# Surface Reactivity of OH Molecules during Deposition of SiO<sub>2</sub> from Siloxane-Based Plasmas

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The surface interactions of OH(X<sup>2</sup>Π) radicals during SiO<sub>2</sub> deposition from 1,3,5,7-tetramethylcyclotetrasiloxane (TMCTS)/oxidant (O<sub>2</sub> or N<sub>2</sub>O) and dimethyldimethoxysilane (DMDMOS)/oxidant (O<sub>2</sub> or N<sub>2</sub>O) plasmas have been measured by using the imaging of radicals interacting with surfaces (IRIS) method. The reactivity of OH at the surface of a growing SiO<sub>2</sub> film has been determined as a function of the applied rf plasma power (*P*), the precursor-to-oxidant ratio, and the substrate temperature (*T*<sub>s</sub>). For both Si precursors, the surface reactivity (*R*) of OH during SiO<sub>2</sub> deposition on a 300 K Si substrate is ~0.60 and is unaffected by changing precursor:oxidant ratio but does increase slightly with *P*. In contrast, at higher substrate temperatures (*T*<sub>s</sub> > 350 K), *R* decreases to  $0.16 \pm 0.10$  for 1:10 TMCTS/O<sub>2</sub> plasma (*P* = 100 W) and to  $0.42 \pm 0.03$  for 1:10 DMDMOS/O<sub>2</sub> plasma (*P* = 100 W). The rotational ( $\Theta_R$ ) and translational ( $\Theta_T$ ) temperatures of the OH radicals have also been determined. The formation and role of OH in SiO<sub>2</sub> deposition are discussed and compared with previous results for TEOS/O<sub>2</sub> plasmas.

# 1. Introduction

Organosilane precursors, such as tetraethoxysilane (TEOS), are widely used to deposit SiO<sub>2</sub> and other silicon-based materials in plasma-based processes.<sup>1-3</sup> An oxidant such as O<sub>2</sub> or N<sub>2</sub>O is commonly added to the precursors to deposit stoichiometric SiO<sub>2</sub>. In plasma-enhanced chemical vapor deposition (PECVD) processes, the role of the oxidant is to oxidatively remove organic components from both the gas phase and the growing film, resulting in the production of high-quality  $SiO_2$ .<sup>2,4-12</sup> In the gas phase, oxygen oxidizes and enhances fragmentation of precursor molecules. Moreover, oxidation of adsorbed precursor fragments on the film-forming surface is important to form hydrocarbon-free SiO<sub>2</sub>. However, a moderate concentration of the undesirable silanol (-SiOH) species is also incorporated.<sup>4-12</sup> In the reactions of oxygen with hydrocarbon species, OH is an important oxidation product as well as a reactant.<sup>13,14</sup> Thus, studies of gas-phase OH molecules and their surface reactivity during SiO<sub>2</sub> deposition provide insight into hydrocarbon removal in both gas-phase and gas-surface interactions, and reveal a possible source of silanol groups in the film.

The imaging of radicals interacting with surfaces (IRIS) technique<sup>15,16</sup> used in our laboratories characterizes gas-phase plasma species as well as their surface reactivity during plasma processing of a substrate. The IRIS method combines plasma and molecular beam technologies with laser-induced fluorescence (LIF) to provide spatially resolved two-dimensional images of radical species during plasma processing. Buss and co-workers<sup>17</sup> applied the IRIS technique to study the gas-phase and surface reactivity of OH in a H<sub>2</sub>O plasma system interacting with a Si<sub>3</sub>N<sub>4</sub> surface. Note that the H<sub>2</sub>O plasma only hydrates the Si<sub>3</sub>N<sub>4</sub> substrate surface and it is a nondepositing and nonetching system. It is hypothesized that the OH radical was involved in an exchange mechanism with silanol groups present on the substrate surface. The surface reactivity (*R*) of OH was

measured as 0.57  $\pm$  0.05 when the substrate temperature ( $T_s$ ) was 300 K. *R* decreased to approximately zero (100% scatter) at  $T_s \geq 500$  K. The decrease in *R* was attributed to the loss of silanol surface coverage at high  $T_s$  and to the decrease in the activation energy for desorption relative to the activation energy for reaction.<sup>17</sup>

We have previously investigated the source and role of OH in a film deposition system, specifically PECVD of SiO<sub>2</sub>, using a 20:80 TEOS/O<sub>2</sub> system.<sup>18,19</sup> With the TEOS/O<sub>2</sub> system, the surface reactivity of OH on a 300 K Si substrate was 0.41  $\pm$  0.04 and was unaffected by changing the applied rf plasma power (*P*). Interestingly, *R* decreased significantly as the substrate temperature was increased, reaching 0.15 at  $T_s > 350$  K. This was attributed to a decrease in reaction partners such as the silanol group (-SiOH) or H atoms on the surface at higher  $T_s$ . Using isotopically labeled <sup>18</sup>O<sub>2</sub> as the oxidant, we also found that oxygen atoms in the O<sub>2</sub> were the source of the oxygen atoms in OH, not oxygen in the TEOS precursor.

In a separate study, we recently investigated PECVD of SiO<sub>2</sub> films from 1,3,5,7-tetramethylcyclotetrasiloxane (TMCTS)- and dimethyldimethoxysilane (DMDMOS)-based plasmas.12 TM-CTS and DMDMOS are relatively new precursors for deposition of SiO<sub>2</sub>, and are of interest for the deposition of porous low dielectric constant films. High-quality SiO2 films can be deposited from these two precursors with sufficient oxidant (O2 or N<sub>2</sub>O) addition. Moderate amounts of -SiOH species were, however, also present in the films. As with most SiO<sub>2</sub> deposition systems, we found that the silanol moieties are reduced or eliminated at elevated  $T_s$ . Similar to the TEOS system, OH radicals in the plasma gas phase may be responsible for silanol species formation and may also be involved in precursor fragmentation and film deposition. We present herein the characterization of OH in both the gas phase and at the gassurface interface in the TMCTS and DMDMOS plasma systems. Deposition parameters studied include applied rf power, precursor-to-oxidant ratio, and substrate temperature. Comparison of the results for TMCTS- and DMDMOS-based plasma systems

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with those for the TEOS/O<sub>2</sub> and  $H_2O:Si_3N_4$  systems expanded our knowledge of sources and roles of OH in SiO<sub>2</sub> deposition plasmas.

## 2. Experimental Details

The IRIS apparatus has been described in detail previously, including details of the plasma generation and chamber specifics.<sup>16</sup> Briefly, in a typical IRIS experiment, feed gases enter the rear of a tubular glass reactor, 13.56 MHz rf power is applied, and an inductively coupled plasma is produced. The expansion of the plasma into a differentially pumped highvacuum chamber through a 1-cm hole and two collimating slits creates a near-effusive molecular beam, which contains virtually all the species present in the bulk plasma. A tunable laser intersects the plasma molecular beam downstream at a 45° angle and excites the species of interest. Spatially resolved laser induced fluorescence (LIF) images are collected with a gated intensified charge-coupled device (ICCD) camera located perpendicular to both the laser beam and the plasma molecular beam. A substrate that is oriented parallel to the laser beam is rotated into the path of the plasma molecular beam and LIF images are again collected. The difference between LIF images collected with the substrate in and out of the path of the molecular beam is attributable to the species scattered off the substrate surface. Comparisons between the spatial distribution of scattered and incident molecules are used to determine the surface reactivity of the species of interest.

In the present study, plasmas were produced from mixtures of silicon precursors [TMCTS (Gelest, >95%) or DMDMOS (Gelest, >95%)] and oxidant gases [O<sub>2</sub> (General Air, >99.99%) or N<sub>2</sub>O (General Air, >99%)]. The TMCTS and DMDMOS vapors were delivered and controlled with a Nupro bellowssealed metering valve. O2 or N2O was introduced into the reactor through an MKS mass flow controller and allowed to stabilize prior to the addition of the silicon precursors. The total pressure in the reactor was maintained at 50  $\pm$  1 mTorr. The flow rate of O2 or N2O varied from 10 to 22 sccm and the ratio of precursor to oxidant was calculated from their partial pressures and varied from 1:4 to 1:30. The applied rf power was varied from 50 to 150 W. Substrates were 25 mm  $\times$  40 mm *p*-type Si (100) wafers with the polished side facing the molecular beam. The wafer was mounted on a heatable substrate holder and  $T_s$ was varied from 295 to 573 K. The distance between the laser beam and the substrate surface was 3 mm for all reactivity experiments.

Tunable laser light ranging from 500 to 1000  $\mu$ J/pulse was produced from a frequency-doubled excimer (XeCl, 170 mJ, 30 Hz) pumped dye laser system, using Rhodamine B dye. For fluorescence excitation experiments, the plasma molecular beam was collimated by a single 1.5-mm-wide slit. The laser was stepped from 307.6 to 309.0 nm in 0.001-nm increments and the LIF of the OH  $A^2\Sigma^+ - X^2\Pi$  (0,0) transition was collected and plotted as a function of laser wavelength. At a given laser power and given laser wavelength, the fluorescence signal is proportional to the OH ground-state population.<sup>15,17</sup> We have previously examined wider spectral ranges and find that excitation data taken in this limited wavelength range are representative of the OH population.<sup>18,19</sup> For reactivity measurements, the plasma molecular beam was collimated by two slits, 1.0 and 1.25 mm wide, with the second slit located 12 mm downstream from the first slit. The first slit was mounted on a liquid N2 cold shield to minimize desorption of molecules from the slit surface. The laser was tuned to 307.853, 308.164, or 308.528 nm corresponding to the J = 1.5, 3.5, and 5.5 states of

the Q<sub>1</sub> branch of the OH  $A^2\Sigma^+ - X^2\Pi(0,0)$  transition, respectively. Except for the *J*-state substrate temperature dependence study, all data were collected with the laser tuned to 307.853 nm, corresponding to the Q<sub>1</sub> (*J* = 1.5) state of OH.

The LIF signals were imaged onto the ICCD camera gated at 100 ns after the excitation to avoid laser light interference. A U340 band-pass filter was placed between the ICCD camera and the vacuum chamber to reduce spurious signals from scattered laser light and plasma emission. A gate width of 1000 ns was used (the OH  $A^2\Sigma^+$  radiative lifetime is  $688 \pm 7 \text{ ns}^{20}$ ) and the pixels were  $4 \times 4$  binned to increase the signal-tonoise ratio. Each image consists of 6000 or 7200 laser pulses. Multiple sets of data were taken with the surface alternating in and out of the molecular beam path. Background images were taken with the laser tuned to a nonresonance wavelength and subtracted from each image. One-dimensional cross sections were formed by averaging 15 pixel columns along the laser axis and plotting signal intensity as a function of distance along the laser path.

A numerical simulation is used to quantify the spatially resolved LIF data to obtain the surface reactivity of the OH radicals. The simulation program has been described in detail previously.<sup>18</sup> It is based on the known experimental geometry and calculates the spatial distribution of the OH number density in the molecular beam at the interaction region as well as those for the molecules desorbing from the substrate surface. The scattering coefficient, *S*, defined as the ratio of the flux of scattered molecules to that of the incident beam, is adjusted to best fit the experimental data. The surface reactivity, *R*, is defined as 1 - S.

IRIS experiments measure the relative densities of molecules in the incident molecular beam and scattered molecules from a surface. If the velocity distributions of the two populations (i.e., the molecular beam molecules and the scattered molecules) are significantly different, this can affect their densities in the laser.<sup>15</sup> This can be accounted for by scaling *S* by the ratio of the velocity of the scattered molecules to the velocity of the molecular beam,  $F_s = V_{scat}/V_{mb}$ .<sup>21,22</sup> With methods described in detail previously,<sup>23,24</sup> we have utilized the IRIS instrument to measure the velocities of OH in our plasma molecular beams. For velocity distributions of scattered molecules, we assume thermal equilibration with the surface has occurred. Thus, the velocity of scattered molecules is assumed to be characterized by a Maxwell–Boltzmann distribution at  $T_s$ .

# 3. Results

3.1. Spectroscopy. LIF is a nonintrusive and highly selective technique that allows for the identification and study of one type of species among many others in the plasma molecular beam. Panels A and C in Figure 1 show the fluorescence excitation spectrum for OH obtained from 1:10 TMCTS/O2 and DMDMOS/O<sub>2</sub> plasmas at P = 100 W, respectively. Calculated spectra for the OH  $A^2\Sigma^+$  –  $X^2\Pi$  (0,0) transition using the molecular constants of Coxon<sup>25</sup> are shown in Figure 1, panels B and D. The excellent agreement in the line positions verifies the fluorescing species is indeed OH. A comparison of the relative line intensities between the experimental spectrum with the spectra calculated at different rotational temperatures, using a linear least-squares method, yields  $\Theta_R=325\pm20$  K for OH in the TMCTS plasma. With the same method, the OH rotational temperatures for plasmas of 1:20 TMCTS/N<sub>2</sub>O, 1:10 DMD-MOS/O<sub>2</sub>, and 1:20 DMDMOS/N<sub>2</sub>O at P = 100 W are 365  $\pm$ 25, 380  $\pm$  25, and 355  $\pm$  20 K, respectively. Thus,  $\Theta_{\rm R}({\rm OH})$ values in these plasmas are approximately the same within



**Figure 1.** (A) Experimental fluorescence excitation spectrum of OH in a TMCTS:O<sub>2</sub> (1:10) (P = 100 W) plasma molecular beam. Peaks at 307.853, 308.164, and 308.528 nm correspond to the Q<sub>1</sub> branch 1.5, 3.5, and 5.5 *J*-state of the OH A<sup>2</sup> $\Sigma^+$  - X<sup>2</sup> $\Pi$  (0,0) transition, respectively. (B) Calculated fluorescence excitation spectrum of OH A<sup>2</sup> $\Sigma^+$  - X<sup>2</sup> $\Pi$  (0,0) transition, using the molecular constant of Coxon<sup>25</sup> at  $\Theta_R = 325$  K. (C) Experimental fluorescence excitation spectrum of OH in a DMDMOS:O<sub>2</sub> (1:10) (P = 100 W) plasma molecular beam. (D) Calculated fluorescence excitation spectrum of OH in a DMDMOS:O<sub>2</sub> (1:10) (P = 100 W) plasma molecular beam. (D) Calculated fluorescence excitation spectrum of OH in a DMDMOS:O<sub>2</sub> (1:10) (P = 100 W) plasma molecular beam. (D) Calculated fluorescence excitation spectrum of OH in a DMDMOS:O<sub>2</sub> (1:10) (P = 100 W) plasma molecular beam. (D) Calculated fluorescence excitation spectrum of OH in a DMDMOS:O<sub>2</sub> (1:10) (P = 100 W) plasma molecular beam. (D) Calculated fluorescence excitation spectrum of OH in a DMDMOS:O<sub>2</sub> (1:10) (P = 100 W) plasma molecular beam. (D) Calculated fluorescence excitation spectrum of OH A<sup>2</sup> $\Sigma^+$  - X<sup>2</sup> $\Pi$  (0,0) transition, using the molecular constant of Coxon<sup>25</sup> at  $\Theta_R = 380$  K.



#### **Precursor : Oxidant**

**Figure 2.** LIF intensity of OH as a function of precursor-to-oxidant ratio at P = 100 W for plasmas of TMCTS:O<sub>2</sub> (solid circles), TMCTS: N<sub>2</sub>O (open circles), DMDMOS:O<sub>2</sub> (solid triangles), and DMDMOS: N<sub>2</sub>O (open triangles). Based on reproducibility, estimated errors in these values are  $\pm 10\%$ .

experimental error, with the greatest disparity occurring between the TMCTS/O<sub>2</sub> system and the DMDMOS/O<sub>2</sub> system. The values derived in these systems are, however, significantly lower than that measured for OH in the 20:80 TEOS/O<sub>2</sub> plasma at *P* = 80 W, which yielded  $\Theta_{\rm R} = 440 \pm 50$  K.<sup>18</sup> These differences are discussed further below.

Figure 2 shows the OH LIF intensities as a function of the precursor-to-oxidant ratio for TMCTS/O<sub>2</sub>, TMCTS/N<sub>2</sub>O, DM-DMOS/O<sub>2</sub>, and DMDMOS/N<sub>2</sub>O plasmas with P = 100 W. Note that no OH LIF signals were detected for plasmas comprising 100% precursor, similar to results in the TEOS/O<sub>2</sub> system. OH LIF intensities become measurable with addition of oxidant and



**Figure 3.** LIF intensity of OH as a function of *P* for plasmas of TMCTS:O<sub>2</sub> (1:10) (solid circles), TMCTS:N<sub>2</sub>O (1:20) (open circles), DMDMOS:O<sub>2</sub> (1:10) (solid triangles), and DMDMOS:N<sub>2</sub>O (1:20) (open triangles). Based on reproducibility, estimated errors in these values are  $\pm 10\%$ .

increase dramatically when the ratio exceeds 1:2 for  $O_2$  or 1:8 for  $N_2O$ . The OH LIF intensities reach maxima at ratios of 1:6 for  $O_2$  and 1:20 or 1:30 for  $N_2O$ . These results demonstrate that production of OH is directly related to the oxidant concentration in the plasma. Figure 3 shows the OH LIF intensities as a function of *P* for plasmas of 1:10 TMCTS/ $O_2$ , 1:20 TMCTS/ $N_2O$ , 1:10 DMDMOS/ $O_2$ , and 1:20 DMDMOS/  $N_2O$ . In all of the plasma systems, OH LIF intensities increase with *P*. Note that film quality under these high oxidant conditions is quite good, with little to no carbon incorporation observed. At lower *P* values, however, we observe significant contributions from silanol species in the films.



**Figure 4.** Two-dimensional ICCD images of OH LIF signals in (A) a TMCTS:O<sub>2</sub> (1:10) (P = 100 W) plasma molecular beam and (B) with an Si substrate rotated into the path of the molecular beam at a laser-surface distance of 3 mm. Image C is the difference between images A and B and shows only OH molecules scattered from the surface. Dashed lines indicate the locations of the molecular beam and the laser beam.



Figure 5. Cross sections (solid curves) of OH LIF images A and C in Figure 4. Dashed curves represent the simulation results with R = 0.38.

3.2. Surface Reactivity. Surface reactivity in IRIS experiments is measured by comparison of ICCD images obtained with the substrate surface in and out of the path of the plasma molecular beam. Figure 4 shows a typical set of 2-dimensional ICCD images of LIF signals for OH in a 1:10 TMCTS/O2 plasma at P = 100 W. Signals from OH in the incident molecular beam are shown in Figure 4A. In Figure 4B, the substrate is placed in the path of the molecular beam and the LIF signal includes both OH in the incident molecular beam and any OH scattered from the substrate surface. Figure 4C is the difference between panels B and A in Figure 4, showing only the signal resulting from OH desorbing from the surface. By averaging several columns of pixels along the laser beam axis, 1-D cross sections of the LIF images shown in Figure 4A,C can be created (Figure 5). The simulation results, shown as dashed curves in Figure 5, yield a scattering coefficient, S = $0.62 \pm 0.05$ , which results in a surface reactivity of R = 0.38 $\pm$  0.05. Averaging three sets of data gives  $R = 0.40 \pm 0.03$  for OH from 1:10 TMCTS/O<sub>2</sub> plasma at P = 100 W at the surface of a depositing SiO<sub>2</sub> film.

As noted in Section 2, changes in translational temperature upon interaction with the substrate can significantly affect the observed scatter coefficient. Here, we have measured the

TABLE 1:	$\Theta_{\rm T}$ for	OH as a	a Function	of F
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		$\Theta_{\mathrm{T}}\left(\mathrm{K}\right)$	
plasma conditions	50 W <sup>a</sup>	100 W	150 W
TMCTS:O <sub>2</sub> (1:10)	308	$508\pm 64$	$708 \pm 110$
TMCTS:N <sub>2</sub> O (1:20)	383	$573 \pm 55$	$763 \pm 41$
DMDMOS:O <sub>2</sub> (1:10)	498	$670 \pm 78$	$842\pm77$
DMDMOS:N <sub>2</sub> O (1:20)	541	$725\pm78$	$909 \pm 94$

<sup>*a*</sup> As signal levels were extremely low at 50 W, these values were estimated to a first-order approximation assuming a linear relationship between  $\Theta_{\rm T}$  and *P*.

velocity of OH radicals in our molecular beams using methods described previously.<sup>23,24</sup> Values for  $\Theta_{\rm T}$  are listed in Table 1. These values have been used to calculate correction factors for our scattering coefficients, which are listed in Table 2, along with the corrected *S* values. For comparison, results from the TEOS/O<sub>2</sub> system are also given in Table 2.

The effects of *P* and the precursor-to-oxidant ratio on the surface reactivity of OH have also been examined and the resulting *R* values are listed in Tables 3 and 4, respectively. These values have also been corrected based on the differences in velocity distributions. For both silicon precursors, and for O<sub>2</sub> and N<sub>2</sub>O, OH reactivity on the SiO<sub>2</sub> film forming surface is essentially the same:  $R = 0.59 \pm 0.05$  under all conditions at P = 100 W. However, OH reactivity increases from  $R = 0.50 \pm 0.06$  at P = 50 W to  $R = 0.64 \pm 0.04$  at P = 150 W. For comparison, results from the TEOS/O<sub>2</sub> system are also listed in Tables 3 and 4.

Substrate temperature is another important deposition parameter in SiO<sub>2</sub> PECVD processes, specifically with respect to the incorporation of SiOH groups. Thus, the surface reactivity of OH molecules as a function of  $T_s$  can provide additional insight into deposition mechanisms. Measurement of the J-state dependence of S on  $T_s$  can also be used to determine the  $\Theta_R$  of  $OH.^{17,18,21,22,26}$  As noted above, S is defined as the ratio of the flux of scattered molecules to that of the incident beam. If OH radicals in the incident molecular beam adsorb on the surface, thermally equilibrate, and desorb, then the desorbed OH will have the temperature characterized by  $T_s$ . If  $\Theta_R \neq T_s$ , the population of a specific J state in the incident molecular beam will be different from that in the scattered molecules from the surface. There will, therefore, be an apparent change in the observed S values for different J states. The observed S values of different J states will be the same only when  $\Theta_{\rm R} = T_{\rm s}$ . Figure

TABLE 2: OH Translational Temperatures, Correction Factors, S, and R Values at P = 100 W

		correction factor <sup>a</sup>				
plasma conditions	$\Theta_{\mathrm{T}}\left(\mathrm{K}\right)$	$(V_{\rm scat}/V_{\rm mb})$	S	R	$S_{ m cor}$	$R_{\rm cor}$
TMCTS:O <sub>2</sub> (1:10)	$508 \pm 64$	0.77	$0.60 \pm 0.03$	0.40	0.46	0.54
TMCTS:N <sub>2</sub> O (1:20)	$573 \pm 55$	0.72	$0.57 \pm 0.05$	0.43	0.41	0.59
DMDMOS:O <sub>2</sub> (1:10)	$670 \pm 78$	0.67	$0.59 \pm 0.05$	0.41	0.40	0.60
DMDMOS:N <sub>2</sub> O (1:20)	$725 \pm 78$	0.64	$0.67 \pm 0.12$	0.33	0.43	0.57
TEOS:O <sub>2</sub> $(1:4)^{b}$	$912 \pm 20$	0.57	$0.59\pm0.04$	0.41	0.34	0.66

<sup>*a*</sup> These values assume a Maxwell–Boltzmann distribution of  $T_s = 300$  K for scattered OH. <sup>*b*</sup> Values for the TEOS/O<sub>2</sub> system were measured at P = 85 W.<sup>18</sup>

TABLE 3: R Values for OH as a Function of Applied rf Power<sup>a</sup>

	reactivity coefficients, R			
plasma conditions	50 W	100 W	150 W	
TMCTS:O <sub>2</sub> (1:10)	$0.40(0.41) \pm 0.11$	$0.40(0.54) \pm 0.03$	$0.33(0.57) \pm 0.03$	
$DMDMOS:O_2$ (1:20)	$\begin{array}{c} 0.46 \ (0.52) \pm 0.04 \\ 0.42 \ (0.55) \pm 0.06 \end{array}$	$0.43 (0.59) \pm 0.05$ $0.41 (0.60) \pm 0.05$	$0.46(0.66) \pm 0.04$ $0.41(0.65) \pm 0.04$	
$DMDMOS:N_2O(1:20)$	$0.34(0.51) \pm 0.17$	$0.33(0.57) \pm 0.12$	$0.40(0.66) \pm 0.10$	
DMDMOS:O <sub>2</sub> (1:10) DMDMOS:N <sub>2</sub> O (1:20) TEOS:O <sub>2</sub> (1:4) <sup>b</sup>	$\begin{array}{c} 0.42 \ (0.55) \pm 0.06 \\ 0.34 \ (0.51) \pm 0.17 \end{array}$	$\begin{array}{c} 0.41 \ (0.60) \pm 0.05 \\ 0.33 \ (0.57) \pm 0.12 \\ 0.41 \ (0.66) \pm 0.04 \end{array}$	$\begin{array}{c} 0.41 \ (0.65) \pm 0.\\ 0.40 \ (0.66) \pm 0. \end{array}$	

<sup>*a*</sup> Numbers in parentheses are values corrected for the different velocity distributions of the incident and scattered OH. <sup>*b*</sup> Values for the TEOS/O<sub>2</sub> system were measured at P = 85 W.<sup>18</sup>

TABLE 4: R Values for OH as a Function of Precursor-to-oxidant Ratio at  $P = 100 \text{ W}^a$ 

		reactivity coefficients, R			
plasma conditions	1:4	1:10	1:20	1:30	
TMCTS:O <sub>2</sub>	$0.40~(0.54)\pm0.04$	$0.40~(0.54)\pm0.03$	$0.40~(0.54)\pm0.03$	$0.39(0.53) \pm 0.04$	
TMCTS:N <sub>2</sub> O	-	$0.48~(0.63)\pm0.05$	$0.43~(0.59)\pm0.05$	$0.50(0.64) \pm 0.04$	
DMDMOS:O <sub>2</sub>	$0.35(0.56) \pm 0.15$	$0.41(0.60) \pm 0.05$	$0.40(0.60) \pm 0.06$	$0.37(0.58) \pm 0.07$	
DMDMOS:N <sub>2</sub> O		$0.39(0.61) \pm 0.17$	$0.33(0.57) \pm 0.12$	$0.37(0.60) \pm 0.11$	
$TEOS:O_2^b$	$0.41~(0.66)\pm0.04$				

<sup>*a*</sup> Numbers in parentheses are values corrected for the different velocity distributions of the incident and scattered OH. <sup>*b*</sup> Values for the TEOS/O<sub>2</sub> system were measured at P = 85 W.<sup>18</sup>

6 shows the measured S values as a function of  $T_s$  for J states of 1.5, 3.5, and 5.5, as well as the numerical simulations of S (solid lines) that account for the relative J-state population changes with substrate temperature. These values have been corrected based on the differences in velocity distributions. For OH, in a 1:10 TMCTS/O<sub>2</sub> plasma at P = 100 W (Figure 6A), the best fit to the experimental results yields  $S = 0.84 \pm 0.10$ for all J states and for substrate temperatures  $T_s > 350$  K (S = 0.40 for  $T_{\rm s} = 295$  K), which gives  $R = 0.16 \pm 0.10$ . The intersection of the simulated lines for all three J states gives an estimation of  $\Theta_R = 345 \pm 30$  K. For OH in a 1:10 DMDMOS/  $O_2$  plasma at P = 100 W (Figure 6B), the simulation results yield  $S = 0.58 \pm 0.03$  ( $R = 0.42 \pm 0.03$ ) for  $T_s > 350$  K and  $\Theta_{\rm R}$  = 360 ± 30 K. In both systems, the OH rotational temperatures estimated with this method are in excellent agreement with those obtained from the fluorescence excitation spectra. In addition, the data also suggest that there is no J-state dependence for the OH reactivity.

# 4. Discussion

The deposition mechanism for PECVD of SiO<sub>2</sub> with organosilanes or organosiloxanes with O<sub>2</sub> or N<sub>2</sub>O is commonly proposed to consist of several steps: (1) precursor fragmentation and oxidation in the plasma; (2) adsorption of the precursor fragments onto the surface followed by surface diffusion; (3) gas-surface oxidation to further remove hydrocarbon species and to form inorganic film precursors; and (4) final SiO<sub>2</sub> network formation through condensation of these inorganic precursors.<sup>2,8</sup> Data from our complementary study of SiO<sub>2</sub> PECVD from TMCTS- and DMDMOS-based plasmas<sup>12</sup> also support the above deposition mechanism. The addition of an oxidant is essential to the deposition of high-quality SiO<sub>2</sub> films, through oxidative removal of hydrocarbon substituents from the precursor in both the gas phase and through gas—surface reactions.<sup>2,4–11</sup> Given that OH is a well-known and important product in hydrocarbon oxidation reactions,<sup>13,14,27</sup> studies of gas-phase OH and its surface interactions during film formation are important to understanding of the overall SiO<sub>2</sub> deposition processes.

In the TMCTS/O<sub>2</sub>(N<sub>2</sub>O) or DMDMOS/O<sub>2</sub>(N<sub>2</sub>O) plasmas, the precursor molecules and O2 or N2O molecules are dissociated, resulting in precursor fragments and O atoms. OH is formed in the reactions between O atoms and the hydrocarbon species of the precursor fragments. In TEOS/O2 plasmas, isotopically labeled <sup>18</sup>O<sub>2</sub> studies effectively identified the oxygen source for OH as the O<sub>2</sub> gas, not the oxygen in the TEOS precursor.<sup>18</sup> In the plasma systems studied here, we believe the oxygen source for the OH is also the oxidants, O<sub>2</sub> and N<sub>2</sub>O. This is supported by the observation that no OH LIF signals were detected for 100% precursor plasmas and that the OH LIF intensities are directly correlated with oxidant addition (Figure 2). Hydrocarbon oxidation studies have determined that ground-state  $O(^{3}P)$  atoms typically react with small alkanes in the gas phase through H-atom abstraction to form OH.27 Electronically excited O(1D) atoms react with alkanes by either H-atom abstraction or insertion into the C-H bond.<sup>28,29</sup> In general, all of these OHforming reactions between O atoms and alkanes involve strong interactions only between the O atom and individual C-H bonds, rather than with the entire hydrocarbon molecule.<sup>27-30</sup>

Similarly, hydrogen abstraction to form OH is a major reactive pathway for reactions of O atoms with hydrocarbon moieties in precursors such as TMCTS, DMDMOS, TEOS, and their fragments.<sup>18</sup> As noted in Section 3.1 and listed in Table



**Figure 6.** Substrate temperature dependence of the observed scattering coefficient, *S*, for OH rotational states of J = 1.5 (closed circles), 3.5 (open circles), and 5.5 (closed triangles) for plasmas of (A) TMCTS: O<sub>2</sub> (1:10) and (B) DMDMOS:O<sub>2</sub> (1:10) at P = 100 W. Solid lines are the results from simulations, assuming  $R = 0.16 \pm 0.10$  (A) and 0.42  $\pm$  0.03 (B) for  $T_{\rm s} > 350$  K. The intersection of the simulation lines yields the rotational temperatures of  $\Theta_{\rm R} = 345 \pm 30$  (A) and 360  $\pm$  30 K (B).

1, the rotational and translational temperatures of OH in TEOS/ O<sub>2</sub> plasmas are significantly higher than those in TMCTS- and DMDMOS-based plasmas under similar conditions. The difference in the precursor structures, mainly the difference in the hydrocarbon C-H bonds, may account for the difference in the OH temperatures. Specifically, the exothermicities of H-atom abstraction by O(<sup>3</sup>P) are -9.6, -29.3, and -43.1 kJ/mol for primary, secondary, and tertiary H atoms.<sup>27</sup> The TEOS molecule has both primary and secondary H atoms, whereas DMDMOS and TMCTS contain only primary H atoms. Thus, the differences in rotational and translational temperatures may be linked to the significantly higher exothermicity for H-abstraction from TEOS than from TMCTS or DMDMOS.

As noted above, the OH concentration in the gas phase is directly correlated to the concentration of O atoms and precursor molecules. As shown in Figure 2, it takes substantially more N<sub>2</sub>O than O<sub>2</sub> to form the same amount of OH. Increasing the oxidant concentration increases O atom concentrations<sup>1</sup> as does increasing the applied rf power in the plasma (Figure 3). Both of these actions lead to a concomitant increase in OH concentration. The decrease in OH LIF intensities observed at precursor: oxidant ratios above 1:8 for O2 systems, and above 1:20 for N<sub>2</sub>O plasmas, Figure 2, is likely the result of decreasing concentration of precursor molecules in the plasma. OH is an initial reaction product of O atoms with hydrocarbons and may abstract another H atom to produce H<sub>2</sub>O.<sup>13,14</sup> These reactions also produce more reactive radical species susceptible to further O atom attacks, which may eventually lead to production of CO and CO2.31,32 Our optical emission spectroscopy (OES) and mass spectrometry (MS) studies have confirmed the presence of these species in the gas phase.<sup>12</sup> Gas-phase reactions that produce OH are important because they enhance fragmentation

of the precursor species. This is significant as these precursor fragments are considered the active deposition precursors in alkoxysilane deposition systems.<sup>2,4–6,8</sup> Thus, the deposition of high-quality  $SiO_2$  is directly affected by formation of OH radicals.

The OH surface reactivity of ~0.60 on a 300 K SiO<sub>2</sub> filmforming surface (Tables 2-4) indicates that  $\sim$ 60% of the incident OH molecules react with the surface and 40% scatter or desorb from the surface. As the IRIS experiment does not track individual molecules, the reactivity value could be the result of a combination of gas-surface interactions that consume and generate OH. Gas-surface interactions can be reactive and nonreactive and can be described in terms of two limiting cases, thermal and nonthermal. In a thermal, or Langmuir-Hinshelwood (LH), reaction, a gas-phase reactant species becomes trapped on the surface and reacts with another surface species.<sup>33</sup> The product then desorbs from the surface at energies dictated by a Maxwell-Boltzmann distribution at the surface temperature. In a nonthermal, or Eley-Rideal (ER), reaction, the incident species reacts with another species at the surface on a time scale too short for thermal equilibrium to be established, and the product leaves the surface with nonthermal energy.<sup>33,34</sup> Analogous nonreactive processes are adsorption/desorption (thermal) and direct inelastic scattering (IS) (nonthermal). When OH is incident on the surface, it may directly scatter away from the surface (Process 1a) or adsorb on the surface, thermally equilibrate, and subsequently desorb (Process 1b).



For reactive cases, OH may react with other surface species such as H atoms to form  $H_2O$  (Process 2) or Si atoms to form -SiOH (Process 3). These are reactions that consume OH at the surface of the growing SiO<sub>2</sub> film.



Gas-surface reactions that could produce OH include surface H atom abstraction by gas-phase and/or surface-bound O atoms (Processes 4).



Alternatively, gas-phase O atoms can undergo multiple H-atom abstractions from hydrocarbon moieties on a surface, forming OH and then  $H_2O$ .<sup>13,14,35,36</sup> Other gas—surface processes that

could involve OH radicals include ion-mediated reactions<sup>37</sup> such as Process 5, which would produce OH at the surface, and Process 6, OH surface recombination to produce  $H_2O_2$ ,<sup>38</sup> which would consume OH at the surface.

$$\xrightarrow{\Theta} OH \longrightarrow OH$$

$$\xrightarrow{O} OH$$

$$\xrightarrow{(5)}$$

$$2 \text{ OH}(s) = H_2O_2(s)$$
 (6)

Processes such as 4 and 5 that produce OH should be enhanced by increasing either oxidant addition or *P*. Both of these actions increase the gas-phase O-atom concentration, whereas increasing *P* also increases ion flux and energy.<sup>1</sup> The apparent OH surface reactivity would thereby decrease with increasing oxidant addition or *P*. The measured *R* values are, however, unaffected by changes in oxidant addition and slightly increased with *P* (Tables 2–4). This suggests that the overall OH surface reactivity is primarily governed by the chemistry of OH and that O-atom reactions with the surface to produce OH as well as ion-mediated surface processes are not significant compared to the overall interactions of OH with the depositing SiO<sub>2</sub> film. Note that the internal and translational energy of OH increases with *P*, which may also increase the reactivity of OH.

Past IRIS studies in our laboratories have shown significant differences when altering the plasma chemistry, plasma parameters, or substrate materials.<sup>17,18</sup> Thus, the OH surface reactivity could be dramatically different for different systems due to differences in the surfaces with which OH is reacting. Lunsford and co-workers38 have investigated the reactions of OH on TiO2 (anatase and rutile), SiO<sub>2</sub> (fused quartz), α-Al<sub>2</sub>O<sub>3</sub>, and Au surfaces and observed different OH surface reactivity on each of these surfaces. They reported the OH reactivity of  $2 \times 10^{-3}$ on the SiO<sub>2</sub> (fused quartz) surface, which was quite different from our results using a TEOS/O<sub>2</sub> plasma,<sup>18,19</sup> and from the results presented here for TMCTS and DMDSO-based plasmas. This difference was attributed to variations in the different SiO<sub>2</sub> surfaces when comparing their fused quartz surface with our TEOS/O2 PECVD SiO2. The reactivity of OH during SiO2 film formation in the plasma systems of TMCTS/O2(N2O) and DMDMOS/ $O_2(N_2O)$  is very similar to that measured in the TEOS/O<sub>2</sub> plasma system,<sup>18</sup> i.e., R = 0.60. This is not surprising as these systems are all depositing systems with similar deposition processes resulting in high-quality SiO2 films. Indeed, films deposited under the plasma parameters studied in this article and in the TEOS/O2 system have very similar composition.10-12 Therefore, the surfaces that OH molecules interact with during film formation are nearly identical. At elevated  $T_{s}$ , however, OH has somewhat different surface reactivity in each of the alkoxysilane systems:  $R = 0.15 \pm 0.05$ ,  $0.16 \pm 0.10$ , and  $0.42 \pm 0.03$  at  $T_s > 350$  K for TEOS/O<sub>2</sub>, TMCTS/O<sub>2</sub>, and DMDMOS/O<sub>2</sub>, respectively. This indicates that the concentrations of active species on the surface that react with OH have different  $T_s$  dependence. At elevated  $T_s$ , the concentrations of surface-active species decrease (but not to zero even at  $T_s =$ 573 K), which leads to decreased R values. This is different from the system of H<sub>2</sub>O plasma interacting with Si<sub>3</sub>N<sub>4</sub> surface,<sup>17</sup> which is a nondepositing and nonetching system. In the H<sub>2</sub>O system, OH has surface reactivity of  $R = 0.57 \pm 0.05$  at  $T_s =$ 300 K and R = 0 at  $T_s \ge 500$  K, where the surface concentration of active species (e.g., -SiOH) decreases with increasing  $T_s$ ,

and is effectively zero at  $T_s \ge 500 \text{ K}$ .<sup>17</sup> In SiO<sub>2</sub> deposition systems, reactions of OH with surface Si atoms produce undesirable –SiOH species. Increasing  $T_s$  leads to a decrease in the surface reactivity of OH, thus a decrease of the probability of forming surface –SiOH. This is consistent with the observation that increasing  $T_s$  decreases or eliminates silanol species in SiO<sub>2</sub> films.<sup>11,12</sup> It should be noted, however, that one additional cause of the decreased OH reactivity at elevated  $T_s$ is that the relative adsorption-to-desorption ratio of OH from the surface is different at different  $T_s$  values. This, however, assumes that the OH is not reacting at the surface, but is merely participating in adsorption–desorption processes. The relative importance of these two mechanisms cannot, however, be directly explored with IRIS experiments.

# 5. Summary

We have investigated the relative gas-phase concentration and surface reactivity of OH in the SiO<sub>2</sub> depositing plasma systems of TMCTS/O<sub>2</sub>(N<sub>2</sub>O) and DMDMOS/O<sub>2</sub>(N<sub>2</sub>O). In all systems, OH is formed by O-atom abstraction of hydrogen atoms from hydrocarbon moieties in precursor molecules or fragments. Our gas-phase data show that the relative OH concentration is directly correlated to gas-phase concentrations of precursor species and O atoms. The reactivity of OH at the surface of a growing SiO<sub>2</sub> film is  $\sim$ 0.60 at  $T_s = 300$  K and P = 100 W in all four plasma systems, and is independent of changes in the precursor-to-oxidant ratio. However, the OH surface reactivity slightly increases with P and R decreases significantly to 0.16  $\pm$  0.10 for the TMCTS/O<sub>2</sub> system and to 0.42  $\pm$  0.03 for the DMDMOS/O<sub>2</sub> system at elevated  $T_s$  (350 to 573 K). Comparison to previous results for TEOS/O2 plasma systems indicates that OH participates in SiO<sub>2</sub> film deposition and contributes to hydrocarbon removal, precursor fragmentation, and surface silanol formation.

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