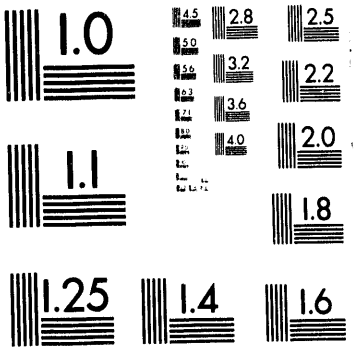
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Surface Chemistry of Boron-Doped SiO_2 CVD: Enhanced Uptake of Tetraethyl Orthosilicate by Hydroxyl Groups Bonded to Boron

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Abstract

Insight into how dopants can enhance deposition rates has been obtained by comparing the reactivities of tetraethyl orthosilicate (TEOS, $Si(OCH_2CH_3)_4$) with silanol and boranol groups on SiO_2. This comparison has direct relevance for boron-doped SiO_2 film growth from TEOS and trimethyl borate (TMB, $B(OCH_3)_3$) sources since boranols and silanols are expected to be present on the surface during the thermal chemical vapor deposition (CVD) process. A silica substrate having coadsorbed deuterated silanols (SiOD) and boranols (BOD) was reacted with TEOS in a cold-wall reactor in the mTorr pressure regime at 1000K. The reactions were followed with Fourier transform infrared spectroscopy. The use of deuterated hydroxyls allowed the consumption of hydroxyls by TEOS chemisorption to be distinguished from the concurrent formation of SiOH and BOH that results from TEOS decomposition at this temperature. It was found that TEOS reacts with BOD at twice the rate observed for SiOD, given equivalent concentrations of BOD and SiOD. This demonstrates that hydroxyl groups bonded to boron increase the rate of TEOS chemisorption. In contrast, additional results show that surface ethoxy groups produced by the chemisorption of TEOS decompose at a slower rate in the presence of TMB decomposition products. Possible dependencies on reactor geometries and other deposition conditions may determine which of these two competing effects will control deposition rates. This has significant implications for microelectronics fabrication since the specific dependencies would be expected to affect process reliability. In addition, this may explain (in part) why the rate enhancement effect is not always observed in boron-doped SiO_2 CVD processes.

Introduction

The addition of trimethyl borate (TMB, $B(OCH_3)_3$) to a thermal tetraethyl orthosilicate (TEOS, $Si(OCH_2CH_3)_4$) chemical vapor deposition (CVD) process produces boron-doped oxide films.[1] Boron-doped films require a lower temperature than undoped SiO_2 films to achieve reflow in the surface planarization step during very-large-scale-integrated (VLSI) device fabrication.[1] Interestingly, the addition of dopant precursors has been observed to enhance the rate for SiO_2 deposition.[2,3] However, this effect is not always observed.[4] Surprisingly, there have not been any studies designed specifically to determine if there is a chemical basis for the rate enhancement effect.

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It has been shown that surface boranol groups (BOH) react at a significantly higher rate than silanols when exposed to trimethoxymethylsilane ($H_3CSi(OCH_3)_3$), a TEOS homologue.[5] In view of this reactivity, boranol groups may be anticipated to influence the thermal TEOS deposition chemistry on SiO_2. This is a relevant consideration since silanols (SiOH) and boranols are expected to be present on the surface during boron-doped SiO_2 CVD. For example, silanol groups are known to be consumed and then reformed during the chemisorption and decomposition of TEOS.[6,7] In addition, boranols as well as silanols can be formed from the decomposition of TMB on SiO_2.[8] Boranols can also be produced either by the hydrolysis of TMB chemisorption products[9] (water is produced from TEOS decomposition[10]), or by a more direct reaction between the reaction products of TMB and TEOS chemisorption.[10]

This study is designed to compare the reactivity of TEOS with surface silanol and boranol groups. Reactions were carried out in a cold-wall reactor in the mTorr pressure regime at 1000K using a high surface area silica substrate. The surface contained a mixture of both silanol and boranol groups, formed by the hydrolysis of the products of an initial TMB chemisorption step. The reactions were monitored by moving the substrate into adjoining chambers for Fourier transform infrared spectroscopy (FTIR) and x-ray photoelectron spectroscopy (XPS) analyses.

Experimental

Reactions and surface analyses were carried out in a vertically oriented three-chamber system.[11] The ultra-high vacuum (UHV) surface analysis chamber is located at the top of this system, the reactor is in the middle, and the IR cell is at the bottom. Reactions were carried out in a static mode (flow rate of zero) in the mTorr pressure regime. Changes on the surface were followed by interrupting the reaction, allowing the substrate to cool down, and then moving the substrate into either the UHV chamber for XPS or the IR cell for FTIR. A new background spectrum was acquired before each IR transmission spectrum. The substrate was then moved back into the reactor, and the reaction was resumed. Five mg of high surface area silica, supported on a tungsten screen for resistive heating, was used for the SiO_2 substrates. Cleaning and annealing were accomplished by heating at 900K for 30 minutes in 50 mTorr of O_2.[12] The methods used for preparing the precursors and verifying their purity have been reported.[11]

Results and Discussion

Boranol Formation and the Reactivity of TMB on Silica at 300K

The vibrational spectra associated with the initial step for boranol formation on the silica substrate is presented in fig. 1. As shown in spectrum A, annealing the D_2O treated surface at 1200K prior to TMB exposure forms isolated Si-OD groups (2763 cm^{-1} [7]) and two-membered siloxane ($(Si\text{-}O)_2$) rings (888 and 908 cm^{-1}).[12] As shown in spectrum B, TMB reaction at 300K and 10 mtorr for 6 sec. results in the formation of methoxy groups (labeled "Ome" in the figure). The vibrational features indicate that methoxy groups are bonded to boron ($B(OCH_3)_n$) as well as

silicon ($Si(OCH_3)_m$) on the surface.[8] This reaction diminishes the area of the Si-OD peak by less than 5% while reducing the $(Si\text{-}O)_2$ peak by 95%. This suggests that $(Si\text{-}O)_2$ rings are ~20 times

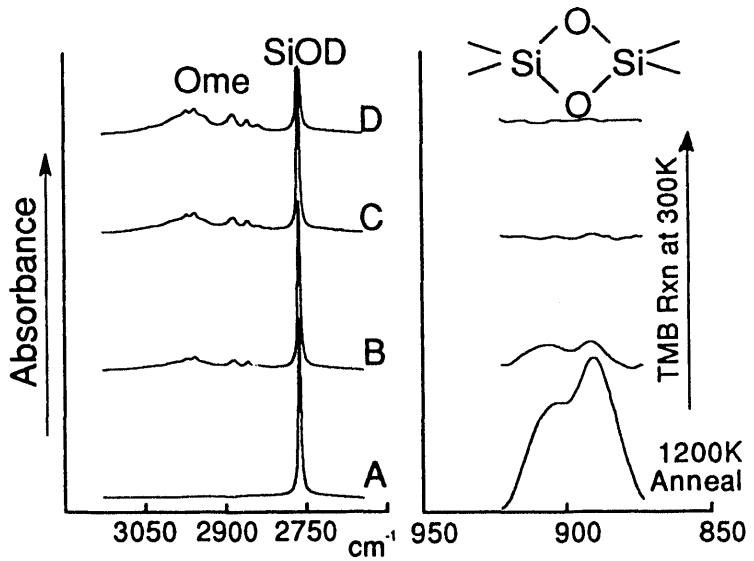

Figure 1. Vibrational spectra for the reaction of TMB at 300K and 10 mTorr on silica pre annealed at 1200K. Surface methoxy groups are marked as "Ome". The SiOD peak in spectrum D has been truncated.

more reactive than silanols with respect to TMB reactions. Further TMB reaction for 10 sec. removes all evidence of the $(Si\text{-}O)_2$ rings (spectrum C). Although not shown in the figure, TMB reaction at 100 mTorr for 300 sec. decreases the Si-OD concentration to half of the initial concentration.[9] It has also been shown that subsequent reaction with H_2O at 900K regenerates some of the silanols and produces boranols at the expense of nearly all of the methoxy groups.[9]

This study is designed to compare the relative reactivities of silanols and boranols with TEOS. For this comparison to be valid, it is critical for the relative populations of surface silanols and boranols to be uniform throughout the porous substrate. Achievement of this requirement will be determined by the reactivity of TMB, since TMB is used for the initial boranol preparation step. For example, if the TMB reaction rate with silanols was greater than the TMB diffusion rate, the reactions would be diffusion-rate limited. This would result in undesirable concentration gradients of boranols from the outer to the inner surfaces of the porous substrate. In this regard, the relative reactivities of $(Si\text{-}O)_2$ rings and silanols with TMB is particularly significant. Since $(Si\text{-}O)_2$ rings are uniformly distributed throughout the porous substrate, the fact that the greater reactivity of $(Si\text{-}O)_2$ rings can be observed is clear evidence that TMB reaction is not diffusion-rate limited. This suggests that *TMB exposure will produce a uniform distribution of boron methoxy species throughout the silica substrate* for subsequent hydrolysis to form boranols.

Reactivity of TEOS with Deuterated Silanols and Boranols at 1000 K

The chemisorption of TEOS at 450K followed by heating to progressively higher temperatures has shown that TEOS first consumes hydroxyls and then reforms hydroxyls as a result of the decomposition of ethoxy groups on the surface.[6] In order to measure the rate of hydroxyl consumption without the interference of concurrent hydroxyl formation at 1000K, a surface with deuterated hydroxyls (SiOD and BOD) was used for the TEOS reactions. This surface was prepared by exposing a substrate with SiOH and BOH groups to 500 mTorr of D_2O for 5 minutes at 900K. This was then annealed for 5 minutes in vacuum at 1000K, and then examined with IR and XPS to ensure that the surface was stable on a time-scale comparable to the longest reaction with TEOS at 1000K. Neither the formation of $(Si\text{-}O)_2$ rings nor a change in the relative intensities of the hydroxyls, deuterated or otherwise, was observed. As shown by the spectrum at

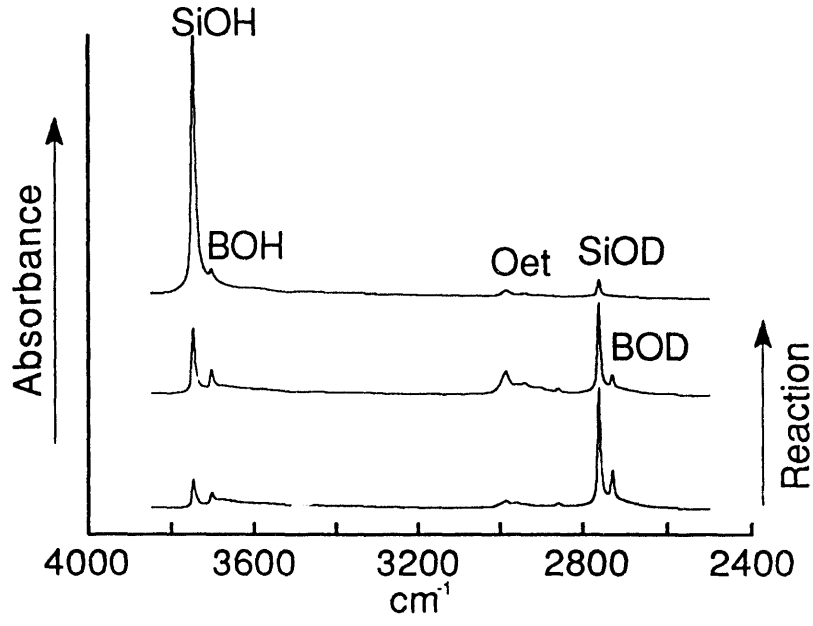

Figure 2. Vibrational spectra representative of the trends observed for fifteen TEOS reaction segments at 1000K. "Oet" denotes surface ethoxy groups.

the bottom of fig. 2, D_2O exposure did not convert all of the SiOH (3748 cm^{-1} [12]) and BOH (3703 cm^{-1} [5]) to SiOD (2763 cm^{-1} [7]) and BOD (2731 cm^{-1} [9]). Additional experiments using extended D_2O exposures suggest this incomplete conversion is due to the initial H/D exchange being reversed by secondary reactions with HOD.[7]

The first reaction segment was carried out at 1000K in 10 mTorr TEOS for 14s. Subsequent reactions were also performed at 1000K using progressively higher pressures and longer reaction times. 200 mTorr and 150s were used for the final reaction segment. The middle spectrum and the top spectrum in fig. 2 are associated with the reaction midpoint and the reaction

endpoint, respectively, and are representative of the general trends observed during a total of fifteen reaction segments. As expected, exposure to TEOS clearly reduces the populations of both SiOD and BOD groups while increasing the number of SiOH groups on the surface. Interestingly, there is also an increase in the BOH concentration on the surface, as shown in the middle spectrum. Deuterium-hydrogen exchange reactions could be the cause of the depletion of BOD and the formation of BOH. This could result from reactions with TEOS decomposition products (water or ethanol[10]) formed in the gas-phase or on the surface. However, this possibility is unlikely since both the BOH and BOD concentrations decrease steadily during the initial reaction segments (as made evident by vibrational spectra not shown in the figure). It is more likely that the products from the dissociative chemisorption of TEOS on BOD undergo further reaction and in this way make boranols again available for reaction with TEOS. Although much lower in concentration, the spectrum at the top of the figure shows that BOH groups are still present on the surface when all of the BOD groups have been removed.

At the same time that the BOH concentration reaches a maximum, the ethoxy concentration also reaches a maximum. Evidence of the ethoxy group accumulation can be seen in the middle spectrum in the frequency region labeled with "Oet". Since ethoxy groups maintain a low concentration on a surface which has been exposed to only TEOS at 1000K and not exposed previously to TMB,[7] the relatively high concentration of ethoxy groups seen in the middle spectrum of fig. 2 is evidence that *boron, boranols, or some other product from TMB chemisorption and hydrolysis decrease the rate of ethoxy group decomposition on* SiO_2.

Integrations of the SiOD and BOD vibrational peaks for the initial reaction segments followed by normalization to compensate for their dissimilar initial concentrations allows the SiOD and BOD reactivities with TEOS to be compared directly. These data are plotted in fig. 3. Comparison of the initial slopes shows that the rate constant for TEOS reacting with BOD is twice

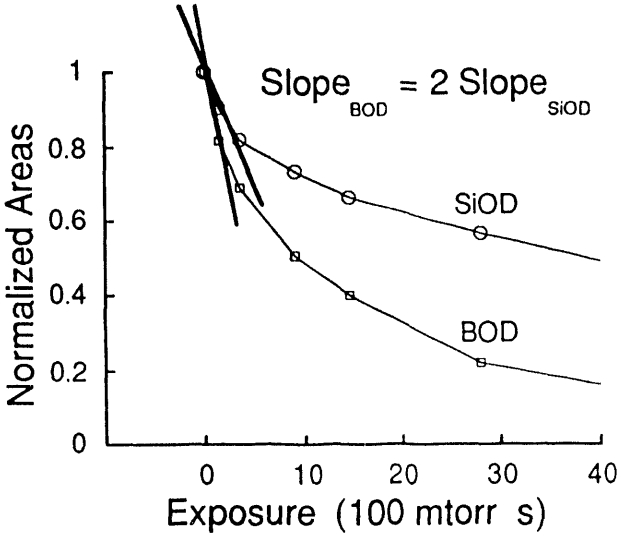

Figure 3. Normalized integrations of the SiOD and BOD vibrational peaks for the initial TEOS reaction segments at 1000K.

that of SiOD. This result is the first quantitative determination that *boranols increase the rate of TEOS chemisorption on SiO_2 at 1000K.*

Summary

New information about the deposition of doped SiO_2 films from TEOS and TMB sources has been obtained using FTIR. Specifically, the first direct measurements of the relative reaction rates of surface silanols and boranols with TEOS at 1000K have been achieved. To circumvent limitations imposed by the concurrent hydroxyl consumption and reformation which accompany TEOS reaction at 1000K, coadsorbed deuterated silanol and boranol groups were used to study the reaction rates. It was determined that the initial chemisorption of TEOS is *enhanced* by BOD relative to SiOD by at least a factor of two at this temperature. In contrast, the decomposition rate of ethoxy groups (the product of TEOS chemisorption) is *decreased* by the products of TMB chemisorption. Possible dependencies on reactor geometries and other deposition conditions may determine which of these two competing effects will control deposition rates. This has significant implications for microelectronics fabrication since the specific dependencies would be expected to affect process reliability. In addition, this may explain (in part) why the rate enhancement effect is not always observed in boron-doped SiO_2 CVD processes.

Acknowledgements

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