Investigation of Self-Assembled Monolayer Resists for Hafnium Dioxide Atomic Layer Deposition

Rong Chen,[†] Hyoungsub Kim,[‡] Paul C. McIntyre,[‡] and Stacey F. Bent*[,§]

Department of Chemistry, Department of Materials Science and Engineering, and Department of Chemical Engineering, Stanford University, Stanford, California 94305

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In this paper, a series of self-assembled monolayers (SAMs) has been investigated as deactivating agents for the atomic layer deposition (ALD) of HfO_2. Three important factors that determine the capacity of self-assembled monolayers to prevent ALD of HfO_2, chain length, tailgroup structure, and reactive headgroup, have been investigated. We show that to achieve satisfactory deactivation toward atomic layer deposition, it is crucial to form densely packed, highly hydrophobic monolayers. This in turn requires deactivating agents with high reactivity and nonbulky tailgroups comprised of a minimum chain length. A mechanism for the blocking process is proposed in which the role of the SAMs is both to remove reactive Si−OH/Si−O−Si groups at the SiO_2 surface and to prevent ALD precursors from reaching the SiO_2−SAMs interface.

Introduction

As the scaling of metal-oxide-semiconductor field-effect transistors (MOSFETs) continues and higher switching speed is required, the thickness of the SiO_2 gate dielectric must be substantially decreased. For example, the SiO_2 gate dielectric thickness must be decreased to ∼1.5 nm for 100 nm channel length devices.[1] However, for oxide thicknesses below 2 nm, the leakage current caused by direct electron tunneling from the gate to the channel becomes substantial.[2,3] To solve this problem, gate dielectrics with permittivities greater than that of SiO_2 are required, because high-κ dielectric layers allow deposition of thicker films while retaining a capacitance equivalent to that of very thin SiO_2.[3,4] Among many potential materials, hafnium dioxide (HfO_2) has drawn significant attention due to its high-κ value (20−25), wide band gap (∼5.7 eV), and apparent compatibility with conventional poly-Si gate electrodes without any barrier layers.[5] In addition to its potential application in integrated circuits, HfO_2 is also a high refractive index, low absorption material for optical coatings in the near-UV (below 300 nm) to IR (∼10 μm) regions.[6] HfO_2 films with excellent uniformity and accurate film thickness control at the nanometer scale are required for these applications.

Atomic layer deposition (ALD) has received considerable attention as a means of depositing ultrathin films of materials such as HfO_2. It is a powerful film growth technique that employs a sequence of self-limiting surface reaction steps to afford subnanometer control of the growth process.[7−10] ALD can be used to deposit thin films of numerous semiconducting, insulating, and metallic materials. Moreover, the self-limiting nature of ALD ensures the precise control of film thickness and uniformity over large areas, including nonplanar surfaces. ALD appears to be well suited to many applications, especially those in which a low-thermal budget synthesis of thin inorganic films with exquisite structural control is desired. The adsorption-controlled layer-by-layer reactions produce excellent conformality and uniformity.[7] At the same time, ALD is a method in which surface reactions play an important role for both surface nucleation and film growth. The ALD process is based upon chemical reactions between the precursors and a substrate, and the reactions depend strongly on the specific reactive functional groups present on the surface prior to the deposition.

Recently, self-assembled monolayers (SAMs) have been demonstrated to act as an effective monolayer resist toward several ALD processes which involve water as a precursor.[11−13] This approach provides a promising way to enable a process called area-selective ALD, in which the deposition process is controlled spatially using selective modification of the growth substrate. Area-selective ALD differs from conventional, subtractive lithographic patterning; it is an additive

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* To whom correspondence should be addressed. Phone: 650-723-0385. Fax: 650-723-9780. E-mail: sbent@stanford.edu.

[†] Department of Chemistry.

[‡] Department of Materials Science and Engineering.

[§] Department of Chemical Engineering.

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process in which material is deposited only where needed. Because of this distinction, area-selective ALD promises to provide a number of advantages, including reducing the number of etch and lithography steps for systems utilizing multiple depositions, eliminating difficult etching steps, and minimizing the use of expensive reagents. This paper primarily discusses the modification of a silicon substrate using SAMs as the deactivating agents to block the HfO_2 thin film ALD process and investigates the properties of the SAMs that are required for full deactivation against ALD.

SAMs are monolayer organic films that form spontaneously on solid surfaces. The self-assembling nature provides the design flexibility to obtain a range of desired materials properties. SAMs have been investigated for a few decades and are well known to modify the physical, chemical, and electrical properties of semiconducting, insulating, and metallic surfaces.[14] Furthermore, SAMs have been demonstrated to be high resolution, ultrathin resists in photolithography,[15,16] electron beam lithography,[3,17,18] scanning probe lithography,[19,20] and micro-contact printing at subnanometer scale.[21,22] In this work, we have investigated organosilanes as deactivating agents toward the ALD process. Organosilanes of the general formula R_nSiX_{4-n} ($n = 1-3$) are widely used as effective surface modification agents for a variety of applications including MEMS,[23,24] biomaterials,[21,25] and optical and electronic devices.[21,22,26] Due to the robust, covalent Si−O linkage between molecules and the surface, films formed by organosilanes demonstrate good chemical and thermal stability. For example, we have previously demonstrated that octadecyltrichlorosilane (ODTS) films can act as effective monolayer resists for ZrO_2 and HfO_2 ALD processes.[11] Others have also shown that ODTS SAMs can block ALD of ZnO[12] and TiO_2.[13]

Although these initial studies have demonstrated that self-assembled monolayers can block against the ALD process, the criteria for choosing SAMs to achieve the most effective deactivation are still unknown. In addition, how the choice of ALD precursors impacts the deactivation process, as well as the blocking mechanism itself, is still undetermined.

In this paper, we will propose a model to explain the blocking mechanism. The model is based on the investigation of a series of SAMs as monolayer resists for the HfO_2 ALD process. The study reveals that several important factors decide whether a particular agent will be effective in deactivating the ALD process: chain length of the molecular precursors, reactive headgroup, and tailgroup structure. The initial blocking mechanism toward the ALD process is also discussed to understand the requirement for different parameters that determine the formation of an efficient monolayer resist.

Experimental Section

1. SAMs Preparation. Sample substrates were cut from Si (100) wafers purchased from Si-Tech, Inc. (p-type with boron dopant; resistivity of 1.0−10.0 Ω cm). All chemicals used to form self-assembled monolayers were purchased from Aldrich (Milwaukee, WI) and were used directly without further treatment. We chose toluene (anhydrous, 99.8%, Aldrich) as the solvent for all of the solutions. All procedures for SAM formation were performed in a dry, air-purged glovebox. To form all of the self-assembled monolayers in this study, the silicon substrates were dipped into a 10 mM solution of the deactivating agent in toluene, and the bottles containing the submerged substrates were then sealed and held in the glovebox for 2 days without disturbance. We found that the use of long reaction time in a dry environment is essential to formation of high-quality SAMs.[11,27,28] After SAM formation, the samples were rinsed sequentially with toluene, acetone, and chloroform and dried by nitrogen flow. All of the samples were stored in the glovebox for more than 10 h before the analysis and subsequent experiments.

2. ALD Process. The ALD precursors for HfO_2 deposition were high-purity hafnium tetrachloride ($HfCl_4$) powder and deionized water. The HfO_2 ALD process includes two self-limiting chemical reactions, repeated in alternating ABAB sequences shown below.

The chemistry for HfO_2 deposition was:

$$\text{A:}\ \ \text{Hf}-\text{OH}^* + \text{HfCl}_4 \rightarrow \text{Hf}-\text{O}-\text{HfCl}_3^* + \text{HCl}\uparrow$$

$$\text{B:}\ \ \text{Hf}-\text{Cl}^* + \text{H}_2\text{O} \rightarrow \text{Hf}-\text{OH}^* + \text{HCl}\uparrow$$

where the asterisks represent the surface species. In both reactions, a gas-phase molecular precursor reacts with the surface functional species and saturates the entire surface in a self-limiting manner. Each AB reaction cycle produces an HfO_2 layer terminated by hydroxyl groups, with the hydrochloride byproduct pumped away.

The base pressure of the ALD reactor was kept at 5×10^{-8} Torr to obtain an initial clean surface before the film deposition. During the ALD process, the reactor was operated at 0.5 Torr. The source temperatures were 20 and 150 °C for the H_2O and $HfCl_4$ precursors, respectively. The sample surface was alternately exposed to $HfCl_4$ and water vapor. After each exposure, the reaction chamber and the gas manifold were purged with nitrogen to avoid possible gas-phase reactions and to eliminate the possible physisorption of the precursors on the substrates. Deposition was carried out at a substrate temperature of 300 °C. The exposure times for $HfCl_4$ and water vapor were both 2 s, followed by 3 min of nitrogen purging after each precursor was introduced into the chamber. The entire 50 cycles of $HfCl_4$ and water vapor precursors form a 36−38 Å thickness HfO_2 high-κ dielectric film on reference chemical oxide passivated Si (100) substrates. The physical thickness of HfO_2 was determined by ellipsometry after prior calibration by transmission electron microscopy (TEM).

3. Film Characterization. Measuring the wetting properties of a SAM-coated substrate is one of the most surface-sensitive and

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rapid techniques for judging the quality of the SAM. Ellipsometry and X-ray photoelectron spectroscopy (XPS) provide information on film thickness and elemental composition, respectively. All three of these techniques provide a macroscopic view of the film properties averaged over a relatively large sampling area. Atomic force microscopy (AFM) and cross-sectional TEM analysis, on the other hand, provide nanoscale information on the film, which is useful in understanding the blocking mechanism of organosilanes toward the ALD precursors.

A FTA 2000 dynamic contact angle analyzer has been used to measure the water contact angle. The water contact angles (WCAs) we report in this paper are static angles. A sessile drop of Millipore-Q water (resistivity = 18.2 MΩ cm) with constant volume (20 μL) was applied onto the surface of each sample. At least four different points of each sample were measured to get the average value for the WCAs.

A Gaertner Scientific Corp. L116C He−Ne ellipsometer was used to measure the film thickness for this study. The incident angle for the ellipsometer is 70°. For the alkylsiloxane monolayers, we use a refractive index of $n = 1.46$.[29] More than five points were measured on each sample to check the uniformity and to obtain an average value for the film thickness.

The XPS, AFM, and TEM analyses were carried out in the facilities of the Geballe Laboratory for Advanced Materials (GLAM) at Stanford University. The XPS system used is an SSI S-Probe monochromatized spectrometer, which uses Al (Kα) radiation (1486 eV) as a probe. This instrument permits high sensitivity and good energy resolution. All of the spectra shown in this paper have a detection sensitivity of $\sim$0.1 at. %. Surface morphology was investigated by AFM (Digital Instruments Inc., Santa Barbara, CA). The surface morphology of the samples before and after ALD processing was compared to help elucidate the blocking mechanism and the film nucleation process. Tapping mode was used for both SAM and HfO_2 surfaces.

The TEM used in this work is a Philips CM20 field emission gun (FEG) microscopy. The operating voltage for this high-resolution TEM is 200 kV, with 2.4 Å point-to-point resolution and 2 Å line resolution.

Results and Discussion

To investigate which properties of the self-assembled monolayer are required for full deactivation of a SiO_2 surface against ALD, a series of deactivating agents has been investigated for use as ALD resists. The series includes linear aliphatic alkyltrichlorosilanes of different chain lengths; trichlorosilanes with different tailgroup types, including linear, branched, and aromatic tails; and molecules with different reactive headgroups, such as trialkoxysilanes and mono-, di-, and trihalosilanes. A comparison is made between the type of deactivating agent, the quality of the SAM formed, and its ability to block the ALD process. This comparison provides insight into the blocking mechanism of organic monolayer resists toward the ALD process.

1. Tailgroup Chain-Length Dependence. A series of *n*-alkyltrichlorosilanes of chain lengths ranging from 1 to 18 carbon atoms was used to form self-assembled monolayers on the oxide-covered silicon substrates. The SAMs formed by the different *n*-alkyltrichlorosilanes were characterized by ellipsometry and contact angle measurements, and were then loaded into the ALD reactor where the HfO_2 ALD process was carried out. The hafnium atomic percentage (Hf at. %) after the ALD process was analyzed by XPS to provide information on the amount of HfO_2 deposited onto the SAM-coated substrates.

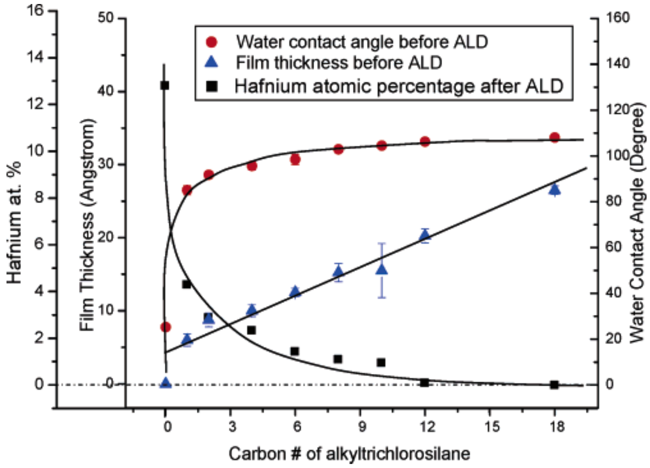

Figure 1. Chain-length dependence of alkyltrichlorosilane blocking efficiency. The plot shows the water contact angle and film thickness before ALD, and hafnium atomic percentage by XPS analysis after the ALD process.

As shown in Figure 1, the film thickness of the self-assembled monolayers increases linearly with the number of carbon atoms in the alkyltrichlorosilane. On the other hand, the water contact angle increases abruptly when adding the first one and two methyl units to the alkyl chain, and then grows moderately before reaching a plateau (static water contact angle WCA = 110°). The data show that when the alkyl chain is sufficiently long (in this case, a 12-carbon atom alkyl chain), the monolayer completely converts the surface wetting property to hydrophobic, and the WCA does not increase further. These results are consistent with a previous report.[29] The blocking efficiency of the film is represented in Figure 1 by the hafnium atomic percentage (Hf at. %) after the ALD process as determined by XPS analysis. On the unmodified chemical oxide passivated substrate, the Hf at. % is approximately 12.4% after the deposition.[30] As seen in Figure 1, the Hf at. % decreases when the substrate is coated with the organic monolayer prior to ALD. Furthermore, the magnitude of the decrease depends on the chain length of the SAM. Inspection of Figure 1 shows that the Hf at. % is inversely proportional to the WCA for various chain-length alkyltrichlorosilanes, indicating that the blocking efficiency approximately tracks the WCA. Only those molecules with alkyl chain lengths greater than 12 can completely block the HfO_2 ALD process, as indicated by the absence of Hf on those samples after ALD within the XPS detection limit.

The HfO_2 ALD process using $HfCl_4$ and H_2O precursors depends strongly on the presence of surface hydroxyl groups.

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(30) This number is less than the 33.3% that was expected for a stoichiometric bulk HfO_2 film. We attribute this discrepancy to three possible effects. First, because the HfO_2 film is so thin, there is a contribution to the XPS spectrum from the substrate silicon. In addition, one of the Hf peaks overlaps with the oxygen peak, which increases the apparent O at. % and decreases that of Hf. Finally, there is carbon and oxygen surface contamination on the sample surface that occurs before it is put into the XPS chamber.

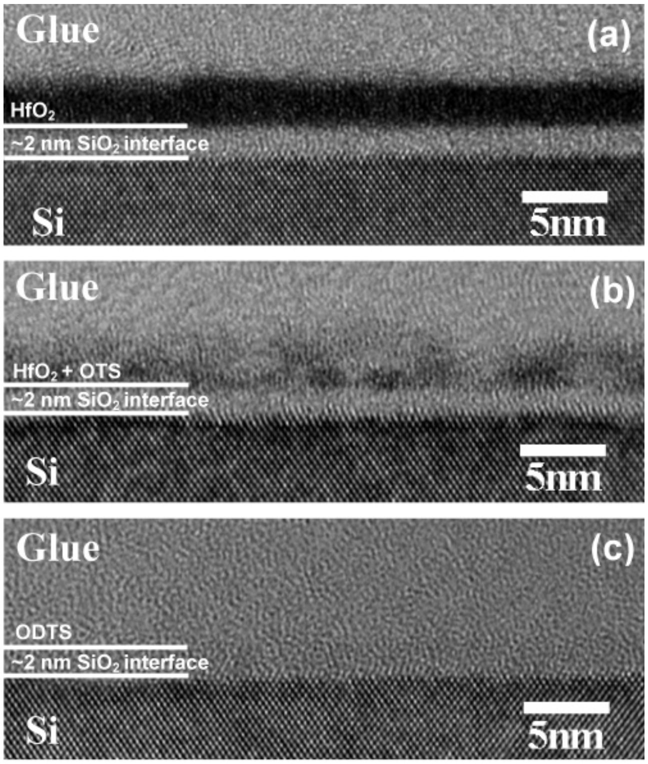

Figure 2. Cross-sectional HR-TEM image of HfO_2 deposition on (a) chemical oxide silicon wafer; (b) densely packed OTS-coated silicon wafer; and (c) densely packed ODTS-coated silicon wafer.

The process is believed to occur by initial reaction of $HfCl_4$ with Si−OH groups at the SiO_2 surface.[31] We might expect, therefore, that deactivating the surface hydroxyl groups would effectively block the ALD process. If the only requirement for deactivation was that the surface hydroxyl groups had to be replaced by siloxane bonds at the surface by reaction with an alkyltrichlorosilane, there should be no major difference between shorter-chain and longer-chain molecules if the surface silylation goes to completion. However, the chain-length dependence results described above demonstrate that the blocking mechanism is not as simple as the deactivation of surface hydroxyl groups. To further elucidate the mechanism of the deactivating effect, an interface analysis by cross-sectional TEM and surface morphology analysis by AFM has been performed.

The cross-sectional, high-resolution (HR) TEM images in Figure 2 compare the HfO_2 deposition on a chemical oxide silicon wafer, an octyltrichlorosilane (OTS) deactivated silicon wafer, and an ODTS-coated silicon wafer. There is a uniform HfO_2 layer on the chemical oxide substrate, as revealed by the dark band above the SiO_2 layer [Figure 2a]. On the other hand, we observe some aggregation of the HfO_2 film on the sample coated with OTS, which is an eight-carbon alkyl chain trichlorosilane molecule, as seen by the inhomogeneous contrast between the SiO_2 and glue layers [Figure 2b]. Finally, no HfO_2 is detected on the ODTS (18-carbon chain alkyltrichlorosilane) deactivated sample [Figure 2c]. The TEM analysis is consistent with the XPS results, in that the blocking efficiency of HfO_2 increases with the longer-chain deactivating agents; hence, only partial blocking is achieved with the eight-carbon chain. The most important information obtained from the cross-sectional TEM images, however, is that on the OTS deactivated sample, the HfO_2 film grows directly at the SiO_2 interface instead of on top of the organic film.

An AFM analysis has been performed on the above three samples (both before and after the ALD process) as well. For the chemical oxide substrate, the starting surface is atomically flat, and the HfO_2 film is also quite uniform after the ALD process, with a 1.5 Å root-mean-square (RMS) roughness. For the ODTS-coated substrate, the sample is also atomically uniform both before (RMS = 1 Å) and after (RMS = 1 Å) the ALD process. Nevertheless, for the OTS-coated substrate, the sample is much rougher after the deposition [Figure 3b] (RMS = 7 Å) than before the ALD process [Figure 3a] (RMS = 1 Å). We believe the islands shown in Figure 3b form as a result of HfO_2 nucleation and growth, as discussed below.

2. Mechanism of Growth and Deactivation. On the basis of the above analysis, a possible mechanism can be proposed to explain the dependence of the deactivating process on chain length (Scheme 1a and b). We believe that surface defects, likely, nonreacted hydroxyl groups, are the initial sites for the HfO_2 growth. In addition, nucleation may also occur at Si−O−Si bonds. The role of the SAM appears, then, to be 2-fold: (1) to remove reactive Si−OH groups at the SiO_2 surface, and (2) to prevent precursors from reaching the SiO_2 surface where they may otherwise react with remaining Si−OH defects and Si−O−Si type bonds.

The organic deactivating agents are known to react with surface hydroxyl groups, leaving the alkyltrichlorosilanes bonded to the surface through Si−O covalent bonds. However, due to local bonding mismatch between the organic layer and the Si−O−Si interface, together with the complex surface structure of the SiO_2 surface, there are always some nonreacted hydroxyl groups or defects left.[14,32] Consequently, the underlying SiO_2−organic interface is relatively reactive due to the remaining hydroxyl groups, other defects, and Si−O−Si bridge oxygen atoms.[32] If the ALD precursors reach this interface, they can bond to the reactive surface sites and begin the ALD process. Both water and $HfCl_4$ precursors might potentially bond to the oxygen atoms to start the ALD cycles. For example, the $HfCl_4$ precursors can react with the surface hydroxyl groups and subsequently nucleate growth, which would propagate through the ALD half reactions. Furthermore, theoretical calculations have demonstrated that the $HfCl_4$ precursors could initiate reaction through the Si−O−Si bridge oxygen atoms.[33] Moreover, recent experiments have shown the precursors that react with surface hydroxyl groups can also bond to oxygen atoms in polymer films to start ALD nucleation. For example, reported ALD growth on polyurethane and low-κ SILK demonstrates that the film can grow on polymers with bridging oxygen atoms.[34,35]

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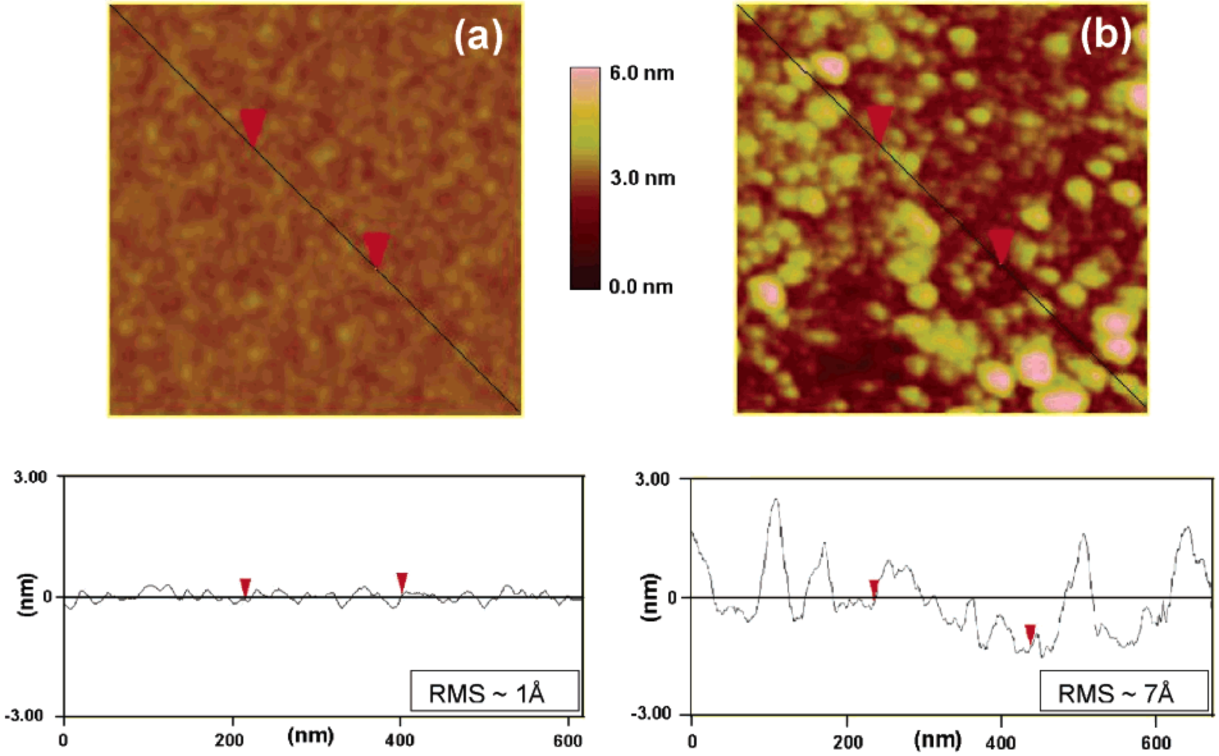

Figure 3. AFM plan view and sectional analysis of a closely packed octyltrichlorosilane (OTS)-coated silicon wafer (a) before HfO_2 ALD deposition; and (b) after HfO_2 ALD deposition.

The packing density of the SAMs depends on intermolecular van der Waals (VDW) dispersion forces, which are proportional to the strength of the induced dipole. There are two main factors that determine the strength of the induced dipole between molecules: the size and the shape of the molecules. Because all of the molecules in the chain-length dependence experiment are *n*-alkyltrichlorosilanes, they have the same structure. Therefore, the strength of the van der Waals interaction in this case is a function of the size, that is, chain length, of the molecules. The longer-chain molecules have stronger VDW interactions because they have more electrons and more distance over which induced dipoles can develop. For the shorter-chain deactivating agents, the interchain VDW attraction is relatively weak. This is seen in the reduced packing density and lower hydrophobicity (WCA) for the shorter-chain SAMs.

We postulate here that to effectively block the ALD process, it is important that the SAM be densely packed and highly hydrophobic to repulse the ALD precursors' permeation [Scheme 1a]. Otherwise, the precursors can penetrate the organic layer to reach the organic−SiO_2 interface. Once at the interface, they can bond with the hydrophilic surface sites such as the remaining hydroxyl groups and oxygen atoms, and nucleate growth as illustrated in Scheme 1b. Even for densely packed shorter-chain SAMs, however, the majority of hydroxyl sites have been deactivated. Hence, the precursors can bond only at the relatively few individual, nonreacted hydroxyl sites, or at oxygen bridge sites, which may be of lower reactivity. This mechanism would lead to nucleation primarily at defects and subsequent growth from these sites. Therefore, the amount of HfO_2 deposited will be much less than on the clean chemical oxide substrate, with the resulting HfO_2 layer nonuniform and discontinuous. This model is consistent with the TEM image shown in Figure 2b, in which the HfO_2 is seen to aggregate at the interface and the film density is much lower than that on the chemical oxide SiO_2 [Figure 2a]. Furthermore, the roughness observed in AFM for HfO_2 films grown on samples deactivated by short-chain molecules [Figure 3b] also supports this model.

As the chain length of the organic layer increases, the interchain van der Waals (VDW) attraction becomes stronger and the SAMs become better packed and more hydrophobic. Under current ALD conditions, once the chain length increases to a certain point, indicated by the plateau in the value of the contact angle in Figure 1, the SAM is able to completely block the penetration of precursors to the reactive organic−SiO_2 interface. At the same time, the long purging times between each precursor pulse allow the removal of any physisorbed ALD precursors from the substrates. The result is complete (or near-complete) inhibition of the ALD reactions. In summary, we propose that it is precursor penetration through the SAMs and interface nucleation that lead to HfO_2 film growth on shorter-chain SAMs. To achieve satisfactory deactivation, a minimum chain length is therefore necessary.

3. Tailgroup Structure Effect. According to the mechanism proposed above, the packing density of the self-assembled monolayers determines their blocking efficiency toward the ALD process. The longer is the alkyl chain, the stronger is the van der Waals interaction. Therefore, for molecules with the same tailgroup structure, the longer chain

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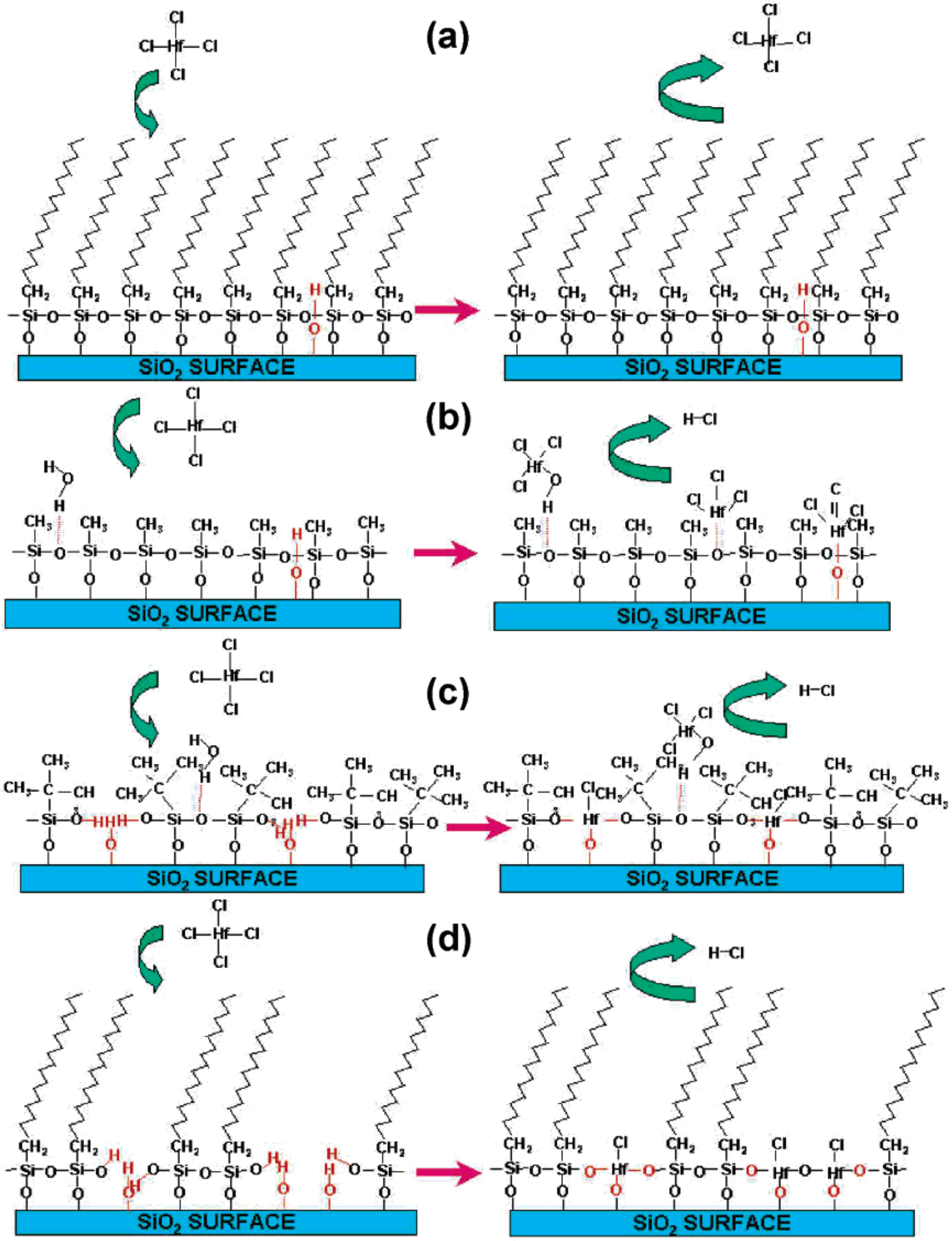
Scheme 1. Schematic Illustration of the ALD Deactivating Mechanism for Different Types of SAMs[a]



[a] (a) Densely packed, long-chain, self-assembled monolayer; (b) densely packed, short-chain, self-assembled monolayer; (c) self-assembled monolayer with bulky tailgroups; and (d) loosely packed, self-assembled monolayer with pinholes.

can provide better deactivating efficiency. However, because molecular structure can also influence the strength of intermolecular van der Waals interactions, the shape of the tailgroup on the SAM is another important consideration for choosing effective deactivating agents.

To examine the effect of tailgroup structure on deactivation efficiency, three different butyltrichlorosilanes, *n*-butyl-, iso-butyl-, and *tert*-butyltrichlorosilane, have been studied. Their properties (WCA, thickness) and the results of a post-ALD elemental analysis are compared in Table 1. The hydrophobicity and the thickness of the organic films are found to decrease when the alkyl chain groups become bigger. The Hf at. % measured after the ALD process increases as the SAM constituent changes from *n*-butyl to *iso*-butyl to *tert*-butyl, indicating that the deactivation efficiency also becomes worse as the tailgroups become more bulky. It is likely that the observed effect is a result of reduced packing density with the bulkier tailgroups. The bulky tail structures decrease

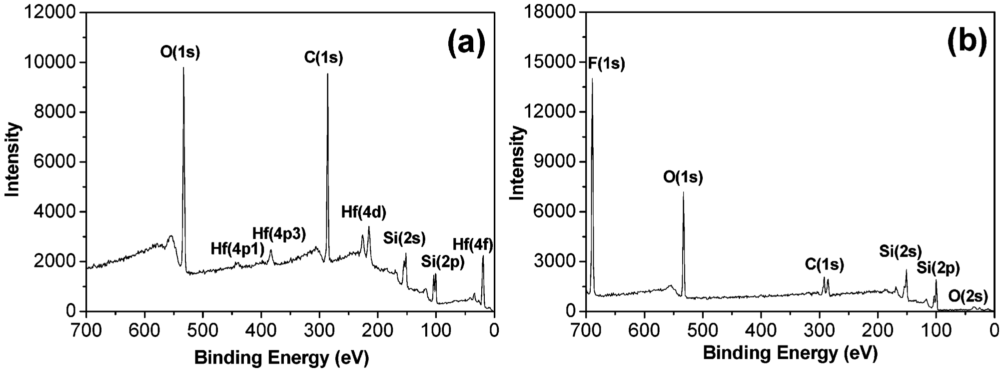


Figure 4. XPS spectra following (a) HfO_2 deposition on chemical oxide silicon substrate; and (b) HfO_2 deposition on FOTS-coated silicon substrate.

Table 1. Water Contact Angle and Film Thickness for Multiple Deactivating Agents before the ALD Process, and XPS Elemental Analysis after the HfO_2 ALD Process

deactivating agents	water contact angle (deg)	film thickness of deactivating agents (Å)	element at. % analysis by XPS	
			hafnium	carbon
none	5.2−38.7	none	12.4	22.5
ODTS	109.8 ± 1.1	26.8 ± 0.6	<0.1	60.1
$SiMeCl_3$	85.1 ± 1.9	6.5 ± 0.8	4.3	25.6
$SiMe_2Cl_2$	95.3 ± 3.6	10.5 ± 0.5	2.5	26.5
$SiMe_3Cl$	79.0 ± 0.8	3.9 ± 0.8	11.7	29.4
$SiMe_3Br$	79.4 ± 2.1	4.8 ± 1.3	11.6	31.9
$SiMe_3I$	78.3 ± 1.4	3.9 ± 1.4	11.9	31.9
HMDS	82.0 ± 1.3	5.6 ± 1.0	10.1	26.7
n-$BuSiCl_3$	95.7 ± 2.5	13.0 ± 0.8	2.4	31.3
iso-$BuSiCl_3$	88.7 ± 2.4	9.5 ± 1.7	7.7	30.0
tert-$BuSiCl_3$	83.5 ± 3.4	7.4 ± 1.3	10.4	19.3
benzyl-$SiCl_3$	94.0 ± 3.3	12.6 ± 2.2	9.9	39.2
ODTM	96.8 ± 2.6	10.7 ± 2.5	11.7	29.8
ODTE	97.4 ± 2.3	12.3 ± 1.5	11.3	31.4
FOTS	112.1 ± 1.7	15.3 ± 2.1	<0.1	24.6[a]

[a] Carbon atomic percentage for FOTS is small as compared to OTS; this is because the hydrogen atom cannot be detected by XPS while the fluorine atom can.

the interchain VDW attractions. Therefore, to obtain the most closely packed film, simple, linear alkyl chain groups are necessary.

All of the compounds discussed above have hydrocarbon tailgroups. Fluorinated carbon chain trichlorosilanes have also been chosen in this study as a comparison to hydrocarbon alkyltrichlorosilanes. In contrast to hydrocarbon alkyltrichlorosilanes, fluoroalkyltrichlorosilanes are much more reactive toward SAM formation. This higher reactivity is because of an inductive effect of the fluorine substituents on the γ-C.[36] In addition to higher reactivity, the fluoroalkyltrichlorosilanes can form more highly hydrophobic films than hydrocarbon alkyltrichlorosilanes. Here, tridecafluoro-1,1,2,2-tetrahydrooctyltrichlorosilane (FOTS) has been investigated as a deactivating agent and compared to octyltrichlorosilane (OTS). Both FOTS and OTS have eight-carbon chain tails. However, for FOTS, the static water contact angle of the dense SAM is 112°, while for OTS, the static water contact angle of the densely packed film is only 103°. The difference between contact angles results from the fact that fluorocarbon chains possess higher hydrophobicity than the corresponding hydrocarbon analogues.[37] An empirical rule states that with respect to the cmc (critical micellar concentration) value, one CF_2 unit brings as much hydrophobicity as 1.5 CH_2 units.[38] Fluorine atoms are much bigger than hydrogen atoms. The interchain VDW attraction energy of fluorocarbon chains is hence stronger than that of hydrocarbon chains of the same length. Therefore, fluoroalkyltrichlorosilanes can provide denser and more hydrophobic film with fewer required carbon units in the SAM tailgroups, which may lead to better inhibition of ALD growth.

The XPS spectra in Figure 4 compare the HfO_2 ALD process on a chemical oxide silicon substrate and an FOTS monolayer-coated silicon substrate. It is evident that there are no hafnium peaks on the FOTS-coated substrate within the sensitivity of the spectrometer. For the OTS monolayer, the hafnium atomic percentage on the sample after the ALD process is 1.2%, as shown in Figure 1. The fluoroalkyltrichlorosilanes therefore provide better deactivation and encompass another category of promising deactivating agents toward the ALD process.

Besides the aliphatic chain molecules, aromatic tail molecules have also been investigated. Neither could the bulky phenyl rings form closely packed films, nor does the amorphous SiO_2 surface help to orient them for forming stable $\pi-\pi$ stacking. Therefore, they would not be expected to form efficient deactivating films against the ALD process. We have examined benzyltrichlorosilane to verify this point. The data in Table 1 for benzyltrichlorosilane reveal a low contact angle and a correspondingly high Hf at. % following ALD.

To summarize the tailgroup structure investigation, the packing of the molecules in a self-assembled monolayer depends on the VDW attraction between tailgroups. As the tail structure becomes more complex and bulkier, the VDW attraction is weakened, and consequently the packing density is degraded. In SAMs that are not densely packed, there are more defects and pinholes left on the surface, and these defects and pinholes make it possible for the precursors to penetrate into the organic film and bond with the interface hydroxyl groups or oxygen atoms [Scheme 1c]. On the other hand, by substituting the hydrocarbons of the tailgroups with a fluorocarbon, the monolayer film becomes denser and more hydrophobic. The results of the FOTS study suggest that fluorocarbon tail chain molecules can provide a deactivating effect similar to that of a hydrocarbon chain molecule but with a shorter chain length. To use SAMs as ALD resists,

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(37) Oda, R.; Huc, I.; Danino, D.; Talmon, Y. *Langmuir* **2000**, *16*, 9759.

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films with high packing density are necessary. The optimum deactivating agents, therefore, appear to be those with simple, linear alkyl tail chains without branches.

4. Reactive Headgroup Dependence. All of the compounds discussed above are alkyltrichlorosilanes. These compounds have reactive headgroups containing three chlorine atoms, which provide high reactivity toward surface hydroxyl groups and the ability to cross-link with other alkyltrichlorosilanes under solution-phase reaction. To obtain a better understanding of the ALD blocking mechanism, molecules with different reactive headgroups have also been investigated in this study. To separate the effect of the SAM headgroup from that of the tail, we chose to focus primarily on SAM precursors containing methyl tailgroups to represent the alkyl chain analysis while the headgroup was varied.

a. Number of Chlorine Substituents. SAM formation and ALD deactivation with alkyldichlorosilanes and monochlorosilanes have been compared to that using alkyltrichlorosilanes. Films formed by trimethylchlorosilane (TMCS), dimethyldichlorosilane (DMDCS), and methyltrichlorosilane (MTCS) are analyzed in Table 1. These three molecules have similar molecular structure, Me_nSiCl_{4-n} ($n = 1-3$), with different numbers of chlorine substituents at the headgroup.

It has been shown by previous experimental analysis and ab initio calculations[39,40] that as the number of Cl substituents increases, the reactivity of the compounds toward the surface also rises. It is evident from Table 1, however, that the hydrophobicity does not follow the same trend as the surface reactivity. Although MTCS has the highest reactivity among these three molecules, the film formed by DMDCS has the highest hydrophobicity and the best blocking effect. We suggest, therefore, that the organosilane with two methyl groups (and two chlorine atoms) forms a denser film than the film formed by the compound with one methyl group (and three chlorine atoms). There are two competing factors leading to this behavior: VDW attraction or repulsion between tailgroups and reactivity of the headgroup. Although the VDW attraction is expected to become stronger with increasing number of methyl groups, too bulky a tail will lead to steric repulsion. In addition, the decreasing number of chlorine atoms reduces the reactivity of the headgroup at the surface. Consequently, the most dense, hydrophobic SAM is formed by the intermediate alkylchlorosilane, DMDCS, with two CH_3 and two Cl groups.

b. Other Reactive Groups. In addition to chloride compounds, other reactive groups have been compared in this study as shown in Table 1. These include alkylbromosilane, alkyliodosilane, and alkyldisilazane, as well as alkylalkoxysilanes.

The electronegativity and the Si−X bond energy decrease according to the sequence Cl > Br > I. Therefore, the reactivity of Me_3Si-X toward the hydroxyl groups should increase along the same series; that is, bromo- and iodotrimethylsilanes should exhibit higher reactivity with hydroxyl groups than chlorotrimethylsilane. This prediction is consistent with results of theoretical calculations.[40] However, the experimental results do not reveal a significant difference in reactivity under current reaction conditions. According to Table 1, trimethylchlorosilane, trimethylbromosilane, and trimethyliodosilane form SAMs of similar hydrophobicity (WCA) and thickness. Hf at. % values are nearly 12%. Meanwhile, hexamethyldisilazane, another commonly used SAM compound, demonstrates a water contact angle, film thickness, and blocking effect that are similar to those of the trimethylhalosilanes.

None of these compounds containing trimethyl tailgroups appear able to form densely packed, hydrophobic films that can effectively block the ALD process. Low reactivity of the headgroup and steric effects between the tailgroups are possible reasons for the resultant loosely packed films and inefficient blockage. With each of these compounds, the hafnium atomic percentage after ALD is comparable to that on the unprotected, chemical oxide substrate, indicating that none of these SAMs prevents HfO_2 ALD to a significant degree.

TEM studies were also carried out on substrates protected by trimethylhalosilane SAMs. The TEM image after the ALD process on trimethylhalosilane-coated samples looks similar to the TEM image collected after ALD growth on a chemical oxide substrate [Figure 2a]. In particular, the HfO_2 film is continuous and uniform. However, the trimethyl groups are known to be stable at the ALD reaction temperature (300 °C), and consequently they must still be present at the interface. To explain the TEM results showing that a continuous HfO_2 film is formed even in the presence of the SAM, we postulate the following model. For these bulkier trimethylsilane compounds, there may be a significant density of unreacted surface hydroxyl groups left on the samples even after formation of the SAM. Consequently, some of these hydroxyl groups are likely to neighbor one another. The $HfCl_4$ precursors can bond to these sites and nucleate the film growth. With networking through the Hf−O−Hf bonds, growth can occur laterally within a few ALD cycles. Eventually, the cross linking of the Hf−O−Hf may completely cover all of the methyl groups.

Another headgroup commonly used in formation of SAMs is that of alkoxysilanes. Here, the *n*-alkyltrialkoxysilanes are compared to *n*-alkyltrichlorosilanes. Both octadecyltrimethoxysilane (ODTM) and octadecyltriethoxysilane (ODTE) have been investigated, and the results of the solution-phase SAM formation and Hf at. % following ALD are compared in Table 1. It is evident that the degree of blocking is poor for these compounds as compared to a chlorosilane with the same 18-carbon chain tailgroup.

We attribute the poorer blocking of ODTM and ODTE for ALD process to submonolayer film formation. The *n*-alkyltrialkoxysilane molecules polymerize on the surface by a two-step mechanism: the polar trialkoxy headgroup first hydrolyzes into trihydroxy groups, and then the polymerization occurs as a second step by intermolecular condensation between neighboring silanol groups with the elimination of a water molecule.[41] Because the SAM formation in these studies was carried out under extremely dry conditions to

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[39] Tripp, C. P.; Hair, M. L. *Langmuir* **1995**, *11*, 149.

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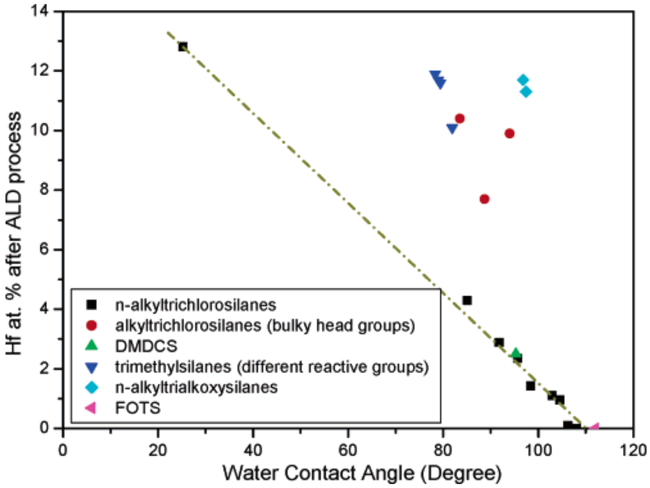

Figure 5. Plot of the Hf at. % post-ALD versus water contact angles measured for a variety of self-assembled monolayers before the ALD process. The Hf at. % is a measure of the blocking efficiency toward the ALD process.

ensure consistency with chlorosilanes SAM formation, there might not have been enough water present to fully convert the trialkoxy reactive groups into trihydroxyl groups. Furthermore, the *n*-alkyltrialkoxysilanes have lower reactivity as compared to the chlorine reactive headgroup and may require longer SAM formation time. Consequently, the reactivity of this type of molecules was likely limited by the water concentration and reaction time of the present experimental condition.

We postulate that SAMs formed by long-chain molecules at submonolayer coverage generate pinholes in the film that can readily trap the ALD precursors. These results are consistent with the model shown in Scheme 1d. The ALD process begins at discrete nucleation sites, where these sites likely correspond to defects (pinholes) in the SAM where unreacted hydroxyl groups at the surface are exposed to the ALD precursors. Similar effects were observed with loosely packed SAMs in our earlier study.[11]

5. Correlation between Hydrophobicity and Deactivation. To summarize all of the different parameters related to the formation of an efficient deactivation layer, a plot of the hafnium atomic percentage after the ALD process versus water contact angle before the ALD process has been constructed for all of the self-assembled monolayers examined in this study. The resultant plot is shown in Figure 5. An interesting correlation between Hf at. % and WCA is apparent in the figure. There is a general trend for decreasing Hf at. % with increasing hydrophobicity (WCA) for densely packed SAMs.

On the other hand, there is a clear difference in deactivation potential (Hf at. %) for those compounds which form densely packed SAMs as compared to those that form poorly packed SAMs. For example, for the series of *n*-alkyltrichlorosilanes, which are known to form densely packed monolayers, the deactivating efficiency is inversely proportional to the WCA, and the Hf at. % values follow the dashed line in Figure 5. Other molecules that also pack well, such as DCDMS and FOTS, also fall on this line. However, for the molecules with bulky tailgroups or low reactivity headgroups (including the alkyltrichlorosilanes with bulky tails groups, trimethylhalosilanes, and *n*-alkyltrialkoxysilanes), closely packed monolayers cannot be formed. Consequently, these SAMs cannot effectively deactivate the ALD process, and the Hf at. % is much larger on these films as compared to densely packed SAMs with the same WCA value.

The data in Figure 5 are consistent with the deactivation mechanism that was proposed in Scheme 1. For the densely packed SAMs, most surface hydroxyl groups have been removed by reaction, and those sites that have not been reacted are protected from the ALD precursors by the hydrophobic organic layer above the interface. In this case, the ALD precursors can bond only to a very few defect hydroxyl groups or bridge oxygen atoms. These defect sites are sparsely concentrated, and the resultant film, if it grows, is discontinuous. For the loosely packed films, there may be larger concentrations of surface hydroxyl groups left because fewer SAM molecules are attached to the surface. The ALD precursors can bond to these sites, nucleating the film growth. At higher concentrations of nucleation sites (defects), neighboring precursors can cross-link with each other, and after several cycles, the deposited film may completely cover the organic layer and change the surface properties, facilitating further ALD growth.

Conclusions

In this paper, we have investigated a series of self-assembled molecules as monolayer resists for HfO_2 atomic layer deposition. The self-limiting nature of the ALD process provides an ideal method to manipulate the surface functional groups to achieve selective deposition by monolayer resists. Three important factors influence the blocking efficiency of the monolayer organic films: chain length, tailgroup structure, and headgroup reactivity. This investigation shows that to achieve satisfactory deactivation toward the ALD process, it is crucial to form densely packed, highly hydrophobic organic monolayers. This in turn requires deactivating agents with high reactivity, low steric effect tailgroups, and minimum chain length.

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