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TEOS Surface Chemistry on SiO_2 at CVD Temperatures and Pressures

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We have developed a significantly improved understanding of thermal TEOS (tetraethylorthosilicate, $Si(OCH_2CH_3)_4$) surface chemistry at CVD (chemical vapor deposition) temperatures and pressures. This was accomplished using GCMS (gas chromatography-mass spectroscopy) and FTIR (Fourier transform infrared spectroscopy) to examine how TEOS reaction rates are influenced by factors critical to the heterogeneous reaction. This included determining the TEOS pressure dependence, testing if reaction by-products inhibit TEOS decomposition, evaluating functional groups on the SiO_2 surface as potential reaction sites, and establishing the functional group coverage dependencies. Our results show that TEOS decomposition rates are first-order in TEOS pressure and independent of the surface reaction by-products and the relative coverages of siloxane bridges (Si-O-Si) and hydroxyls on SiO_2. These conclusions suggest that a precise knowledge of functional group coverages on SiO_2 is not essential for modeling thermal TEOS decomposition rates at 1000 K. In the absence of gas-phase reactions, growth rates should be directly proportional to TEOS pressure. Therefore, it is likely that non-uniform SiO_2 depositions observed in thermal TEOS CVD are due to depletion of TEOS in the gas-phase and/or thermal gradients on the surface.

INTRODUCTION

TEOS (tetraethylorthosilicate, $Si(OCH_2CH_3)_4$) is used in numerous microelectronics processes for the deposition of conformal SiO_2 films (1). Good conformality is achieved only if the SiO_2 deposition rate is uniform over the entire deposition surface. For this reason, a knowledge of the factors that influence the deposition rate is essential for improving TEOS processes and maintaining their reliability. Specifically needed to support the advancement of TEOS-based CVD (chemical vapor deposition) technologies is a detailed kinetic model. This requires the identification of individual reaction pathways and the measurements of their kinetics (2). Importantly, the results must pertain to the chemistry as it takes place under CVD conditions for the model to be relevant.

There are many important aspects of TEOS CVD such as surface chemistry, gas-phase chemistry, and reactor geometry. In this paper, we focus on the surface chemistry of thermal TEOS decomposition. This has been the subject of numerous fundamental investigations (3-9) as well as growth rate studies in research reactors (10-13) and production reactors (14). These studies and others have contributed to our understanding of TEOS surface chemistry. It is particularly difficult, however, to bridge the gap between the results obtained in idealized environments necessary for fundamental studies and the results obtained in real-world CVD environments. Conspicuously absent is a rate expression for the heterogeneous reaction of TEOS on SiO_2 at CVD temperatures and pressures.

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. To minimize complications from gas-phase reactions such as the formation of gas-phase intermediates (11, 15-17), our experiments were carried out using cold-wall reactors. To observe the chemistry and measure the reaction kinetics at CVD temperatures and pressures, GCMS (gas chromatography-mass spectroscopy) and FTIR (Fourier transform infrared 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 determining the TEOS pressure dependence, testing if reaction by-products (ethylene, ethanol, and water) inhibit TEOS decomposition, evaluating functional groups (siloxane bridges (Si-O-Si) and hydroxyls) on the surface as potential reaction sites, and establishing the functional group coverage dependencies.

EXPERIMENTAL

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 at room temperature using the FTIR in a transmission mode. (18)

GCMS experiments were performed using a cold-wall batch reactor (zero flow rate) attached directly to a GCMS via a sampling valve. Samples were taken from the reactor every three minutes to monitor the reaction of TEOS on an SiO_2 substrate. Argon was used as an internal standard to compensate for signal fluctuations and depletion due to sampling. (19)

RESULTS AND DISCUSSION

Development of the heterogeneous TEOS rate expression requires the reaction rate dependence on SiO_2 reaction site coverages and TEOS pressure to be determined at CVD temperatures and pressures. However, the reaction sites involved in the reaction under these conditions must first be identified. For this reason, this section first describes the functional groups present on SiO_2 surfaces. We then compare the reactivities of these species with TEOS and determine the dependence of the reaction rate on their coverages with FTIR. After this, 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.

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 surface is well-characterized (20, 21) 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 (20). Coverages produced by the annealing temperatures used in our studies are given in Table 1. The functional 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 ≈850K, this leads to low coverages of strained, highly reactive two-membered siloxane ($(Si\text{-}O)_2$) rings of shared-edge SiO_4 tetrahedra (22). All of these species have been identified and studied extensively with FTIR. Higher-order, less-strained siloxane rings such as three-membered ($(Si\text{-}O)_3$) species and larger are also formed (23). 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 (21).

Table 1. Coverages of functional groups on SiO_2 at the annealing temperatures used to prepare the substrates used in this study (20-23).

	Coverages ($100 Å^2$)			
Annealing temperature / K	SiOH (isolated)	SiOH (H-bonded)	$(Si\text{-}O)_2$	$(Si\text{-}O)_3$
1000	1.2	0.1	<0.1	2.0
1150	0.85	0.0	0.10	2.2
1400	0.2	0.0	0.15	2.3

TEOS reactions with $(Si\text{-}O)_2$ rings

The reactivity of $(Si\text{-}O)_2$ rings with TEOS has been studied previously (3, 8). $(Si\text{-}O)_2$ rings were shown to be nearly an order of magnitude more reactive than hydroxyls at CVD temperatures and pressures (3). Because of their fast rate of reaction and their slow rate of formation, it was suggested that $(Si\text{-}O)_2$ rings would make a negligible contribution during TEOS CVD (3). The greater reactivity of $(Si\text{-}O)_2$ 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 the $(Si\text{-}O)_2$ ring surface species are distributed uniformly throughout the silica substrate (21), their depletion rate effectively establishes a lower bound on the rate of diffusion. Therefore, the fact that the $(Si\text{-}O)_2$ 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 at a rate that is much faster than the time-scale of the hydroxyl reaction.

Hydroxyl coverage dependence

Previously, labeling hydroxyls with deuterium on SiO_2 has been used successfully with FTIR to distinguish TEOS reactions with hydroxyls (SiOD consumption) from TEOS decomposition (SiOH formation) during reactions at high temperatures (3). These events are associated with initial TEOS chemisorption and subsequent ethoxy siloxane decomposition, respectively (3, 5). We used this same approach to study the hydroxyl reaction rate dependence on hydroxyl coverage in this study. To prepare the surface, the substrate was first exposed to D_2O and then annealed in vacuum at 1000K. This produced an initial total silanol coverage of 1.3 hydroxyls/$100 Å^2$, less than 10% of which were hydrogen-bonded (20, 21). This coverage was used to calibrate the FTIR measurements. The substrate was then given a series of 10 s exposures to 20 mTorr TEOS at 1000 K. FTIR spectra of the surface were measured between each reaction segment. The integrated peaks for the SiO-H (3748 cm^{-1}) and SiO-D (2764 cm^{-1}) stretching modes were then converted to coverages. As shown in fig. 1, the surface began with coverages of 0.87 SiOD/$100 Å^2$ and 0.43 SiOH/$100 Å^2$. These decreased with respect to SiOD and increased with respect to SiOH as the reaction proceeded. However, the total SiOD + SiOH coverage remained essentially constant throughout the reaction. A maximum of 1.4 hydroxyls/$100 Å^2$ was produced after extended TEOS exposures at 500 mTorr.

The TEOS reaction dependence on silanol coverage was studied by using a series of substrates having systematically lower SiOD coverages. The reactions were performed at 1000 K in the same manner described above with the exception that the substrates were annealed in vacuum at 1150K and 1400K after the D_2O treatments. These temperatures lowered the initial silanol coverages to 0.85 hydroxyls/100Å^2 and 0.2 hydroxyls/100Å^2, respectively, prior to the TEOS reaction. In both of these experiments, approximately three-quarters of the hydroxyls were labeled with deuterium (SiOD) prior to reaction with TEOS.

Data obtained on the 1000 K, 1150 K, and 1400 K substrates (18) revealed that TEOS reactions with hydroxyls (SiOD consumption) have a first-order dependence on hydroxyl coverage. In contrast, TEOS decomposition (SiOH formation) is zero-order with respect to hydroxyl coverage. Detailed plots of the data sets have shown that they can be fit quite well to integrated first-order and zero-order rate expressions (18). ($d[SiOD]/dt=-k_1[SiOD]$ where $k_1=5.7\text{x}10^{-3}/s$ and $d[SiOH]/dt=-k_0$ where $k_0=1.4\text{x}10^{-12}$ mol TEOS/cm^{2}s at 1000 K and 20 mTorr.)

If the formation of SiOH is directly proportional to TEOS decomposition ($d[TEOS]_{decomp}/dt=\gamma_{TEOS}\,d[SiOH]_{total}/dt$), then our data also suggest that TEOS decomposition on SiO_2 is independent of hydroxyl coverage at CVD temperatures. This is graphically represented in fig. 2 where the average rate of SiOH formation (TEOS decomposition) is plotted as a function of total hydroxyl (SiOD+SiOH) coverage. Data from all three reaction series are presented, showing that the zero-order dependence extends over a wide range of coverages. Scatter in the data is observed with respect to the abscissa since the increase in the total hydroxyl coverage results from progress in the TEOS reaction. The data converge on the 1000 K annealed data set since the 1000 K reaction temperature ultimately limits the hydroxyl coverage (18).

Nature of the surface reaction and indirect evidence for reactions with $(Si\text{-}O)_3$ rings

The fact that hydroxyl consumption has a first-order dependence on hydroxyl coverage leaves little doubt that hydroxyls are involved in the TEOS reaction on SiO_2. However, detailed analyses of this observation has shown that this could be the result of either a site-specific reaction or a site-independent reaction (18). If we first postulate that the reaction is site-specific, then TEOS must also react with surface species in addition to hydroxyls for the overall decomposition rate to remain constant. Since $(Si\text{-}O)_2$ rings are completely removed from the surface during the first reaction segment at 20 mTorr (18), we speculate based on Table 1, that Si-O-Si bridges in $(Si\text{-}O)_3$ rings could be additional reactive sites on the surface. Certainly this suggestion is based only on indirect evidence, since the reactivity of these IR-inactive species with TEOS has yet to be studied with Raman spectroscopy. However, the coverages of $(Si\text{-}O)_3$ rings are relatively high and the strain energy of 19 kcal/mole for $(Si\text{-}O)_3$ rings (23) makes them attractive candidates for TEOS reactions. Nevertheless, for the reaction rate to remain constant, availability of $(Si\text{-}O)_3$ rings would have to compensate, exactly, for the changes in the hydroxyl coverage. This seems unlikely considering the wide range of hydroxyl coverages shown in fig. 2. It is more likely, that there is a common rate determining step for the reaction of TEOS with hydroxyls and $(Si\text{-}O)_3$ rings - if the reaction is site-specific.

Our data are also consistent with a site-independent mechanism (18). In this case, the reaction would be controlled by intramolecular decomposition of TEOS. The low sticking coefficient we measure ($6\text{x}10^{-7}$) suggests this type of chemistry in our cold-wall reactors would be thermally activated by the SiO_2 surface and not by reactions in the gas-phase (11). Once activated, reactions with hydroxyls (SiOD) would then follow as secondary events. Secondary reactions could also include $(Si\text{-}O)_3$ rings.

TEOS Pressure Dependence

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.3. 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 decrease with time and the reaction products peaks increase. The products were the same for each TEOS reaction and were identified as ethylene, ethanol, acetaldehyde, and water. This agrees with previous reports (24, 25). Calibration curves indicate that ethanol and ethylene are the major fraction of reaction products while water and acetaldehyde are minor products (4, 19). 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 (4, 19). The data are shown in fig.4 and are consistent with a first-order rate constant of 7.1×10^{-13} mol TEOS/cm^{2}mTorrs. The plots also suggest that the TEOS reaction rate is directly proportional to TEOS pressure over a wide range of pressures from 0.10 to 1.50 Torr. The dependence we observe 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 (13). 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 (12) in which a reaction-order of one with respect to TEOS pressure was clearly observed.

Evaluation of By-Product Inhibition

The linearity of the data in fig.4 suggests that the build-up of by-products which occurs in each reaction does not inhibit the TEOS reaction rates. This contradicts previous conclusions reached by modeling (12) and experiment (10). To test our results more thoroughly, we performed a series of experiments in which 1.00 Torr TEOS was mixed with $\geq$ 1.00 Torr of each of the by-products (except acetaldehyde) prior to reaction. Even under these extreme conditions, the reaction rate of TEOS was unaltered by the presence of these species (4). 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 can be expected to be minimal. As a result, this conclusion is in reference to only the heterogeneous reaction component of the CVD process.

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 acquired. 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 decomposition of TEOS on the surface. 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 $(Si\text{-}O)_3$ rings have yet to be established under CVD conditions. 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 $(Si\text{-}O)_3$ 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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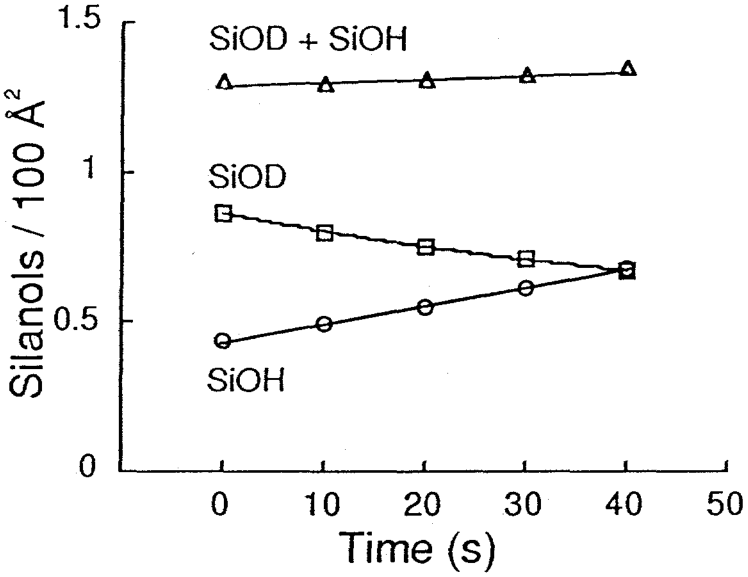

Fig.1 *SiOH and SiOD coverages for 10s segments of a 20mTorr TEOS reaction at 1000K.* The substrate was annealed at 1000K prior to the reaction. Coverages were derived from integrated FTIR absorbances.

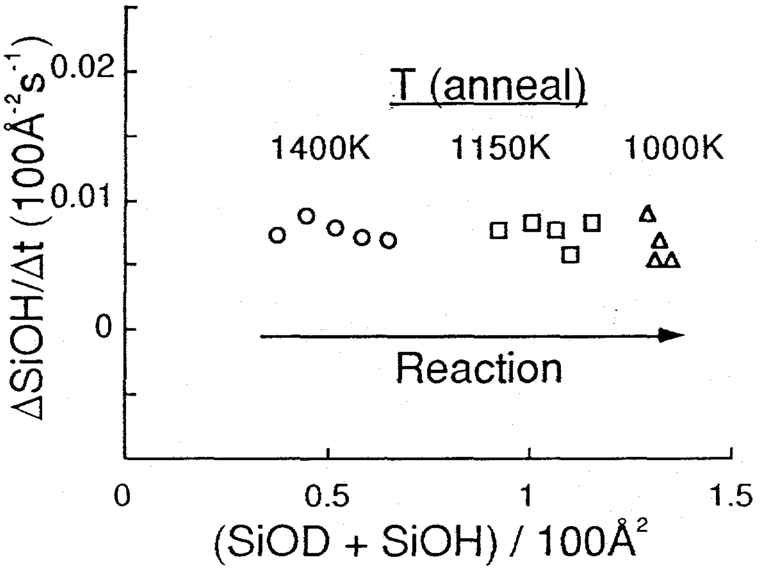

Fig. 2 Average SiOH formation rates as a function of total hydroxyl coverage at 1000K. Increase in the total SiOD+SiOH coverage is due to TEOS reactions on each of the substrates annealed at the temperatures labeled in the figure. This appears as an apparent scatter in the data with respect to the abscissa.

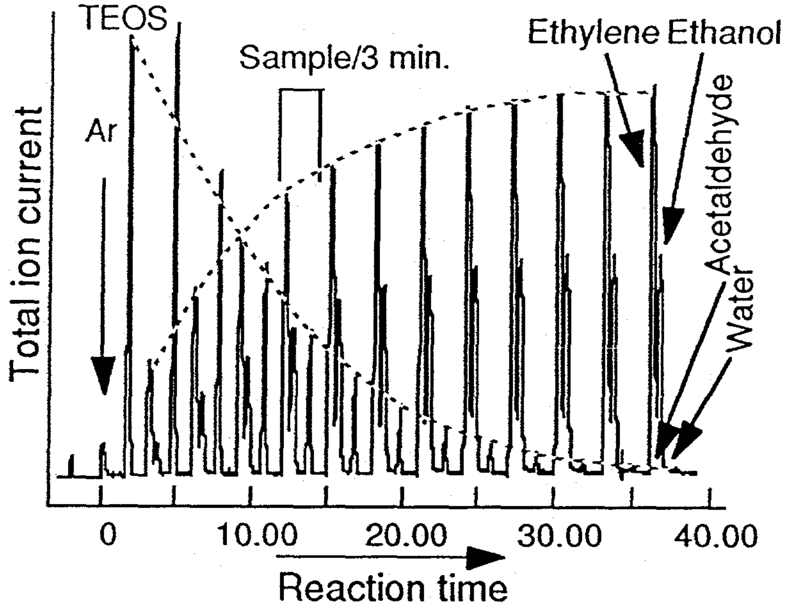

Fig. 3 Repetitive sampling GCMS chromatogram for a TEOS batch reaction at 1.00 Torr and 1000K.

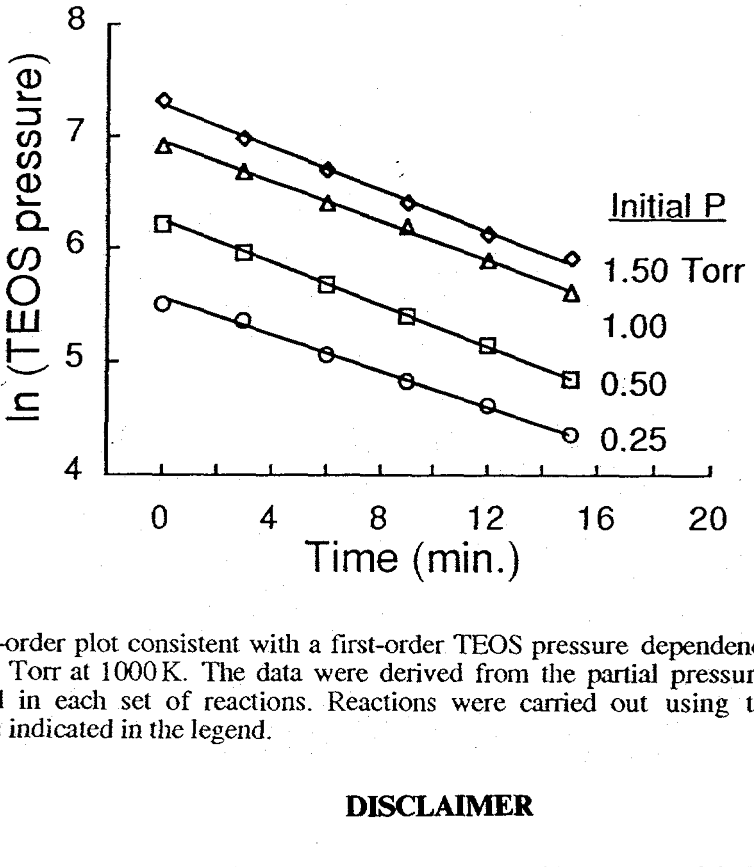

Fig. 4 Reaction-order plot consistent with a first-order TEOS pressure dependence between 0.10 and 1.50 Torr at 1000K. The data were derived from the partial pressures of TEOS left unreacted in each set of reactions. Reactions were carried out using the initial TEOS pressures indicated in the legend.