Plasma oxidation of polyhedral oligomeric silsesquioxane polymers

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Copolymers containing polyhedral oligomeric silsesquioxane (POSSTM) units have been developed to be used as photoresist components in a bilayer resist scheme for 193 nm lithography. This article reports on the behavior of these new POSS based materials under oxygen plasmas. The authors demonstrate using *in situ* ellipsometry and *in situ* x-ray photoelectron spectroscopy that during the first seconds in the plasma a silicon oxide layer is formed on the top surface of the POSS materials. This superficial layer prevents etching and material consumption. An ion-enhanced oxidation model is proposed to describe and explain the experimental data and further investigate POSS etching mechanisms in oxygen plasma. The model shows that the oxide formation rate is reduced exponentially with the oxide thickness. It also predicts that thickness loss has its main roots in the layer densification that occurs when the oxide is formed and shows that the oxide formation is ion enhanced and thus favored at -100 V compared to 0 V bias. © 2006 American Vacuum Society. [DOI: 10.1116/1.2382947]

I. INTRODUCTION

Copolymers containing polyhedral oligomeric silsesquioxane¹ (POSS) units are new promising materials.^{2,3} The POSS unit forms a silicon oxide cage with a chemical formula Si_8O_{12} , which gives to the copolymer hybrid properties between inorganic and organic composite materials. Cage diameter is about 1.5 nm, therefore this moiety belongs to the nano-object family. In general, the nanocomposite formation through the incorporation of POSS into polymeric materials modifies their mechanical and thermal properties. One major application is in lithography.⁴ Next generation of microelectronic circuits requires minimum critical dimensions below 50 nm,⁵ a task achievable through the employment of 193 nm optical lithography, extreme ultraviolet lithography, e-beam lithography, or other next generation lithography (NGL) technologies.⁶ 157 nm lithography is also considered, where most of the polymers based on carbon skeleton, usually employed as resist for lithography, have too high absorbance unless they are at least partially fluorinated.⁷ It has been demonstrated that Si–O bond exhibits a low absorbance at this wavelength as well.^{7,8} In addition, the etch resistance of Si containing polymers to oxygen plasma is excellent.^{9–11} Thus, silicon containing polymers are good candidates as top layer resist materials for bilayer lithography in almost any NGL scheme, supposing that problems related to line-edge roughness (LER) after plasma development are solved.¹² For such a bilayer process, the pattern is imaged on a top layer and transferred to the bottom resist layer by oxygen plasma etching. However, most of the classical silicon polymers such as polydimethylsiloxane $[\text{SiO}(\text{CH}_3)_2]_n$ (PDMS) or poly(methylsilsesquioxane)

$[\text{SiO}_{1.5}(\text{CH}_3)]_n$ (PMSQ) give negative-tone resists. Consequently, positive-tone resists based on silsesquioxane polymers are needed with high resolution and low LER. Towards this target the new class of copolymers containing POSS has been proposed.^{13,14}

Even though etch resistance at oxygen plasma of silicon containing materials is of crucial importance for their performance, experimental results and pertinent modeling are limited. The most known works are that of Watanabe and Onishi¹⁵ and Jurgensen *et al.*¹⁰ They assume that oxygen oxidizes the Si-polymer forming volatile organic compounds and nonvolatile SiO_2 through which oxygen should therefore diffuse. At the same time ions sputter the oxide formed. A possible drawback of these works lies upon the fact that they ignore the ion-enhanced character of the plasma processing of polymers. Nevertheless they do manage to reasonably fit available experimental data.

In this work, we study the chemical and structural modifications of the POSS materials when exposed to an oxygen plasma, both experimentally and theoretically, and compare them with other silicon containing polymers, namely, PDMS and PMSQ (see Sec. III). An analytical, ion-enhanced-consisted model is also proposed to describe the thickness loss and the kinetics of formation of a SiO_2 -like surface layer and its evolution during processing (see Sec. IV). We compare our model with experiments and previous models.^{10,15}

II. MATERIALS AND EXPERIMENTAL SETUP

The molecular structure of an individual unit of ethyl-POSS is shown in Fig. 1(a). It consists of a Si_8O_{12} group arranged in a cage-like structure, with an approximate spherical diameter of 1.5 nm. The core is surrounded by seven ethyl groups and the remaining silicon is linked to the copolymer chain. These copolymers are synthesized at the Institute of Microelectronics in Athens. POSS monomer was

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FIG. 1. Schematic representation of (a) the various constituents of ethyl-POSS copolymers and (b) polymethylsilsequioxane (PMSQ) and polydimethylsiloxane (PDMS)

purchased from Hybrid Plastics and was used as received. It was copolymerized with other monomers, such as methacrylic acid (MA) and *tert*-butyl methacrylate (*t*-BMA) in various compositions [Fig. 1(a)]. Each of them plays a role allowing to optimize lithographic properties. In particular, the POSS cage is important to enhance oxygen plasma etching resistance. *t*-BMA and MA are introduced to obtain a positive-tone behavior resist. Details on synthesis are given elsewhere.^{13,14}

The experiments have been carried out using copolymers containing various weight percentages of the ethyl-POSS monomer, which varied from 20% to 100%. Four ethyl-POSS/*t*-BMA copolymers are studied more particularly: 100/0, 60/40, 40/60, and 20/80. In the following these are labeled as 100%, 60%, 40%, and 20%. Two other copolymers with the addition of MA monomer are also used, with weight percentage in ethyl-POSS/*t*-BMA/MA of 30/50/20 and 40/40/20, respectively; these are further labeled as 30% MA₂₀ and 40% MA₂₀.

The etching reactor used during this study is equipped with an Alcatel inductive coupled plasma source made of a quartz dome and a one turn loop antenna operating at 13.56 MHz. The plasma diffuses in the process chamber where the wafer is located. A second rf generator (13.56 MHz, 600 W) allows to bias the substrate independently. The temperature of the sample is controlled by cooling the sample holder at 20 °C using a cryostat. Heat transfer between the sample and the holder is achieved by mechanically clamping the wafer to the holder and by injection of

helium at the back side of the wafer. If smaller samples are used, thermal paste is employed to ensure a good thermal contact to the wafer. Because of ion bombardment, high gas temperature in high density low pressure plasmas^{16,17} and exothermic oxidation reaction, one could expect a small material temperature increment during plasma processing. However, we estimated that, thanks to the wafer cooling, this temperature increase is not higher than 10 °C. A detailed description of the plasma reactor can be found elsewhere.¹⁸ Plasma conditions used are source power 800 W, pressure 10 mTorr, and flow rate 40 SCCM (SCCM denotes cubic centimeter per minute at STP). Bias voltage has been varied from 0 V(0 W) to −100 V(50 W). *In situ* multiwavelength ellipsometry is used to measure in real time the evolution of the layer thickness. For this a J. A. Woollam M88 ellipsometer running the WVASE software is employed. For each material, ellipsometry data are acquired before any plasma treatment. These data are analyzed using a nonabsorbent Cauchy model. During plasma exposure ellipsometry data are recorded at a rate of one spectrum every 1.5 s. Data analysis is carried out keeping the optical parameters of the material constant and only fitting the total thickness. This procedure is acceptable as long as the material and the plasma-modified material have similar optical parameters, which is the case, and since the modified layer is in any case much thinner than the total thickness. Chemical modification of the surface after plasma exposure is investigated by using *in situ* XPS. Experiments have been carried out with a Leybold LH11 spectrometer, using Mg *Kα* radiation (1253.6 eV). Pass energy was fixed at 50.4 eV. Under this condition the analyzer spectral resolution is 0.5 eV, combined with the linewidth of the Mg *Kα* line the total spectral resolution is 1.0 eV. After etching the reactor is evacuated and the etched sample is transferred via an ultrahigh vacuum buffer chamber into the XPS analysis chamber.

III. COPOLYMER ETCHING IN OXYGEN PLASMA

A. Etch rates

Figure 2 reports the thickness variation in oxygen plasma for 0 and −100 V biases as measured by ellipsometry. For comparison purposes, measurements made on PMSQ and on PDMS materials [which chemical formulas are given in Fig. 1(b)] are also indicated in Fig. 2.

It appears that thickness loss (i.e., etching) rates are not constant during the plasma exposure. Moreover, rate evolution depends on the proportion of ethyl-POSS in the copolymer; the richer the copolymer is in ethyl-POSS, the weaker and slower the evolution becomes. Moreover, different polymers with the same amount of ethyl-POSS, e.g., 40% and 40% MA₂₀, have about the same etch rate and evolution of the etch rate with time.

A larger proportion of ethyl-POSS in the copolymer means a larger concentration of silicon in the material. Figure 3 reports the thickness loss at a given etching time as a function of the inverse of the silicon mass percentage (1/wt %Si) within the various materials. For the 0 V bias

FIG. 2. Copolymer thickness evolution as measured by *in situ* ellipsometry during exposure to oxygen plasma under the following conditions: $P_{\text{source}}=800$ W, pressure=10 mTorr, flow rate=40 SCCM, and bias voltage of (a) 0 V and (b) -100 V.

voltage, we obtain a *quasilinear* evolution at every moment [Fig. 3(a)]. This result shows that all these materials, despite their different chemical compositions, are governed broadly by identical etching mechanisms, in which the silicon atoms play a major role. Yet if one takes a more careful look at Fig. 3(a), it appears that the data for the MA containing materials (40% MA₂₀ and more particularly 30% MA₂₀) are systematically below the purely linear dependence between the thickness loss and the reverse of the silicon mass percentage. Therefore ethyl-POSS/*t*-BMA/MA copolymers exhibit a slightly greater etch resistance than ethyl-POSS/*t*-BMA copolymers. It appears consequently that partial substitution (20%) of MA to *t*-BMA for a given proportion of ethyl-POSS allows to reduce the thickness loss by about 10%, after 10 min.

With a bias of -100 V, one still observes an increasing etch resistance with the inverse of the silicon mass percentage even though a strictly linear dependency between thickness loss and $1/\text{wt \% Si}$ is less clear [Fig. 3(c)]. Again, adding MA seems to reduce the etch rate. However, two main differences are observed at -100 V. First, the 20% material has a particular behavior, showing a thickness loss larger than expected by the linear evolution. Second, the PDMS material behaves at -100 V and with respect to the other materials, in a very different way as compared to 0 V. Curiously, in spite of a larger silicon quantity, thickness loss at

FIG. 3. Thickness loss for various copolymers at various plasma exposure times as a function of the inverse of the silicon mass percentage in the material. (a) 0 V bias, (b) zoom of (a), and (c) -100 V bias.

any etching time is higher for PDMS compared to the 100% ethyl-POSS copolymer [Figs. 2(b) and 3(c)]. In the absence of bias, PDMS does not show this particular behavior [Figs. 3(a) and 3(b)].

As shown in Fig. 2, the copolymer etching rate is maximum at plasma ignition. Figure 4 shows the initial etching rate as a function of $1/\text{wt \% Si}$. Materials rich in silicon exhibit very similar initial etching rates for the two bias conditions. On the contrary, materials with low silicon content, 30% MA₂₀ and more particularly 20%, show significant differences in their initial etch rate between 0 and -100 V.

B. FTIR and XPS analysis

XPS *in situ* measurements were carried out after different exposures to oxygen plasma, from 2 s to 5 min, at 0 and

FIG. 4. Initial etching rates of various copolymers as a function of 1/wt % Si for bias voltage of 0 and -100 V.

-100 V biases. Results were compared with measurements made before etching (see Ref. 19 for complete and detailed analysis before etching). Silicon and oxygen peak intensities increase while the carbon peak intensity decreases. Moreover the carbon peak shape remains unchanged. These facts are a strong indication of a surface oxidation phenomenon as observed with PDMS (Ref. 11) and suggest that no carbon is present in the oxidized layer. Fourier transform infrared (FTIR) analyses have been carried out in order to confirm material oxidation. As an example Fig. 5 reports FTIR spectra for the pure ethyl-POSS material (100%) after different etching times. We observe that the Si-CH₃/Si-O-Si intensity ratio decreases, which corresponds to an oxidation of the material.²⁰ Moreover, the Si-O-Si peak maximum initial position (1105 cm⁻¹) is shifted towards a lower wave number (around 1050 cm⁻¹). This shift can be attributed to material oxidation.^{21,22} Hence, we assume that during oxygen plasma processing, a silicon oxide layer (SiO₂-like) is formed on top of the ethyl-POSS copolymers.

The XPS silicon peak (Si 2p) average full width half maximum (FWHM) before etching is 1.94±0.1 eV for all copolymers. After etching, the silicon peak is significantly broader: 2.43±0.1 and 2.2±0.1 eV for 0 and -100 V bias voltages, respectively. If one considers that the material be-

FIG. 5. FTIR spectra for 100% ethyl-POSS material recorded after various exposure times.

comes oxidized on the surface, one expects the contribution of a silicon oxide Si⁴⁺ component (103.5 eV) in addition to the ethyl-POSS silicon component (102.5 eV). So the increase in width after etching can be explained by the presence of such Si⁴⁺ component. However, peak fitting with two components is rather difficult, the 1 eV gap between the two components being not much larger than the silicon peak FWHM variation (0.5 eV) between before and after etching. Therefore an estimation of the SiO₂-like surface layer by using a deconvolution of the Si peak as was done previously for PDMS (Ref. 11) is not reliable. Thus, we used only peak intensities of the various elements in order to calculate the oxide thickness as well as the silicon to oxygen atomic relative percentage in the oxide layer.

Intensities coming from component characteristic of the copolymer underlayer, or from the oxide top layer, follow classical attenuation laws through a layer thickness e ,

$$I_{\text{pol}} = I_{\text{pol}}^{\infty} \exp\left(\frac{-e}{\lambda \cos(\theta)}\right),$$

$$I_{\text{ox}} = I_{\text{ox}}^{\infty} \left\{ 1 - \exp\left(\frac{-e}{\lambda \cos(\theta)}\right) \right\}, \quad (1)$$

in which I^{∞} refers to the intensity for a semi-infinite material, λ is the photoelectron inelastic mean free path, and θ the photoelectron takeoff angle.

If one considers that the carbon comes mainly from the unmodified copolymer, it is possible to estimate the oxide thickness e_{ox} using the left hand relation in Eq. (1) and the C 1s peak. On what concerns oxygen and silicon concentration in the oxidized layer, we considered that the total O 1s and Si 2p peak intensity after etching is the sum of a contribution coming from the copolymer and another contribution coming from the surface oxide. The calculation of the intensity before and after etching gives the following result:

$$I_{\text{before}} = I_{\text{pol}}^{\infty},$$

$$I_{\text{after}} = I_{\text{pol}} + I_{\text{ox}},$$

$$I_{\text{after}} - I_{\text{before}} = (I_{\text{ox}}^{\infty} - I_{\text{pol}}^{\infty}) \left\{ 1 - \exp\left(\frac{-e}{\lambda \cos(\theta)}\right) \right\}, \quad (2)$$

with the assumption that λ is identical for the copolymer and the oxide materials.

Thanks to this formula, valid for oxygen and silicon peak intensities, we can estimate the oxide infinite intensities for silicon and oxygen, i.e., I_{ox}^{∞} and $I_{\text{Si/ox}}$ and $I_{\text{O/ox}}$ using the right hand relation in Eq. (1). The latter values give the oxygen to silicon ratio in the oxide layer. Table I summarizes atomic percentages and oxide thickness results obtained by XPS after 10 s of etching; thickness loss measured by ellipsometry is also reported. Other analyses were carried out for different etching times (from 2 s to 5 min); data were processed according to the same protocol but not shown in Table I in order to simplify the presentation.

For the two bias conditions, for all materials and etching times, the O/Si ratio in the surface layer is close to 2. This

TABLE I. Atomic percentages, oxide thickness, and O/Si atomic ratio in the oxidized layer, as measured by XPS after 10 s of etching in oxygen plasma with 0 and -100 V bias voltages. The corresponding thickness loss, measured by ellipsometry, is also indicated.

Copolymer	100%	60%	40%	30% MA ₂₀	20%
Theoretical values before etching					
at. % C	48.8	62.8	69.0	69.1	74.7
at. % O	32.6	26.9	24.4	26.1	22.1
at. % Si	18.6	10.3	6.6	4.8	3.2
After etching in O ₂ plasma 800 W, 40 SCCM, 10 mTorr, 10 s, 0 V					
at. % C	20.5	30.6	37.5	39.7	45.0
at. % O	53.2	47.1	44.8	44.2	41.3
at. % Si	26.3	22.3	17.8	16.2	13.7
Thickness loss (nm)	5.0	9.4	12.4	15.7	20.8
Oxide thickness (nm)	2.4	2.0	1.7	1.5	1.4
% Si in oxide	33.1	36.0	33.7	34.4	32.6
% O in oxide	63.4	60.6	62.2	61.9	62.4
Ratio (O/Si) _{ox}	1.9	1.7	1.8	1.8	1.9
After etching in O ₂ plasma 800 W, 40 SCCM, 10 mTorr, 10 s, 100 V					
at. % C	15.8	24.3	31.2	31.9	39.2
at. % O	58.2	53.6	49.8	49.9	45.1
at. % Si	26.0	22.1	19.0	18.2	15.6
Thickness loss (nm)	4.8	10.9	16.6	23.2	53.6
Oxide thickness (nm)	3.2	2.7	2.2	2.2	1.8
% Si in oxide	30.4	31.2	31.4	32.0	32.0
% O in oxide	66.2	65.0	64.3	64.1	63.2
Ratio (O/Si) _{ox}	2.2	2.1	2.0	2.0	2.0

result is therefore another strong indication that exposure to O₂ plasma leads to the formation of a SiO₂-like surface layer containing only a very small proportion of carbon. Variation of the silicon oxide thickness as function of etching time and Si weight percentage is reported in Fig. 6. It appears that the richer the material is in silicon, the thicker the oxide is at a given etching time. However, it appears also that the 20% copolymer presents a particular behavior. Whereas it contains a very small amount of silicon, at very short times the oxide layer is already as significant as for the other copolymers, about 1.5 nm. This anomaly can be attributed to the surface segregation of the ethyl-POSS cages in the as deposited material, which we characterized previously.¹⁹ Therefore, at plasma ignition, surfaces exposed to the plasma are quite similar in composition, which initially leads to a similar oxidation for the various copolymers. After these first seconds, as the etching makes progress in the material bulk, the effect of the ethyl-POSS surface segregation decreases. And for etching times larger than 10 s one observes a thicker oxide layer for materials initially richer in silicon [Table I, Fig. 6(a)].

The thickness of the surface oxide is larger after 10 s of etching with a bias of -100 V [Table I, Fig. 6(b)]. This observation is important as it clearly states that the oxide growth rate is enhanced by the ion bombardment, which is in accordance with previous results from Hartney *et al.*²³ We thus have first evidence of ion-enhanced oxidation. In the section below we attempt to model this behavior.

FIG. 6. Oxide thickness as estimated from XPS: (a) as a function of plasma exposure and in the absence of bias voltage, nonzero initial values result from POSS surface segregation phenomenon; (b) as a function of the silicon mass percentage in the copolymer. Notice the greater thickness at -100 V; an evidence of ion-enhanced oxidation.

TABLE II. Copolymer mass percentage in silicon, parameter δ , and experimental ratio of the total thickness loss over the oxide thickness for 10 s of exposure to the oxygen plasma with 0 V bias.

	PDMS	100%	60%	40%	30% MA ₂₀	20%
wt % Si	37.8	30	18	16	9	6
δ	1.7	2.4	4.7	7.5	10.3	16.0
$\Delta e/e_{\text{ox}}$		2.1	4.7	7.3	10.1	14.7

IV. MODELING OF ETCHING KINETICS: PLASMA OXIDATION MODELS

The overall problem of the oxidation of a film by an oxidant that first diffuses through the nonvolatile products of the oxidation is known as the “shrinking core model.”²⁴ In treating this problem three mass balances must be developed: (i) mass balance of the element that is oxidized and forms the nonvolatile products (Si in our case), (ii) mass balance of the nonvolatile products (SiO₂ in our case), and (iii) mass balance of the oxidant within the nonvolatile products (oxygen species in our case) assuming—in most cases—a pure Fickian diffusive flux. Even though this model has been extensively studied^{22–27} in chemical engineering the nature of the plasma etching process introduces parameters (ion enhancement, ion bombardment, and physical sputtering) that are not present in the conventional chemical engineering problems, where the shrinking core model is widely applied. In the present article, the model developed aims at predicting POSS material thickness loss with time during oxygen plasma. We present the model in two steps. The first step uses the silicon mass balance and links the POSS material thickness loss to the oxide thickness. This does not lead to an explicit dependence with time, but this first step is nevertheless interesting since the model can be compared to experiments (both thickness loss and oxide thickness are measured). The second step completes the first one and takes into account the silicon oxide mass balance. An explicit dependence of the thickness loss with time is obtained and the model can be directly compared to experiments.

A. Silicon mass balance

At the interface between oxide and polymer, carbon, hydrogen, and possibly oxygen atoms from the polymer form volatile compounds with oxygen atoms coming from the plasma and leave the surface, whereas the silicon atoms from the copolymers are oxidized and form a SiO₂ layer; the expression of conservation of the amount of silicon at this interface is¹⁵

$$\rho_{\text{ox}}^{\text{Si}} \left(\frac{de_{\text{ox}}}{dt} \right)_{\text{int}} = - \rho_{\text{ox}}^{\text{Si}} \left(\frac{de_{\text{pol}}}{dt} \right)_{\text{int}}, \quad (3)$$

with $(de_{\text{ox}}/dt)_{\text{int}}$ the thickness variation of the oxide layer at the interface and $(de_{\text{pol}}/dt)_{\text{int}}$ the total thickness variation of the unmodified polymer. $\rho_{\text{ox}}^{\text{Si}}$ and $\rho_{\text{pol}}^{\text{Si}}$ are the silicon mass densities (g/cm³), respectively, in the oxide and in the polymer. These can be calculated thanks to the relation ρ_X^{Si}

$= \rho_X p_X^{\text{Si}}$, where ρ_X is the specific weight and p_X^{Si} is the silicon mass percentage in the material.

The total variation of the oxide layer is the sum of the variation at its two limits at the interface with the copolymer material due to oxidation and at the outer surface due to the sputtering mechanism, with k_{sp} the sputtering rate of this oxide layer.

$$\frac{de_{\text{ox}}}{dt} = \left(\frac{de_{\text{ox}}}{dt} \right)_{\text{int}} - k_{\text{sp}}. \quad (4)$$

Taking into account that the total thickness is the sum of the oxide thickness plus the copolymer thickness, the copolymer thickness variation can be calculated thanks to relations (3) and (4). After integration, one finally obtains

$$e_0 - e(t) = \delta e_{\text{ox}}(t) + (1 + \delta) k_{\text{sp}} t, \quad (5)$$

with e_0 being the initial thickness of the polymer and $\delta = (\rho_{\text{ox}}^{\text{Si}} - \rho_{\text{pol}}^{\text{Si}}) / \rho_{\text{pol}}^{\text{Si}}$.

This last term δ is positive and greater than 1 since the silicon density in the silicon oxide layer is larger than in the copolymers. To calculate δ , we used the specific weight of an oxide deposited by PECVD ($\rho_{\text{SiO}_2} = 2.2 \text{ g/cm}^3$) and the mass percentage in silicon of a perfectly stoichiometric oxide ((wt %) $_{\text{SiO}_2}^{\text{Si}} = 46.7\%$). As regards copolymers, we did not have accurate measurements of the specific weight of all materials. Thus, we considered that the specific weight was similar for all copolymers and close to that of 100% ethyl-POSS: 1 g/cm³. Table II reports calculation of δ for the copolymers and for PDMS.

1. Comparison with experimental results

If we consider that sputtering is negligible at 0 V bias, then relation (5) gives

$$\Delta e(t) = \delta e_{\text{ox}}(t). \quad (5')$$

This equation also allows us to explain qualitatively Fig. 3(a), in which the thickness loss at 0 V follows a linear relationship with 1/wt % Si. According to Eq. (5'), if at a given time we observe roughly the same oxide thickness for all copolymers, the total thickness loss at this instant is a linear function of δ , which is an opposite function of the silicon mass percentage (see δ expression).

Still, following Eq. (5') $\Delta e/e_{\text{ox}}$ the ratio of the thickness loss measured by ellipsometry on the oxide thickness measured by XPS should give an experimental value for param-

FIG. 7. Total thickness loss as a function of the oxide thickness (a) Experimental data obtained at 0 V bias voltage and at 2, 10, 20, and 300 s etching times. The dashed lines are lines with a slope δ for the various copolymers. (b) Comparison between 0 and -100 V bias voltages after 10 s of etching.

eter δ . Such ratio is given in the last line of Table II. The excellent agreement between δ and $\Delta e/e_{\text{ox}}$ makes a good case for the modeling.

Figure 7 represents the total thickness loss as a function of the oxide thickness. Following Eq. (5') the relation between the thickness loss (Δe) and the oxide thickness (e_{ox}) is a straight line of slope δ . In Fig. 7, dashed lines are plotted, which slopes correspond to the parameter δ calculated theoretically for the different copolymers. We also report on this graph experimental data points (Δe vs e_{ox}) for various plasma processing times.

From Fig. 7 one observes that the best agreement is obtained for the 100% ethyl-POSS, which data follow perfectly the model for all etching times. The worst agreement is for the 20% ethyl-POSS that seems to behave very differently from the other materials. For all materials, a linear relation is observed between thickness loss and oxide thickness. For 10 and 20 s, most of the experimental data are close to the theoretical lines. However, for 300 s experimental data are systematically above theoretical lines and for 2 s experimental data are systematically below theoretical lines. Thus, experimental slopes are generally higher than expected from the model (except for the 100% ethyl-POSS material). Some assumptions can be put forward to explain these observations. First of all, after 300 s of etching, the C 1s peak signal is weak which renders the determination of the oxide thickness

imprecise. However, the discrepancy should also appear for the 100% ethyl-POSS. Second, after 2 s of etching, results are still influenced by the initially present surface segregation as discussed before, and oxide thickness is larger than predicted by the model. The pure ethyl-POSS material, which does not present any surface segregation phenomenon, shows a thickness loss versus oxide thickness falling exactly on the theoretical line. Finally, in the absence of bias the model seems to apply correctly, once the issue due to the surface segregation is taken into account and for times lower than a few minutes. In a real bilayer process, these materials will not be exposed to oxygen plasmas more than a few minutes. Thus our model can be used to analyze the behavior of ethyl-POSS copolymers during the pattern transfer to the bottom resist layer. The main interest of this modeling is to show that POSS material thickness loss is mainly due to the formation of an oxide layer denser than the copolymer itself: $\Delta e(t) = \delta e_{\text{ox}}(t)$, where δ quantifies the increase of density.

At -100 V, the experimental points are expected to be above the line of slope δ since in addition to the first term of Eq. (5) ($\delta e_{\text{ox}}(t)$), a sputtering contribution is expected ($((1+\delta)k_s t)$). Figure 7(b) presents experimental points at -100 V for 10 s of etching, and for comparison experimental points without bias, at the same etching time. At -100 V bias, it appears that for most of the materials the experimental points are close to theoretical lines—and even sometimes slightly below—except for the 20% ethyl-POSS material which data are largely above. This astonishing result compared to the prediction seems to indicate that the sputtering of the material is weak at -100 V except for the 20% ethyl-POSS copolymer. In other words, it suggests that the ionic bombardment does not sputter the materials but rather enhances oxidation. Thickness loss measurements support this remark (Fig. 2). Indeed they present abnormally low values at -100 V compared to the PDMS material, although this one contains more silicon. In PDMS all the carbon atoms are linked to silicon, whereas in the POSS copolymers most of the carbon atoms do not present bonds with silicon. This difference in structure could explain etching behavior differences between POSS copolymers and PDMS. Only the 20% ethyl-POSS material, presumably because of its low silicon concentration, seems to undergo sputtering.

Thickness loss is obviously faster at -100 V than at 0 V. However, combined with the oxide thickness results our interpretation is that the ionic bombardment induces only weak sputtering and rather favors material oxidation and thickness loss through the term ($\delta e_{\text{ox}}(t)$).

Let us note that taken as a whole these results turn towards the idea that the oxide growth function depends on the ionic bombardment. This function is studied in the following part.

B. Silicon oxide mass balance and oxidation kinetics

Equation (5) predicts film thickness evolution as a function of time. The initial thickness e_0 and the term δ are readily determined, the sputtering rate k_{sp} is unknown but considered as constant with time. Finally, the oxide thickness

e_{ox} is the only time dependent term. Its determination is necessary to calculate the explicit dependence of total thickness evolution with time. In order to find oxide thickness variation with time ($e_{ox}(t)$), we used the expression (4) rewritten as follows:

$$\frac{de_{ox}}{dt} = f(e_{ox}) - k_{sp}, \quad (4')$$

where $f(e_{ox})$ describes the oxide layer growth rate at the polymer-SiO₂ interface as a function of the oxide thickness. In order to compare our results with existing models, three expressions for $f(e_{ox})$ are studied in the following. We first briefly introduce these three models, and then we describe them in detail and discuss their relevance to describe polymer oxidation in plasmas.

$$f(e_{ox}) = k_{ini} \frac{(e_{ox,final} - e_{ox}(t))}{e_{ox,final}}, \quad (6)$$

this linear model proposed by Watanabe and Onishi¹⁵ assumes that $f(e_{ox})$ is linear to e_{ox} until a limit $e_{ox,final}$ is reached. k_{ini} is the initial formation rate of the oxide.

$$f(e_{ox}) = \frac{B_1}{1 + A_1 e_{ox}}, \quad (7)$$

this model is derived by assuming a net, pure Fickian diffusion of oxygen species through the oxide layer and first-order reaction of oxygen atoms with silicon atoms and organic moieties upon the SiO₂/unmodified-copolymer interface. In fact, this is a small extension of the widely known Deal-Grove model.²⁸ For small e_{ox} Eq. (7) can be Taylor expanded to Eq. (6), i.e., the Watanabe and Onishi model is the limit of the Deal-Grove model at small e_{ox} .

$$f(e_{ox}) = B \exp(-Ae_{ox}), \quad (8)$$

this exponential model is utilized to embody the ion-enhanced character of the process, as will be discussed later. It appears also that Eq. (7) and in consequence Eq. (6) are the limit of this last expression [Eq. (8)] at small e_{ox} .

To compare and validate the above mentioned equations [Eqs. (6)–(8)] we plot polymer thickness losses versus time and fit them using the three models. An example of such fitting is presented in Fig. 8. Discussion pertinent to each case follows in the respective section.

1. Watanabe and Onishi model

First the Watanabe and Onishi model is tested. We obtain the following expression:

$$e_{ox} = e_{ox,final} \left(1 - \frac{k_{sp}}{k_{ini}} \right) \left(1 - \exp \left(- \frac{k_{ini}}{e_{ox,final}} t \right) \right). \quad (9)$$

Albeit the lack of physical basis of this model, it turns out to follow the experimental data quite adequately, especially during the first 3 min (Fig. 8, model A). The problem with this model resides in the lack of physical justification in the oxide growth kinetics which assumes that after a couple of time constant $\tau = e_{ox,final}/k_{ini}$, the thickness loss is linear as a

FIG. 8. Thickness variation of a 40% ethyl-POSS polymer for (a) –100 V and (b) 0 V biases, as measured by ellipsometry (marks), and fit results for the case of: (A) Watanabe and Onishi model (thin line), (B) a pure chemical oxidation model (Deal-Grove) (medium line), and (C) a pure ion-enhanced oxidation model (thick line), for (a) 0 V bias and (b) –100 V bias.

function of time. This behavior is clearly not observed on our measurements even after 8 min of plasma exposure.

2. Chemical oxidation (Deal-Grove) model

This model is a diffusion-reaction scheme primarily set for the thermal oxidation of silicon²⁸ and has been implemented in order to introduce a more physical representation of SiO₂ growth kinetics, compared to Watanabe and Onishi.¹⁵ Here transport of the oxygen species through the SiO₂ obeys a pure Fickian diffusion (let D be the diffusion coefficient) without any reaction. At the SiO₂/unmodified-copolymer interface two kinds of chemical reactions take place: the silicon oxidation and the chemical etching of carbon and hydrogen. These reactions are considered independent one to each other and of the first order. This choice can be justified by the fact that the copolymer consists mainly of carbonaceous groups without silicon (mainly acrylate and aliphatic chains), whose chemical reaction with oxygen undoubtedly influences little reactions on silicon sites (POSS cage). The assumption concerning silicon oxidation is stronger because it supposes that the silicon oxidation is performed in a single step, with carbon withdrawal followed by oxidation of the free bond. The overall oxidation rate, which is assumed equal to the oxygen diffusive flux in this model, is therefore written as follows:

$$F = (k_{\text{ox}}^{\text{Si}} + k_{\text{ox}}^{\text{C}})c_i = k_{\text{ox}}c_i, \quad (10)$$

where $k_{\text{ox}}^{\text{Si}}$ and k_{ox}^{C} are, respectively, the reaction rates in cm/s on silicon and on the carbonaceous species, and c_i in cm^{-3} is the concentration of oxidizing species at the interface.

Taking into account the diffusive transport through the oxide layer and the equality of the oxygen flux to the reaction rate at the SiO_2 -copolymer interface, the $f(e_{\text{ox}})$ function is deduced,

$$f(e_{\text{ox}}) = \frac{k_{\text{ox}}^{\text{Si}}c_i}{\rho_{\text{SiO}_2}^{\text{at}}} = \frac{1}{\rho_{\text{SiO}_2}^{\text{at}}} \frac{k_{\text{ox}}^{\text{Si}}c_0}{1 + (k_{\text{ox}}/D)e_{\text{ox}}} = \frac{B_1}{1 + A_1e_{\text{ox}}}, \quad (11)$$

where $A_1 = k_{\text{ox}}/D$ and $B_1 = k_{\text{ox}}^{\text{Si}}c_0/\rho_{\text{SiO}_2}^{\text{at}}$.

With $\rho_{\text{SiO}_2}^{\text{at}}$ the atomic density of the oxide layer and c_0 the concentration of atomic oxygen at the sample surface, this concentration is supposedly known and fixed by the plasma parameters. The above expression is introduced in Eqs. (4') and (5) to determine $e(t)$ by means of numerical calculations. Thickness loss measurements are then fitted with A_1 and B_1 treated as fitting parameters for each copolymer, and with k_{sp} treated as a fitting parameter depending only on bias voltage and not on copolymer composition (whatever the copolymer, the same oxide material is sputtered). In Fig. 8 the inability of this model (model B) to fit the experimental data is clearly revealed.

3. Ion-enhanced oxidation model

As a result of the inadequacy of the previous models to fit the experimental results and the evidence given for the ion-enhanced character, we resort to the development of a novel, alternative approach to model and simulate the process. In treating this problem we attempt to introduce explicitly the ion-enhanced character of the oxidation by bringing in the ion flux to the reaction kinetics. In general, we may write such a reaction law as

$$f(e_{\text{ox}}) = K_{\text{IE}}^{\text{ox}}(\sqrt{E} - \sqrt{E_{\text{th}}})j_+\theta_i, \quad (12)$$

where j_+ is the ion flux at the polymer/ SiO_2 interface, $K_{\text{IE}}^{\text{ox}}$ is a coefficient of ion-enhanced oxidation of silicon atoms (only a weak function of the ion energy E), E_{th} is a threshold energy for the ion-enhanced reaction [e.g., for Si etching with fluorine atoms $E_{\text{th}} = 4$ eV (Ref. 29)], and θ_i is the surface coverage of oxygen atoms on the polymer/ SiO_2 interface. The ions reaching the surface are decelerated in the SiO_2 layer and energy can be assumed to be a decreasing function of e_{ox} . If we lump together the term $J_+ = (\sqrt{E} - \sqrt{E_{\text{th}}})j_+$, then we may consider the following exponential relation:

$$J_+ = J_+^0 \exp(-Ae_{\text{ox}}), \quad (13)$$

where J_+^0 is the lumped ion energy flux at the top interface (plasma/ SiO_2) and is determined by the plasma conditions, and A is a parameter inversely proportional to the ion projected range. Equation (12) can be written

$$f(e_{\text{ox}}) = K_{\text{IE}}^{\text{ox}}J_+^0\theta_i \exp(-Ae_{\text{ox}}). \quad (14)$$

We should note here that this pure exponential profile for the oxide growth function has been previously utilized within the framework of the silicon oxidation by an oxygen plasma,³⁰ but the explanation of this exponential term is not correct in our opinion and is not based on ion-enhanced oxidation.

Let us now determine the oxide growth function $f(e_{\text{ox}})$,

$$f(e_{\text{ox}}) = B \exp(-Ae_{\text{ox}}). \quad (15)$$

With $B = K_{\text{IE}}^{\text{ox}}J_+^0\theta_i$ in nm/min, where θ_i may be assumed close to unity.

Taking into account the SiO_2 mass balance presented previously [Eq. (4)] the oxide thickness evolution is determined by

$$e_{\text{ox}} = \frac{1}{A} \ln \left[\left(1 - \frac{B}{k_{\text{sp}}} \right) \exp(-k_{\text{sp}}At) + \frac{B}{k_{\text{sp}}} \right]. \quad (16)$$

Parameter B depends on the material through the oxidation rate $K_{\text{IE}}^{\text{ox}}$ and on the plasma conditions through the term J_+^0 . Parameter B is a rate that quantifies silicon oxidation at the oxide/copolymer interface. The larger this parameter is, the faster the oxidation takes place, and the larger the maximum oxide thickness is. Related to the ion projected range parameter A is of course strongly dependent on the bias voltage.

Equation (13) gives the upper limit for the oxide thickness grown under bias $e_{\text{oxlim}} = (1/A) \ln(B/k_{\text{sp}})$. It appears that without sputtering ($k_{\text{sp}} = 0$) this thickness tends towards infinity, since nothing limits the oxide growth.

Again, by having determined $f(e_{\text{ox}})$ we may apply the model to the ellipsometry experimental results by fitting parameters A and B for each copolymer and the sputter rate k_{sp} for each bias voltage (k_{sp} is assumed identical for each copolymer). The ion-enhanced model can fit the data very well (Fig. 8, model C). Agreement is satisfactory for all materials, bias voltages, and time, something that is not obtained by either the Watanabe and Onishi model or the Deal-Grove model. The good quality of the fit in this case reveals the predominant oxidation mechanisms; the ion-enhanced chemical oxidation.

The sputtering rate k_{sp} is found to be equal to 0.2 nm/min at 0 V bias and 0.5 nm/min at -100 V. Under the same experimental conditions we measured a sputtering rate of thermal silicon oxide equal to 2.6 nm/min at -100 V. This weak value of k_{sp} is consistent with previous discussions, in which we suggested that POSS materials are little sputtered in oxygen plasmas.

The values that fitted A^{-1} and B coefficients are portrayed in Fig. 9 as a function of parameter δ , i.e., the inverse of silicon concentration. One can notice a dependency of the two coefficients with the silicon percentage in the material. The richer the material is in silicon (δ small), the weaker the A^{-1} . As mentioned previously A^{-1} is correlated to the projected range of oxygen ions in the context of an ion-enhanced modeling. The fitting results support this correlation in that A^{-1} is lower in the case of 0 V bias.

FIG. 9. Parameter A^{-1} (corresponding to the ion projected range) and B (corresponding to the initial oxidation rate) as a function of parameter δ (POSS content), for two bias voltages of 0 and -100 V.

B is the initial oxidation rate and its value is higher for small δ , since polymers with large silicon content oxidize faster. In Fig. 9, it appears that all copolymers (except the 20% ethyl-POSS) have a coefficient B of the same order of magnitude. According to the model this indicates a constant silicon oxidation rate at both 0 and -100 V. Given the fact that $B = K_{IE}^{\text{ox}} J_+^0 \theta_i$, one would expect B at -100 V to be larger than at 0 V, because J_+^0 is proportional to $(\sqrt{E} - \sqrt{E_{\text{th}}})$. We have no clear explanation for this surprising result. A decrease of θ_i with bias voltage could partially explain this behavior. However, we have no experimental evidence of such decrease.

The 20% ethyl-POSS copolymer shows a different coefficient B for -100 and 0 V, and the coefficient B at -100 V is higher than that of the 30% MA₂₀ and 40% ethyl-POSS materials. This difference between the 20% ethyl-POSS material and the other copolymers has already been discussed in the previous paragraph. This particular behavior undoubtedly comes from the small silicon proportion (at. % Si=3.2) and from the limits of the model under these conditions.

This exponential model applies well to the experiments and provides very interesting information on the oxidation of ethyl-POSS containing copolymers in oxygen plasma. Both at 0 and at -100 V the main mechanism involved to explain thickness loss is the density increase of the layer during its oxidation. We here show that oxidation is strongly supported by ions through an ion-enhanced oxidation process. Ion-

enhanced oxidation is an example of the well known ion-neutral synergetic effect, largely studied in the case of plasma etching,^{31,32} but also in other plasma research fields such as plasma-catalyst interaction,^{33,34} fusion related studies,³⁵ atomic surface recombination,^{36,37} deposition,³⁸ or plasma induced damages on surfaces.³⁹ In addition to these various information, this model could also be used for the development of a pattern transfer simulation code.⁴⁰⁻⁴² These kinds of simulations are increasingly invaluable⁴³⁻⁴⁵ with the shrink of the dimensions of the etch pattern.

V. CONCLUSION

The ethyl-POSS containing materials present some very interesting properties for next generation lithography.^{13,45} With the introduction of a photoacid generator, a positive development scheme can be achieved. Their integration into a bilayer lithography scheme in association with an organic underlayer is possible, because of a high etching selectivity in oxygen plasmas. Indeed we showed that a protective silicon oxide layer is formed on ethyl-POSS materials when exposed to oxygen plasmas, whereas purely hydrocarbonaceous polymers are generally etched very quickly.

In order to understand the etch mechanisms of ethyl-POSS materials under oxygen plasmas, we developed an etching model and confronted it to the experimental results. We showed that the material thickness loss is mainly caused by the formation of the oxide layer which is denser than the copolymer. Thus, the thickness loss can be seen as a densification. We demonstrated that for ethyl-POSS materials ionic bombardment mostly seems to favor oxidation which is higher at -100 V compared to 0 V. Of course this is particularly interesting for the integration of these materials into a bilayer resist scheme. Comparison of three models for the plasma etching was performed; the classic Watanabe and Onishi model, a modified Deal-Grove model for polymers, and an ion-enhanced model introduced here for the first time, which gives a very good prediction of POSS material thickness loss with time.

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