the DAC layer, but the overall etch rate remains stable as the thickness of the DAC layer remains above approximately 2 nm. For the 6 and 10 s oxygen pulse lengths, a greater relative amount of oxygen is present in the plasma, resulting in an enhanced depletion of the DAC layer, which also corresponds to an increasing etch rate. Upon the termination of the oxygen pulse, the monatomic oxygen fraction stabilizes. The oxygen fraction only begins to decrease as it is pumped out of the chamber, in an interval that is determined by the chamber residence time. As the oxygen residence time at the given processing condition is approximately 2 s, we observe the postpulse effects on the DAC layer thickness and etch rate after an initial rapid decrease in the atomic oxygen fraction. In this region, the sharp decline of the atomic oxygen fraction results in the reestablishment of a regime that is dominated by argon ion bombardment, which leads to the reformation of the DAC layer and a corresponding decrease in the etch rate. The key conclusion from this analysis is that a threshold DAC layer thickness of approximately 2 nm is required to maintain a stable etch rate of the PR193 photoresist. The smaller hysteresis in the etch rate versus DAC layer thickness relationship (Fig. 9) compared to the etch rate versus oxygen-to-argon ratio indicates that the etch rate is primarily controlled by the thickness of the DAC layer. As long as there is sufficient oxygen in the plasma, depletion of the DAC layer proceeds, resulting in a sharp increase in the photoresist etch rate when the layer is depleted beyond the threshold thickness. From the narrower hysteresis in the relationship between the etch rate versus the DAC layer thickness compared to the relationship between the etch rate versus the atomic oxygen fraction, we conclude that the etch rate is primarily controlled by the thickness of the DAC layer, rather than the amount of oxygen that is present in the gas phase.

V. SUMMARY AND CONCLUSIONS

In this work, we developed an ellipsometric model to interpret the role of the DAC layer on the photoresist layer structure and overall etch rate. Under an argon plasma with a maximum ion energy of 125 eV, a distinct and reproducible DAC layer with a steady-state thickness of approximately 3.6 nm forms on the surface of the photoresist. At the steady-state condition, the etch rate of the photoresist is maintained at a value of approximately 30 nm/min. Upon introduction of oxygen into the plasma, the surface of the DAC layer becomes oxygen rich, resulting in a greater susceptibility to etching. Depletion of the DAC layer occurs via the incorporation of oxygen into the layer, which is then etched away.

A partial depletion of the DAC layer, up to a remaining thickness of approximately 2 nm, is sufficient to maintain the steady-state etch rate. Further depletion of the layer causes a sharp increase in the etch rate, as the DAC layer can no longer sufficiently mediate the etching of the underlying bulk photoresist layer.

The initial formation of the DAC layer induces stresses within the surface of the photoresist which leads to surface roughening. Because the stress is relaxed upon the formation of roughness, the depletion of the DAC layer from the oxygen pulse does not impact the magnitude of the observed roughness. Reformation of the DAC layer after the oxygen pulse introduces additional stresses which enhance the magnitude of surface roughening.

Overall, we benchmarked the DAC layer properties and the etching behavior for a PR193-type photoresist under varying sets of plasma parameters. A further extension of this work will involve benchmarking the etching behavior of additional photoresists and polymers to develop a model that can connect the DAC layer properties, etching behavior, and chemical composition of the processed materials. This comprehensive model, along with the current work, will allow us to understand the etching behavior of new photoresist materials that are currently in development to achieve sub-10 nm feature sizes using new lithographic techniques.48

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