

Report on the characterization of bonding for surface deactivation layers  
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Task Title : Low-ESH-Impact Gate Stack Fabrication by Selective Surface Chemistry

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### Introduction

Self-assembled monolayers (SAMs) are key to the deposition of multi-layered surface coatings having different properties and functions. SAMs are used to render surfaces hydrophilic or hydrophobic and to terminate with specific functional groups, such as amines and thiols for metal adhesion.<sup>1</sup> In addition to coupling materials, SAMs are used to resist chemical attack permanently to deter corrosion and temporarily either to release another material<sup>2</sup> or to pattern a surface. Patterning has been demonstrated by direct application of a stamp inked with SAMs<sup>3</sup>, as well as by selective deactivation of a portion of a surface.<sup>4</sup> The latter application requires a defect-free SAM that is inactive toward a specific precursor and deposition chemistry.

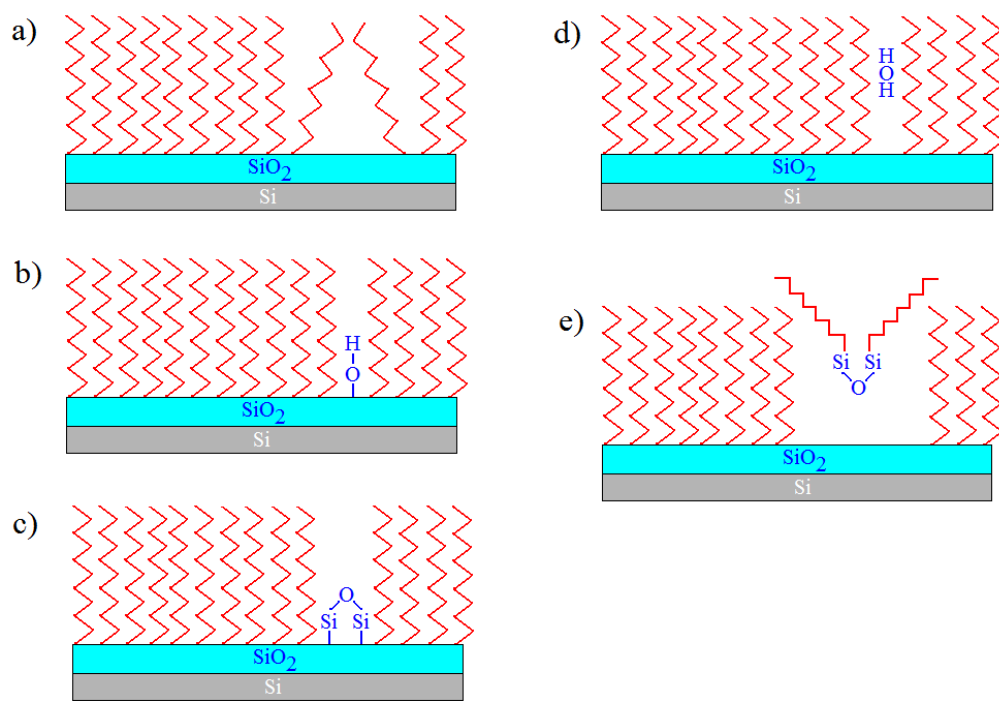
The bonding of the SAM layer with the surface, and specifically the defects that are created in bonding are important for applications where the SAM is used to deactivate the surface. Defect generation in silane-based SAMs could be caused by grain boundaries, misalignment, physical adsorption of SAM molecules, and water in or on a SAM. Islands composed of SAM molecules that grow together imperfectly could expose surface sites to precursor molecules. SAM molecules that are misaligned or misoriented whether at a boundary between islands or within an island could do the same. Silane-based SAMs have a propensity to react together and physisorb on a surface, rather than reacting.

This report details defect generation in SAMs that prevent proper bonding of molecules with the surface. This is the first step to eliminate defects in layers designed to resist chemical attack to pattern surfaces. We chose to study octadecyltrichlorosilane (OTS) because of the success demonstrated using this SAM molecule to selectively deposit metal oxide dielectric layers.<sup>5</sup> The precursor titanium tetrachloride ( $\text{TiCl}_4$ ) was chosen since it is small and reactive.

### Background

Deactivating an atomic layer deposition (ALD) process requires a SAM that is chemically inert to both the metal and oxygen precursors used in deposition. In order to prevent the oxygen precursor,  $\text{H}_2\text{O}$ , from adsorbing on the SAM a hydrophobic molecule is used to form the SAM. Any molecular defects in the SAM will allow nucleation of the metal precursors and begin the ALD growth process. Potential nucleation sites include open or unreacted surface hydroxyl groups, exposed Si-O bonds, water in the SAM, or physisorbed SAM molecules as shown in Fig. 1.

OTS SAMs are typically formed on piranha-etched Si. This method has been shown to deactivate  $\text{HfO}_2$  deposition for up to 50 cycles using either  $\text{HfCl}_4$  or  $\text{Hf}[\text{N}(\text{CH}_3)_2]_4$  and  $\text{H}_2\text{O}$  as ALD precursors.<sup>6-10</sup> Larger metal precursors such as  $\text{CH}_3\text{C}_5\text{H}_4\text{Pt}(\text{CH}_3)_3$ , used for depositing Pt, can be deactivated for up to 400 cycles with this method.<sup>7</sup>



**Fig. 1.** Schematic of potential SAM defects. a) Poor grain boundary between SAM islands due to misaligned molecules. b) Unblocked hydroxyl group, possibly at a grain boundary. c) Open Si-O bond, possibly at grain boundary. d) Water in or on the SAM. e) Polymerized molecules physisorbed on surface.

### Experimental

Degreasing consisted of sonicating p-type Si(100) substrates separately in both acetone and methanol for 5 minutes each, DI rinsing, and blowing dry with N<sub>2</sub>. A chemically hydroxylated surface was prepared by dipping either for 20 min in piranha solution (4 parts H<sub>2</sub>SO<sub>4</sub> to 1 part H<sub>2</sub>O<sub>2</sub> by volume) or for 10 min in nitric acid solution (1 part HNO<sub>3</sub> to 3 parts H<sub>2</sub>O by volume). Before exposing the hydroxylated surfaces to SAM solution, they were heated to 120°C for 5 min in order to remove any residual water left on the surface by the rinse.

Samples were submerged for 48 h in 10 mM OTS dissolved in anhydrous toluene. Samples were rinsed with a solvent, DIW, and N<sub>2</sub> dried. The thickness of the SAM layer was measured using ellipsometry. The water contact angle was measured to determine the hydrophobicity. An additional chlorosilane exposure was made in some cases using smaller molecules to fill in defects in the OTS layer.

The deposition of TiO<sub>2</sub> using an ALD TiCl<sub>4</sub> and water process was used to determine the relative defect concentration in a SAM layer. The ALD experiments were carried out in a custom reactor at a temperature of 170°C. Pulse and purge times were optimized for the best ALD growth rate, ensuring no chemical vapor deposition (CVD) growth. The Ti on the surface was detected using the integrated area of the Ti 2p<sup>3/2</sup> x-ray photoelectron spectroscopy (XPS) peak. The relative Ti peak area is used as a monitor of defect formation.

## Results

OTS SAMs had a monolayer thickness of  $26 \pm 1 \text{ \AA}$ , and a water contact angle of  $110 \pm 1^\circ$  after solvent rinsing. This thickness and water contact angle were obtained after 30 min; however, exposure times of 48 hours were required to form a SAM dense enough to deactivate  $\text{TiO}_2$  ALD. An OTS SAM reduced growth of  $\text{TiO}_2$  by a factor of  $12 \pm 5$ , compared to growth on piranha-etched Si. In contrast to literature results for  $\text{HfO}_2$  ALD, this SAM layer was insufficient to resist  $\text{TiO}_2$  growth for 50 cycles. A fully formed OTS layer was exposed to trimethylchlorosilane (TMCS) to fill in gaps not accessible to the much longer OTS. These surfaces yielded a deactivation factor of  $15 \pm 5$  relative to the chemical  $\text{SiO}_2$  made using piranha. Approximately one-third of the original defects in the OTS layer were filled in with the smaller molecules. Since TMCS binds only to hydroxyl groups, this shows that one-third of the defects in the SAM were unreacted hydroxyl groups, and two-thirds are due to other defects, such as open Si-O bonds or physisorbed molecules. Forming the OTS SAM on nitric acid etched Si eliminated many of the defects by creating a more uniformly hydroxylated surface, which allowed SAM molecules to pack more densely. OTS SAMs formed on nitric acid etched Si had a deactivation factor of  $50 \pm 10$  relative to the chemical oxide formed using piranha. Thus four-fifths of the defects in an OTS SAM formed on piranha-etched Si are avoided by using a better chemical oxidation. This includes open Si-O bonds and unblocked hydroxyl groups at poorly aligned grain boundaries. The remaining one-fifth of the defects in the SAM were due to physisorbed SAM molecules. Eliminating these deactivated a Si surface to 50 cycles of  $\text{TiO}_2$  ALD. The next phase of this work is to extend deactivation to higher numbers of cycles as well as to fabricate a simple device to demonstrate the utility of this chemistry.

## References

1. Dunaway, D. J.; McCarley, R. L. *Langmuir* 1994, 10, 3598-3606.
2. Jung, G.-Y.; Li, Z.; Wu, W.; Chen, Y.; Olynick, D. L.; Wang, S.-Y.; Tong, W. M.; Williams, R. S. *Langmuir* 2005, 21, 1158-1161.
3. Jiang, X.; Bent, S. *Journal of the Electrochemical Society* 2007, 154 (12), 648-656.
4. Hong, J.; Porter, D. W.; Sreenivasan, R.; McIntyre, P. C.; Bent, S. F. *Langmuir* 2007, 23, 1160-1165.
5. Puurunen, R. L.; Vandervorst, W. *Journal of Applied Physics* 2004, 96 (9), 4878-4889.
6. J. Hong, D. Porter, R. Sreenivasan, P. McIntyre, S. Bent. *Langmuir* 2007, 23, 1160-1165.
7. X. Jiang, S. Bent. *Journal of the Electrochemical Society* 2007, 154 (12), 648-656.
8. X. Jiang, R. Chen, S. Bent. *Surface & Coatings Technology* 2007, 201, 799-8807.
9. R. Chen, H. Kim, P. McIntyre, D. Porter, S. Bent. *Applied Physics Letters* 2005, 86, 191910.
10. R. Chen, H. Kim, P. McIntyre, S. Bent. *Chem. Mater.* 2005, 17, 536-544.