TEOS-Based SiO$_2$ Chemical Vapor Deposition: Reaction Kinetics and Related Surface Chemistry

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We have developed a comprehensive understanding of thermal TEOS (tetraethylorthosilicate, Si(OCH$_2$CH$_3$)$_4$) surface chemistry at CVD (chemical vapor deposition) temperatures and pressures. This was accomplished by examining how TEOS reaction rates are influenced by factors critical to the heterogeneous reaction. This includes determining the TEOS pressure dependence, testing if reaction by-products inhibit TEOS decomposition, identifying reaction sites on the surface, and establishing the reaction sites coverage dependencies. We evaluated the pressure dependencies and by-product inhibition with GCMS (gas chromatography-mass spectroscopy). The experiments in a cold-wall research reactor revealed that the TEOS surface reaction at 1000K (1) was first-order with respect to TEOS pressure (0.10 to 1.50Torr) and (2) was not inhibited by surface reaction by-products (ethylene, ethanol, and water). Reactivities of surface sites and their coverage dependencies were compared with FTIR (Fourier transform infrared spectroscopy). Our experiments demonstrated that two-membered siloxane ((Si-O)$_2$) rings on the SiO$_2$ surface were consumed almost instantaneously when exposed to TEOS. However, because their rate of formation is quite slow, we expect that (Si-O)$_2$ rings will play a negligible role during TEOS CVD. Our FTIR experiments also revealed that TEOS decomposition was zero-order with respect to coverages of hydroxyl groups and (by indirect evidence) three-membered siloxane ((Si-O)$_3$) rings. This type of site-independent reactivity is consistent with TEOS reacting with hydroxyl groups and (Si-O)$_3$ rings via a common rate-determining step at 1000K. These results suggest that a precise knowledge of surface site coverages on SiO$_2$ is not essential for modeling thermal TEOS decomposition rates. In the absence of gas-phase reactions, growth rates will be directly proportional to TEOS pressure at 1000K. With respect to deposition uniformity, our results predict that deposition rates will be insensitive to the relative coverages of (Si-O)$_3$ rings and hydroxyls on SiO$_2$ as well as the re-adsorbed by-products of the surface reaction. Therefore, it is likely that non-uniform SiO$_2$ depositions from TEOS reactions are due to depletion of TEOS in the gas-phase and/or thermal gradients.

1. INTRODUCTION

TEOS (tetraethylorthosilicate, Si(OCH$_2$CH$_3$)$_4$) and other alkoxy silanes are central to many SiO$_2$ CVD (chemical vapor deposition) processes [1], whether used alone [2, 3], or with oxygen [4], ozone [5, 6, 7], dopants [8, 9], or plasmas [10]. This utility has made thermal TEOS chemistry the focus of numerous investigations. These include growth rate studies in production reactors [2] and research reactors [3, 11, 12], as well as fundamental investigations of reactions on well-defined surfaces [13, 14] and in the gas-phase [15, 16, 17]. It is particularly difficult, however, for results obtained in the idealized environment necessary for fundamental studies to be extrapolated to real-world CVD environments.

Our efforts attempt to improve the connection between the ideal and real environments by merging carefully controlled fundamental studies with conditions commonly used for TEOS-based SiO$_2$ CVD. While there are many important aspects of TEOS CVD such as surface chemistry, gas-phase chemistry, and reactor geometry, our work focuses on the surface chemistry of thermal TEOS decomposition on SiO$_2$. To minimize complications from gas-phase reactions such as the formation of gas-phase intermediates [3, 15, 16, 17], our experiments were carried out using cold-wall reactors. To observe the chemistry and measure the reaction kinetics at CVD temperatures and pressures, FTIR (Fourier transform infrared spectroscopy) and GCMS (gas chromatography-mass spectroscopy) were used in conjunction with isotopic labeling. With this approach, we have examined how TEOS reaction rates are influenced by factors critical to the heterogeneous reaction. This includes identifying reaction

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sites on the surface, establishing the reaction sites coverage dependencies, determining the TEOS pressure dependence, and testing whether reaction by-products such as ethylene, ethanol, and water inhibit TEOS decomposition.

2. EXPERIMENTAL

GCMS experiments were performed using a cold-wall batch reactor (zero flow rate) attached directly to a GCMS via a sampling valve. The substrate was an SiO_2 film deposited on tantalum foil. Samples were taken from the reactor every three minutes to monitor the reaction of TEOS on an SiO_2 substrate. All of the reactants and products in a given sample could be resolved (except acetaldehyde) and eluted from the column in this time-span. Argon was used as an internal standard.

FTIR experiments were performed in a small cold-wall reactor with BaF_2 windows. The reactor was integrated directly into the standard sample compartment of a Mattson RS/1 spectrometer. The substrate, Cab-O-Sil M5 silica with a surface area of 200 m^2/g, was supported on a tungsten electroformed screen which was used for resistive heating. A new sample of ~5mg was prepared for each set of experiments by pressing the silica into the screen. After each reaction segment, the reactor was evacuated and a spectrum of the surface was recorded using the FTIR in a transmission mode. Further details about the experimental apparatus and procedures are available [18].

3. RESULTS AND DISCUSSION

Insight into the heterogeneous TEOS reaction requires the reaction rate dependence on SiO_2 reactive site coverages and TEOS pressure to be determined at CVD temperatures and pressures. However, the reactive sites involved in the reaction under these conditions must first be identified. For this reason, the first sub-section describes the functional groups present on SiO_2 surfaces. In the sub-sections that follow, we then compare the reactivities of these species with TEOS and determine the dependence of the reaction rate on their coverages from direct and indirect evidence obtained with FTIR. From this, we then develop a discussion of the TEOS chemisorption transition state. In the last sub-section, the GCMS experiments are described. These were used to evaluate the TEOS pressure dependence and to determine if reaction by-products inhibit the TEOS reaction rate.

3.1 Cab-O-Sil M5 SiO_2 Substrate

Cab-O-Sil M5 silica was used as the substrate for the FTIR experiments. Its high surface area allows extremely high signal-to-noise FTIR spectra of surface species to be acquired. In addition, this SiO_2 surface is well-characterized [19, 20] which makes it suitable for conducting well-defined studies of TEOS reactivity.

It is generally accepted that the functional groups identified on Cab-O-Sil M5 silica are present on all SiO_2 surfaces [19]. These groups include hydrogen-bonded and isolated hydroxyl groups. At elevated temperatures, these decrease in coverage by reacting together to produce water and siloxane bridges (Si-O-Si). At temperatures above $\approx 850K$, this leads to low coverages of strained, highly reactive two-membered siloxane $((Si-O)_2)$ rings of shared-edge SiO_4 tetrahedra [21]. All of these species have been identified and studied extensively with FTIR. Higher-order, less strained siloxane rings such as three-membered $((Si-O)_3)$ species and larger are also formed [22]. These have been identified using Raman spectroscopy and NMR spectroscopy. Coverages for all of these surface species as a function of annealing temperature have been summarized [20].

3.2 Reactivities of Silanols and Two-Membered Siloxane $((Si-O)_2)$ Rings

The reactivities of silanols (hydroxyls bonded to Si) and $(Si-O)_2$ rings were compared by measuring the intensities of their vibrational peaks as a function of TEOS exposure. This is shown in fig.1. The initial surface is produced by reacting it with D_2O at 900K to convert SiOH groups to SiOD and then annealing for 30 minutes in vacuum at 1200K to form the $(Si-O)_2$ rings [20]. SiOD groups are used so that the reactions can be followed without interference from concurrent SiOH formation which occurs upon TEOS decomposition. Fig.1 shows that after three consecutive 10 second 10 mTorr TEOS reactions at 1200K, the $(Si-O)_2$ rings are completely removed while the SiOD coverage is decreased only slightly. The integrated areas of the vibrational peaks indicate that the $(Si-O)_2$ rate constant is approximately an order of magnitude greater than the SiOD rate constant for TEOS reactions.
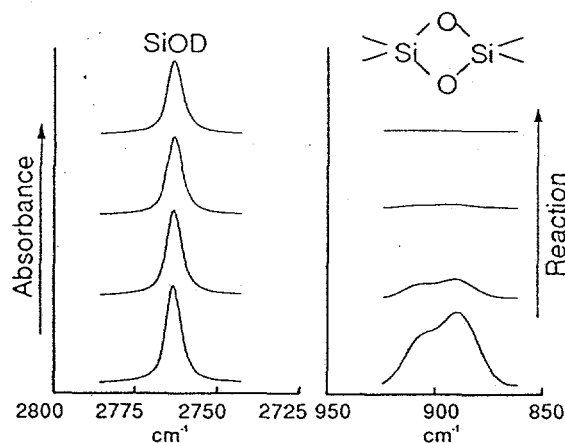
Fig. 1 Vibrational spectra for TEOS reactions with Si-OD and two-membered siloxane ((Si-O)$_2$) rings at 1200 K and 10mTorr.

The time necessary for complete consumption of (Si-O)$_2$ rings ($\approx$30 seconds at 1200 K and 10 mTorr) is quite different from the time necessary to achieve their maximum concentration ($\approx$30 minutes at 1200 K in vacuum [20]). This tremendous difference in consumption and formation rates is also true at 1000K which suggests that the steady-state concentration of (Si-O)$_2$ rings is essentially zero under CVD conditions. As a result, it is expected that reactions between TEOS and (Si-O)$_2$ rings on SiO$_2$ make a negligible contribution to SiO$_2$ deposition.

The greater reactivity of (Si-O)$_2$ rings relative to that of hydroxyls also has significant implications for validating our use of Cab-O-Sil SiO$_2$ substrates for kinetics studies. Specifically, when using porous substrates of this type, the apparent reaction rates are representative of chemical reactivities only if the diffusion rate through the substrate is fast compared to the reaction rate. Since (Si-O)$_2$ rings are distributed uniformly throughout the silica substrate [20], their depletion rate effectively establishes a lower bound on the diffusion rate. Therefore, the fact that the (Si-O)$_2$ ring depletion rate can be observed to be significantly greater than the hydroxyl depletion rate is clear evidence that TEOS can diffuse through the substrate on a faster time-scale than the hydroxyl reaction. It follows that measurements of reaction kinetics that occur on time-scales similar to that of hydroxyl groups also are not mass-transport limited by the porous SiO$_2$ substrate.

3.3 Relationship Between Steady-State Hydroxyl Coverages and Initial Hydroxyl Coverages

The factors that determine the steady-state coverage of silanols can be determined by monitoring TEOS reactions with FTIR as a function of initial hydroxyl coverage. As an example, the vibrational spectra for one of the reactions are presented in fig.2. The spectra are representative of the general trends observed during 30 reaction segments. Before the reaction, the surface was first exposed to D$_2$O and then annealed in vacuum at 1000K. This produced an initial total SiOH and SiOD coverage of 1.3 hydroxyls/100Å^2 [20]. TEOS reaction at 1000K (from the bottom to top in fig.2) decreases the SiOD concentration while increasing the SiOH concentration. The conversion to SiOH can not be the result of hydrogen-deuterium exchange with gas-phase decomposition products such as water and ethanol. We have observed during ethanol and water exposures at 1000K that the rates for secondary reactions with these species are too low for this. It is more reasonable to draw upon previous conclusions from warm-up studies which suggest that TEOS reacts with the surface and consumes silanols. The resulting ethoxy siloxane species on the surface then decompose to regenerate surface silanols [13, 23].
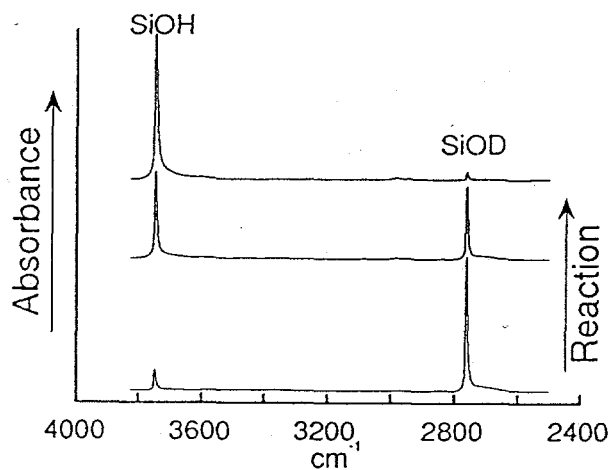

Fig. 2 Vibrational spectra representative of the general trends observed during 30 TEOS reaction segments at 1000 K. The substrate was annealed at 1000K before the reaction.

Detailed comparison of the areas of the SiOH and the SiOD peaks from the vibrational spectra associated with fig.2 show that the respective SiOH-formation:SiOD-consumption relationship is ≈1:1. This is shown by the data with a |slope|=1.2 in fig.3. It follows that the final silanol coverage is nearly identical to the original silanol coverage. However, the reactions were carried out at the same temperature used to anneal the substrate and the annealing temperature defined the initial silanol coverage. Therefore, our observation should not necessarily imply that the steady-state coverage of hydroxyls will be limited by the initial coverage of hydroxyls on the surface.
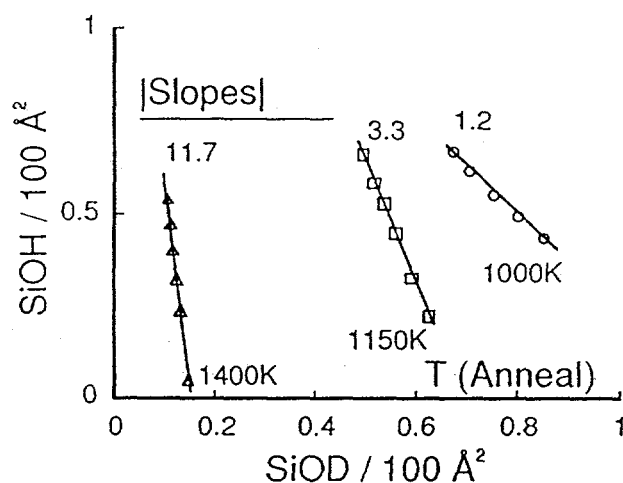

Fig. 3 20 mTorr TEOS reactions at 1000K on three substrates annealed at 1000K, 1150K, and 1400K prior to reaction. The slopes are indicative of the SiOH-formation:SiOD-consumption ratio.

Two additional substrates were exposed to TEOS at 1000K by the same procedure used to acquire the data shown in fig.2. The substrates were annealed in vacuum at 1150K and 1400K prior to the reaction. These temperatures lowered the initial hydroxyl coverages (total SiOH and SiOD) to 0.85 hydroxyls/100Å^2 and 0.2 hydroxyls/100Å^2, respectively [20]. At the end of the reaction series, the total hydroxyl coverages on the substrates annealed at 1150K and 1400K had increased from 0.85 to 1.2 hydroxyls/100Å^2 and from 0.2 to 1.4 hydroxyls/100Å^2, respectively. These final values are close to the 1.3 hydroxyls/100Å^2 well-established for SiO$_2$ surfaces annealed at 1000K [20]. It should also be noted that prolonged annealing at 1000K at the end of each

reaction series decreased the intensities of the hydroxyl peaks by less than 5%. This stability in combination with the dramatic increase in the hydroxyl coverages demonstrates that the steady-state coverage of hydroxyls during TEOS reactions is determined by the deposition temperature and not by the initial hydroxyl coverage.

3.4 Evidence for Three-Membered Siloxane ((Si-O)$_3$) Ring Reactions on SiO$_2$

The SiOH-formation:SiOD-consumption ratios observed during the 1000K TEOS reaction with the substrates annealed at 1150 and 1400K were ≈3:1 and ≈12:1. This is shown by the slopes of the data plotted in fig.3. Considering that the SiOH:SiOD ratio observed on the 1000K substrate was only ≈1:1, these data provide clear evidence that an increase in the SiOH-formation:SiOD-consumption ratio is correlated with a decrease in the initial hydroxyl coverage. Specifically, the maximum ratio of 12:1 indicates that twelve hydroxyls (SiOH) are produced for every hydroxyl (SiOD) that reacts with TEOS. It is not possible to explain the magnitude of this effect if hydroxyl groups are the only surface sites for TEOS chemisorption. For example, it has been proposed that TEOS reacts with an hydroxyl on SiO$_2$ to yield an ethoxy siloxane surface species [13, 23]. This species can have a maximum of only three ethoxy groups as shown in the chemisorption step in fig.4. Each ethoxy has the potential to decompose to an hydroxyl group as shown in the decomposition step. Since the ethoxy groups determine the maximum number of hydroxyls on the surface, the upper limit on the number of hydroxyls produced from the reaction of TEOS with a single hydroxyl would be only 3:1. For this reason, our observation of a 12:1 ratio suggests that reactive sites in addition to hydroxyls are also involved in TEOS surface reactions.
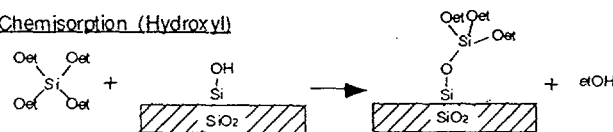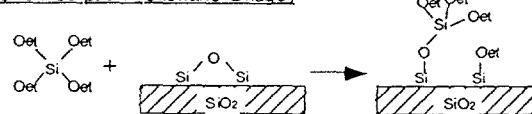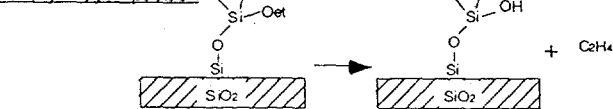

Fig. 4 Possible initial stages of TEOS reactions on SiO$_2$.

We must stress that reactions with the siloxane bridges of highly reactive $(Si-O)_2$ rings initially present on the substrates can not account for the SiOH:SiOD ratios. Although reaction with a siloxane bridge could lead to the formation of four ethoxy groups (fig.4) and therefore a maximum of four hydroxyls, their initial coverage is far too low ($\approx 0.15/100 Å^2$) [20, 21] to result in a 12:1 ratio. In contrast, the initial coverage of three-membered siloxane $((Si-O)_3)$ rings is quite high ($\approx 2.3/100 Å^2$) [20, 22]. The reactivity of siloxane bridges in these IR-inactive species with TEOS, unfortunately, has yet to be studied with Raman spectroscopy. Although we have no direct evidence for their reaction with TEOS, the overwhelming presence of $(Si-O)_3$ rings on the surface lead us to consider that the siloxane bridges in these species may be the additional reactive sites responsible for the formation of additional SiOH groups at 1000K. To a lesser extent, four-membered and five-membered siloxane rings are also present on the annealed SiO_2 surface [22]. We do not exclude the possibility that the siloxane bridges in these species may also be involved in TEOS chemisorption. However, the additional strain energy of 19 kcal/mole for $(Si-O)_3$ rings [22] makes them attractive sites for TEOS reactions.

Additional evidence for reactive sites besides hydroxyls participating in the TEOS reactions is suggested by the zero-order dependence of SiOH formation on the surface. SiOH concentration as a function of reaction time for each of the substrates annealed at 1000, 1150, and 1400K is shown in fig.5. Each of the plots have constant slopes consistent with a zero-order rate expression: $d[SiOH]_{total}/dt = k_{SiOHtotal}$ at 1000K and 20 mTorr TEOS. The three plots are used to derive an average rate constant of $k_{SiOHtotal} = 6.9 \times 10^{-3} SiOH$ $100 Å^{-2} s^{-1}$. Since this pertains to the formation of all SiOH groups from TEOS decomposition at all sites on the surface, we conclude that SiOH formation rates are independent of hydroxyl coverage. If $(Si-O)_3$ rings are additional surface sites responsible for TEOS reactions at 1000K, the data suggest these species have a reactivity ("effective" rate constant) equal to that of hydroxyls over a wide range of hydroxyl coverages.

We can estimate the probability for TEOS-to-SiO_2 decomposition to be 4×10^{-7} at 1000K by dividing the SiOH production rate ($6.9 \times 10^{-3} SiOH 100 Å^{-2} s^{-1}$) by the TEOS flux at 20mTorr ($1.5 \times 10^4 collisions 100 Å^{-2} s^{-1}$). This assumes $d[TEOS]_{decomp}/dt = \gamma_{TEOS} d[SiOH]_{total}/dt$, where γ_{TEOS} is set equal to 1TEOS/SiOH as an example. Reasonable values for γ_{TEOS} are estimated to be between 0.5 and 10. [18] Our

proposal that the formation of SiOH is a close estimate of the TEOS-to-SiO_2 decomposition reaction is supported by the similarity of our TEOS-to-SiO_2 decomposition probability and those of others such as 2×10^{-7} (973K) [3] and 1.3×10^{-6} (calculated from growth-rate data at 1000K and 0.4 Torr published in the reference) [11].
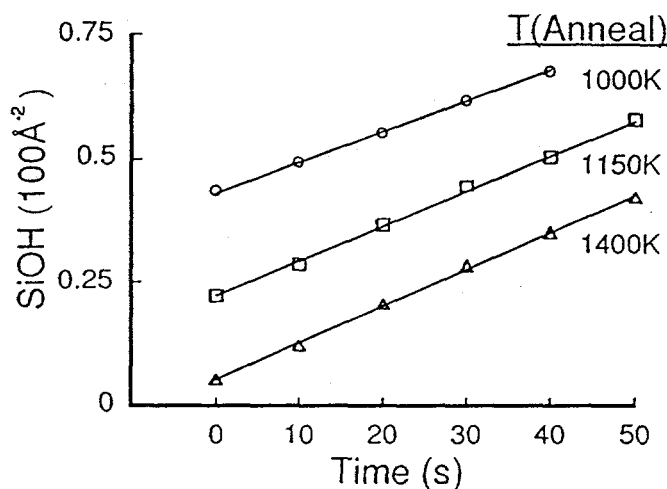

Fig. 5 SiOH formation resulting from 20 mTorr TEOS reactions at 1000K on substrates annealed at 1000K, 1150K, and 1400K.

3.5 The Chemisorption Transition State

The zero-order rate expression for SiOH formation demonstrates that the rate of TEOS decomposition on SiO_2 is independent of hydroxyl coverage at 1000K. This suggests that silanols and siloxane bridges in $(Si-O)_3$ rings have equivalent "effective" rate constants or that SiOD consumption is incidental to chemisorption at elevated temperatures. Either case implies that TEOS reactions with silanols and siloxane bridges occur via a common rate-determining step. This would have to involve a reaction intermediate that does not require a hydroxyl group to react with the surface. This is consistent with the implications of other studies. For example, we have demonstrated that boranols (hydroxyl groups bonded to boron) are infinitely more reactive than silanols at 300K [24]. However, boranols are only a factor of two more reactive than silanols at 1000K [24]. This trend suggests that in spite of the greater reactivity of boranols, TEOS decomposition becomes more insensitive to the difference in boranol and silanol reactivities as the

temperature is increased. In addition, we have used the integrated C-H stretching mode for ethoxy groups as a measure of TEOS chemisorption to compare reaction rates of SiOH and SiOD groups at 765K. This is shown in fig.6 as a function of reaction time at 20mTorr TEOS. Clearly, TEOS reacts with SiOH and SiOD groups at the same rate at 765K [23]. Since this demonstrates there is not a kinetic isotope effect, we conclude that proton transfer, and perhaps direct interaction with hydroxyls, is not critical to the rate-determining step at elevated temperatures. Collectively, these observations suggest that a more facile route for TEOS reaction may become available at higher temperatures that is independent of surface hydroxyls.

instance, the TEOS reaction probability of 4×10^{-7} we measure indicates that only one out every two and a half million collisions with the surface results in TEOS decomposition. A low probability event such as this could be consistent with formation of a thermally activated intermediate being limited by a low thermal accommodation coefficient [25]. Once activated in this critical rate-determining step, a highly reactive species might then react with hydroxyls or $(Si-O)_3$ rings on the surface indiscriminately. As a result, the transition states for TEOS chemisorption and the "effective" rate constants for SiO_2 deposition would be identical for both sites.
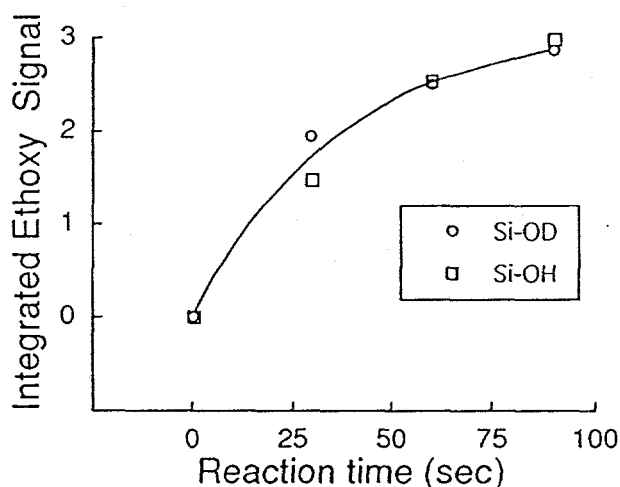

Fig. 6 Comparison of TEOS reactivities with SiOH and SiOD at 765 K and 20 mTorr using the integrated ethoxy group C-H stretching mode as a measure of the TEOS reaction.

The availability of a reactive intermediate for TEOS decomposition at 1000K may allow a new reaction step to be rate-determining for reactions with the siloxane bridges of $(Si-O)_3$ rings as well as with hydroxyls. The reactive species may be either an activated TEOS complex or the result of the intramolecular decomposition of an ethoxy group in TEOS. However, it is unlikely that the formation of the intermediate is the result of a specific interaction with a surface site, since the decomposition rates are site-independent. Nevertheless, it is possible that the critical step may be heterogeneous in nature since the cold-wall reactor used in our experiments is expected to keep gas-phase reactions to a minimum. For
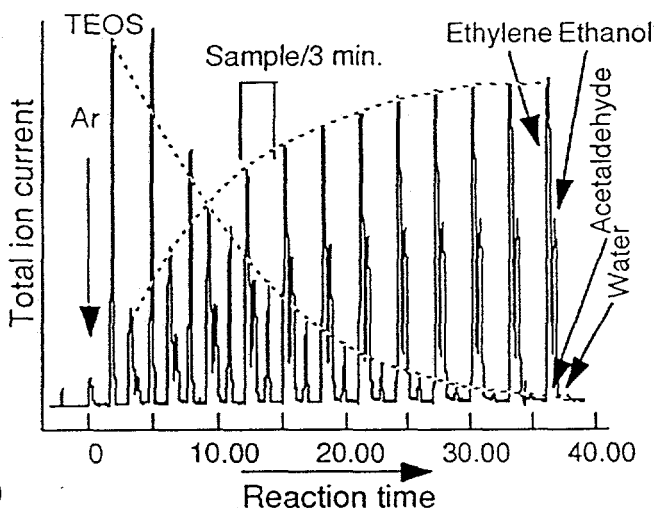

Fig. 7 Repetitive sampling GCMS chromatogram for a TEOS batch reaction at 1.00 Torr and 1000K.

3.6 TEOS Pressure Dependence and Tests for By-Product Inhibition

Repetitive sampling GCMS experiments were used to follow the TEOS decomposition (gas-phase depletion) at 1000K for initial TEOS pressures of 0.25, 0.50, 1.00, and 1.50 Torr. As an example, the total-ion current chromatogram from the 1.00 Torr reaction is shown in fig.7. A sample was taken from the reactor every three minutes. Each sample can be seen as a cluster of peaks in which the individual components have been separated by the chromatographic column. Since the reaction is run in a batch mode (zero flow rate), TEOS peaks are observed to decrease with time and the reaction products peaks are observed to increase. The products were the same for each TEOS reaction and were identified as ethylene, ethanol, acetaldehyde, and water. This agrees with previous reports

[26, 27]. Calibration curves indicate that ethanol and ethylene are the major fraction of reaction products while water and acetaldehyde are minor products [28]. TEOS-based polymers which have been observed by others [16, 17] were not detected in our experiment. However, this is not surprising since we did not use a hot-wall reactor. A reaction-order of one with respect to TEOS pressure was derived by fitting the data to the integrated form of a first-order rate equation ($\ln P_{TEOS} = f(t_{reaction})$).[28] Data from all four of the experiments are shown in fig.8. The linearity of the plots suggests that the rate of TEOS depletion is linear over a wide range of pressures from 0.10 to 1.50 Torr TEOS. The first-order dependence differs from recent results obtained in a cold-wall reactor in which the growth rate data were fit using a fractional order TEOS pressure dependence [12]. We are unable to explain this lack of agreement. However, we can draw direct support from other growth rate measurements taken in a cold-wall reactor [11] in which a unity reaction-order with respect to TEOS pressure was clearly observed.

which 1.00 Torr TEOS was mixed with each of the by-products (except acetaldehyde) prior to reaction. By-product pressures used were 2.00 Torr ethylene, 1.00 Torr ethanol, and 1.00 Torr water. In fig.9, TEOS pressure as a function of reaction time at 1000K is plotted for each of these experiments. Inhibition of TEOS decomposition would be observed as a curve with a decreased slope compared to the plot of TEOS alone. In the extreme case, a slope of zero would indicate that decomposition has been stopped completely. Comparison of the curves does indicate there is some variation among the TEOS pressures at a given reaction time. However, this is within the precision expected for the GCMS measurements. Therefore, we conclude that the decomposition products (ethylene, ethanol, and water) do not inhibit TEOS surface reactions on SiO_2 at 1000K. Since the reactions were carried out in a reactor which had wall temperatures of no more than 100°C, gas-phase reactions would be expected to be minimal. As a result, this conclusion is in reference to only the heterogeneous reaction component of the CVD process.
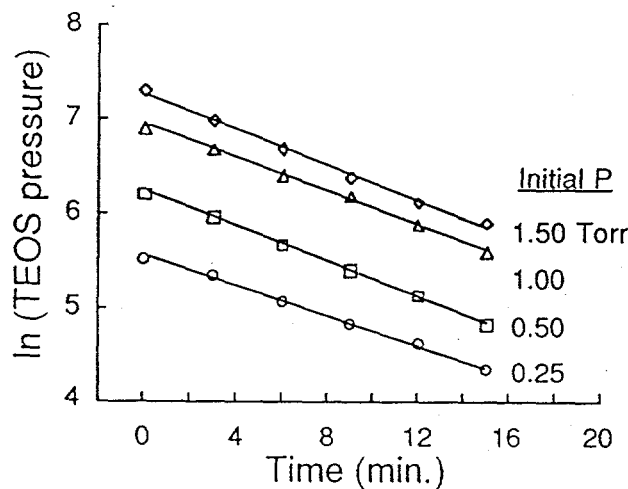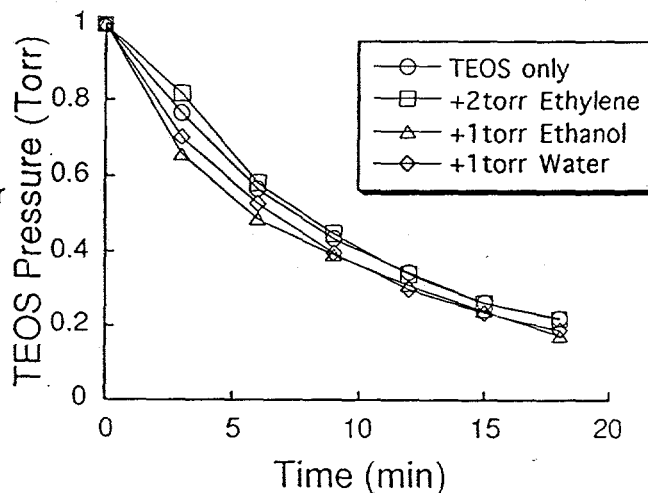

Fig. 8 Reaction-order plot showing that the TEOS reaction-order is one at 1000K and pressure independent between 0.10 and 1.50 Torr. The data were derived from the partial pressures of TEOS left unreacted in each set of reactions which were carried out using the initial TEOS pressures indicated in the legend.

Fig. 9 TEOS depletion as measured with GCMS. Each reaction began with 1.00 Torr TEOS and the reaction by-product indicated in the legend.

The linearity of the data in fig.8 suggests that the build-up of by-products which occurs in each reaction does not inhibit the TEOS reaction rates. However, to test this conclusion more thoroughly, a series of experiments were performed in

4. SUMMARY

Essential reaction kinetics for TEOS-based SiO_2 CVD have been measured using FTIR and GCMS. Reactions were carried out in cold-wall research reactors in a manner

that allowed information specific to the surface chemistry to be determined. Reactions using mixtures of TEOS and ethylene, ethanol, and water show that there is no basis for these species inhibiting the heterogeneous reaction component of a TEOS-based CVD process at 1000K. Of course, since the experiments were designed to address only the surface reaction, these results do not rule out the possibility that by-products could inhibit the gas-phase reactions in a hot-wall reactor.

A thermally activated reaction intermediate may be responsible for the site-independent decomposition of TEOS. The common rate-determining step that results from this may render the consideration of reactive sites and their coverages on SiO_2 inconsequential for TEOS reactions at 1000K. This is particularly significant for predicting SiO_2 growth rates in a CVD environment. Although our work shows that TEOS reactions will produce and then maintain hydroxyl coverages defined by the reaction temperature, coverages of $(Si-O)_3$ and higher-order siloxane rings under CVD conditions have yet to be established. Importantly, the zero-order rate law reveals that a precise knowledge of the coverages of functional groups on SiO_2 is not essential for modeling TEOS surface reaction rates. In the absence of gas-phase reactions, growth rates should be directly proportional to TEOS pressure at 1000K. From the standpoint of deposition uniformity, our results predict that deposition rates will be insensitive to the relative coverages of $(Si-O)_3$ rings and hydroxyls on the SiO_2 surface. Therefore, it is likely that non-uniform SiO_2 depositions from TEOS reactions are due to depletion of TEOS in the gas-phase and/or thermal gradients.

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