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Thin-Film Deposition of Silicon Nitrides and Oxides from Trihydridosilanes

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Trihydridosilanes can provide a route for generating self-assembled monolayers on metal substrates. Under mild conditions, these precursors interact with a variety of clean, hydrogenated and fresh metal and metalloid surfaces, including titanium, silicon and gold. All classes of hydridosilanes have minimal interaction with anhydrous oxide surfaces. After initial deposition, SAMs formed from 2-chloroethyltrihydridosilane may be converted to silicon nitride by pulsing with ammonia or silicon dioxide by pulsing water or oxygen. A proposed mechanism for the initial steps of deposition involves the dissociative adsorption of the silanes with the formation of hydrogen, followed by topmost atom layer insertion and concomitant surface reconstruction.

Introduction

The ever-shrinking real estate available for fabrication of nanofeatures has continued to accelerate the interest in ALD due to its ability to form ultrathin conformal films. The first step in ALD is a controlled and self-limited reaction of a chemical precursor with a substrate, which implies a specific chemical reactivity. Reactivity of this type is readily available in most oxide, nitrogen and chalcogenide films. The opportunities for reaction with pristine and hydrogenated metals and metal alloys that do not form oxides or other simple binary compounds are not as great. Further, in order to induce sites on substrates the presently accepted methodologies such as plasma-induced oxidation may not be desirable since the process typically involves a non-self-limiting degradation of the metal beyond the topmost layer of atoms. If the pristine metal-substrate is itself an ultrathin film, the oxidative process has the potential to degrade the film below the minimum thickness to perform the function for which it was originally deposited. A method for modification of oxide-free metal substrates that maintains film integrity and facilitated ALD growth on the substrates is of obvious utility.

We report here a series of metal substrate reactions which would be more conventionally associated with MOCVD of a Self-Assembled Monolayer (SAM), than ALD. SAM formation and ALD are both self-limiting technologies. The objective of this study is to demonstrate the potential of conversion of trihydridosilane derived SAMs to sites for ALD growth. The general method is a self-limiting injection of atoms into the top-most layer of metal substrates of a silicon atom induced by a trihydridoorganosilane. Depending on the specific precursor, an oxygen, halogen, nitrogen or carbon atom may be bonded to the silicon atom injected into the topmost layer of the substrate.

Observation of trihydridosilane interaction with various metal substrates is not without precedent. In this short paper, the initial observations in our laboratories which led to ALD experiments will be considered in the context of earlier reports which, in retrospect, support the concept that sites with specific reactivity can be induced in

pristine metal substrates. A mechanism for the metal modification is proposed. Preliminary ALD experiments are reported.

Results and Discussion

Observation of the specific interaction of trihydridosilanes with metal substrates

The treatment of oxide-free titanium metal with octadecylsilane and octadecyldimethylsilane in liquid phase at room temperature (depicted in Figure 1) is representative of the interaction of hydridosilanes with many metals. These experiments, reported earlier [1], were not performed under ALD or MOVD conditions, but simply bulk immersion of the metal substrates to neat liquid under a nitrogen atmosphere. Both the alkyldimethylhydridosilanes and the alkyltrihydridosilanes impart hydrophobicity to metal substrates, but trihydridosilanes are more effective than monohydridosilanes. The maximum water contact angle for the trihydridosilanes requires an induction time, while no change with time is observed for the monohydridosilane. These results are similar for neat deposition on gold at 80°C (depicted in Figure 2), although the time to achieve maximum contact angle is shortened. Figure 3 indicates that vapor phase treatments with octylsilane have no significant differences from the liquid phase treatments with the less volatile octadecylsilane and also suggest that the time requirement for optimum surface modification roughly follows the Arrhenius rule.

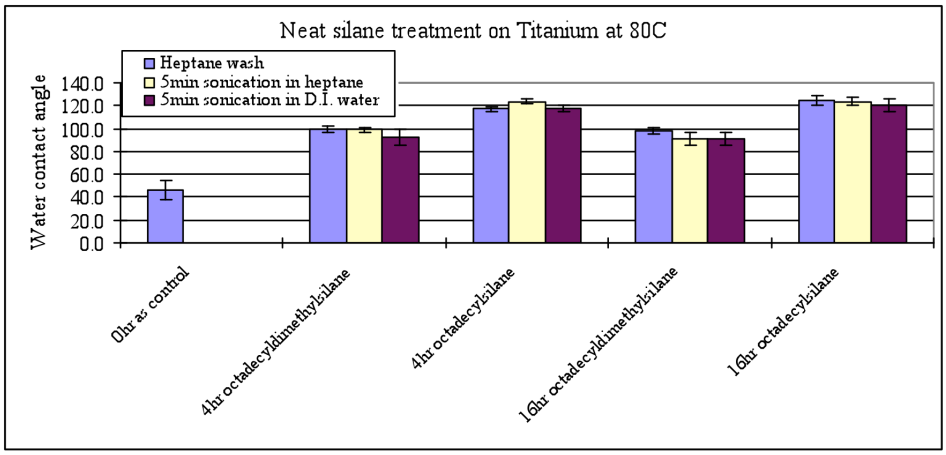


Figure 1. Contact angle of water on titanium metal after 80◦C exposure to neat octadecyldimethylsilane and octadecylsilane, for 4 and 16 h. After exposure substrates were (1) rinsed with heptane, (2) rinsed with heptane followed by sonication in heptane, (3) rinsed in heptane, followed by sonication in heptane, followed by sonication in deionized water.

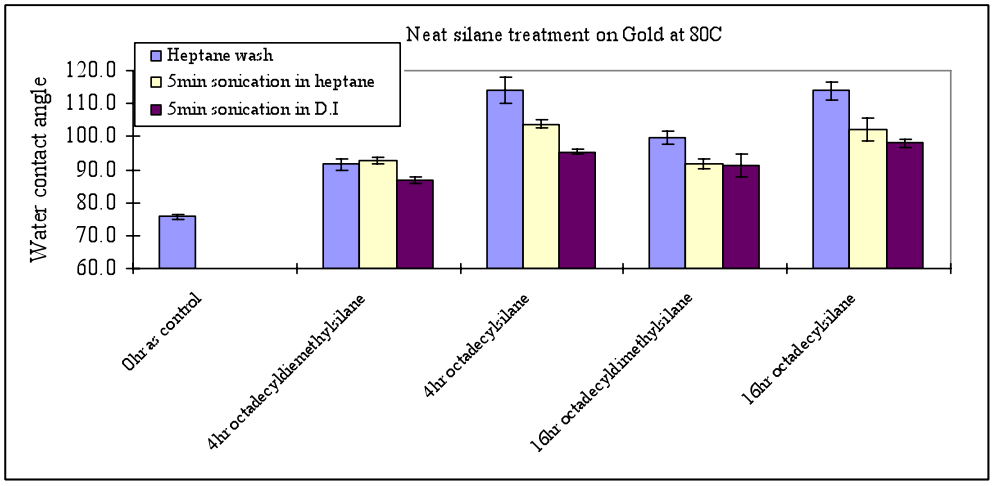


Figure 2. Contact angle of water on gold after 80◦C exposure to neat octadecyldimethylsilane and octadecylsilane, for 4 and 16 h. After exposure substrates were (1) rinsed with heptane, (2) rinsed with heptane followed by sonication in heptane, (3) rinsed in heptane, followed by sonication in heptane, followed by sonication in deionized water.

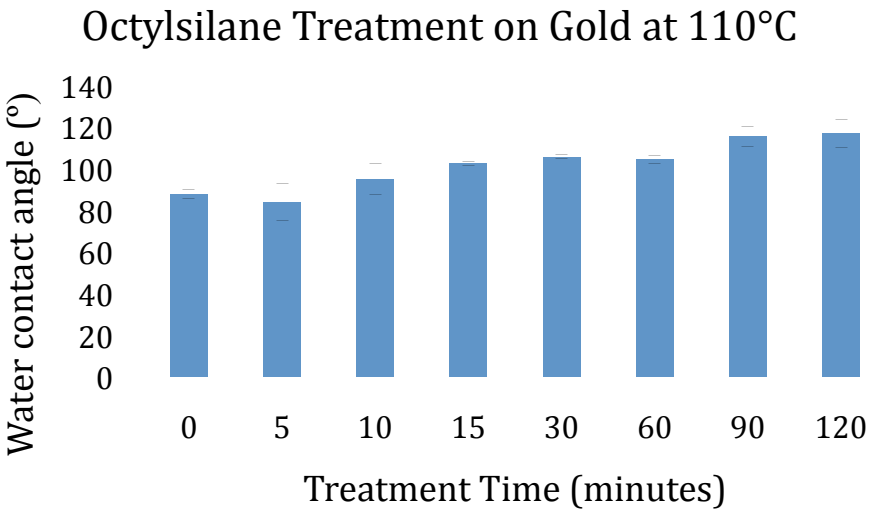
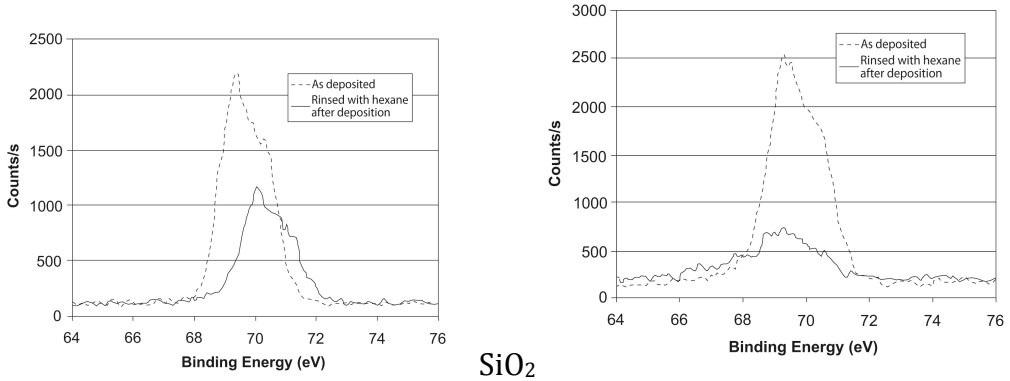


Figure 3. Contact angle of water on gold at 110◦C exposure to octylsilane in the vapor phase.

Preferential Interaction of Hydridosilanes with Metals compared to Metal–Oxides

A series of experiments was undertaken in an attempt to elucidate the mechanism for the modification of substrates by trihydridosilanes. 4-Bromobutylsilane and 11-bromoundecylsilane were synthesized in order to provide a tag for XPS detection. In the second series, α,ω-(trihydridosilyl)alkanes were synthesized in order to amplify the silyl hydride density at the substrate. XPS was used to analyze the Br 3d photoelectron peaks for 11-bromoundecylsilane-treated substrates. The Br fingerprint spectrum indicates that the bromoalkylsilane adsorbed onto all substrates evaluated. After liquid phase treatment, the pre-rinse initial peak intensities of all substrates were roughly equivalent. The greatest difference between pre-rinse and post-rinse Br 3d spectral intensity, employed as an indication of binding strength, was observed between clean silicon and silicon dioxide surfaces. Figure 4 shows the Br 3d pre-rinse and post-rinse XPS spectra of 11-bromoundecylsilane on titanium. The results indicate a moderate to

strong interaction with silicon and only a slight interaction with silicon dioxide. The Br 3d pre-rinse and post-rinse spectra of 11-bromoundecylsilane on titanium are shown in Fig. 8 and are similar to those observed for gold. Among the metals tested, post-rinse intensity strength was in the order Ti > Si > Au. These results are interesting in that they correlate to the relative dissolution volumes of hydrogen in metals [2]. However, it should be noted that there appears to be more than one bonding environment for the bromine atom in the various substrates suggesting that, in addition to the Br–C bond associated solely with the alkyl chain, there are other substrate-dependent interactions of the bromine atom.



Si SiO_2

Figure 4. Surface modification of Si (left) and SiO_2 (right) with 11-bromoundecylsilane. Si: less decrease in the XPS Br 3d peak intensity after rinsing, indicating a stronger surface adhesion/bonding. SiO_2: larger change found in Br peak intensity after rinsing.

Reconstruction of Metal Surfaces induced by trihydridosilanes and Si distribution

A limited number of hydridosilanes with structures analogous to alkylthiols have been reported to modify gold substrates [3]. Octylsilane is strongly chemisorbed onto gold and induces a reconstruction of the Au(111) surface with concomitant formation of Au islands.

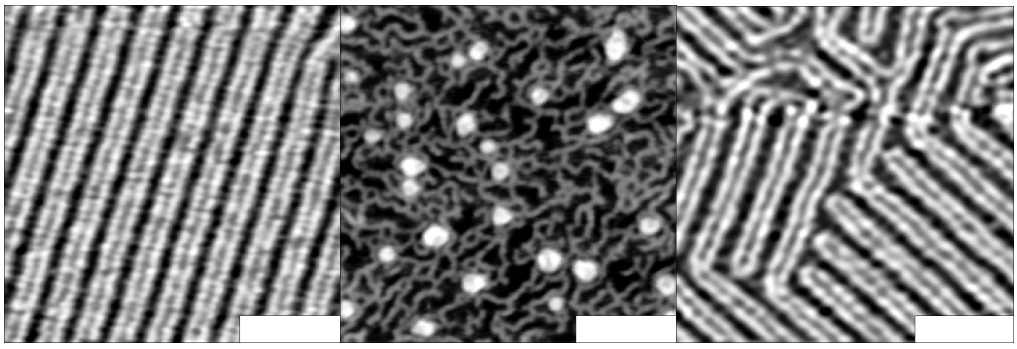
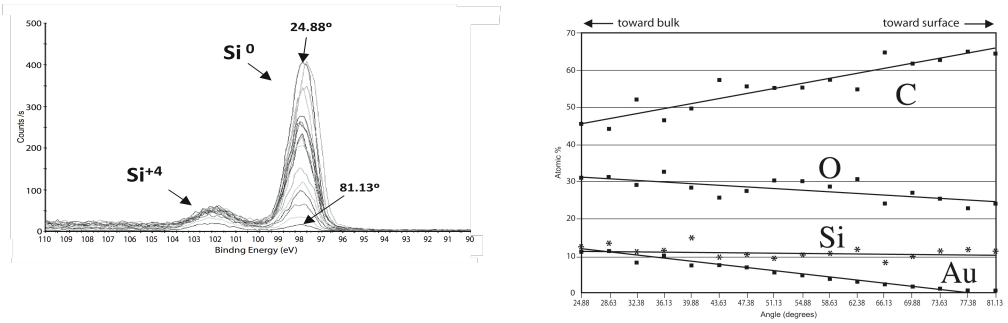


Figure 5. (left) gold unexposed, (center) gold octylsilane exposed, (right) gold, octylsilane exposed, oxidized. Images courtesy of M. Banaszak Holl, University of Michigan.

The second series of experiments utilized 1,10-disiladecane and 1,4-disilabutane treatments on gold substrates. The resulting adsorbed species were profiled using angle-resolved XPS (ARXPS), where the effective information depth is adjusted by changing the relative take-off angle of the sample, thus changing the source of photoelectron species with respect to depth. The results depicted in Fig 6a and 6b can be summarized as follows: The ratio of carbon to Si^{+4} is slightly higher than the stoichiometry required for disiladecane (4:1); Si^{+4} is observed in close proximity to the

surface — at or above it; Si^0 is observed relatively deepe — at or below the surface. Au and O signals also originate from below the surface. Meanwhile, increased C noted above the surface is associated with the hydrocarbon bridge of the disiladecane molecule. Further, while perhaps within the limits of experimental error, the oxygen atom concentration most closely correlates with the silicon atom concentration but has a greater tendency to increase with depth. The presence of oxygen atoms indicates that there is a mechanism for oxidation that must be associated with the silane, since gold does not form oxides under the experimental conditions.

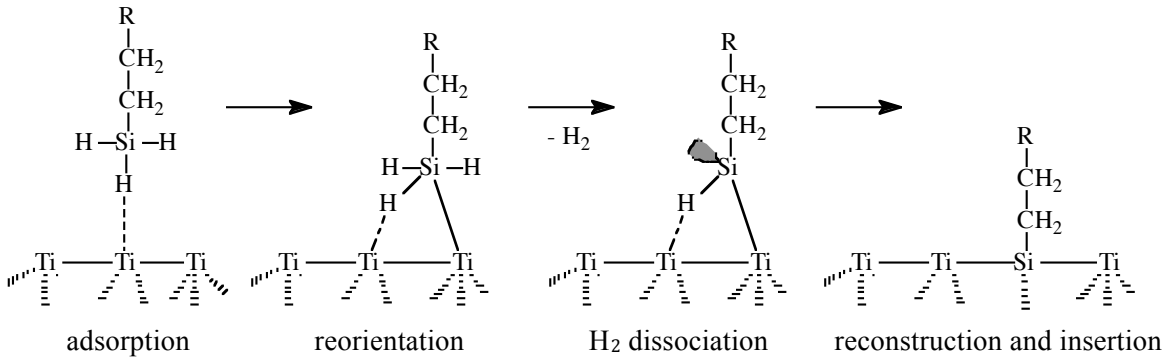


Figures 6. ARXPS spectrum and elemental concentration vs detector angle for 1,10-disiladecane on a Au surface

Proposed Mechanism for Trihydridosilane Adsorption and Silicon Atom Injection

In the context of literature cited here and previously [1], the data obtained in this stud suggest the following mechanism:
(1) Trihydridosilanes adsorb in a perpendicular orientation to the surface with a hydrogen coordinated to a surface atom. Most likely the adsorption is at a site of a surface defect associated with a strained bond.
(2) The silane reorients, allowing coordination with a second surface atom.
(3) Dehydrogenation of the silane occurs with formation of a silylene in what can be regarded as a dissociative-adsorption process.
(4) Restructuring of the surface atoms is induced by the silylene, creating new strained bonds and vacancies allowing insertion of the silicon atom into the topmost layer of the metal.
(5) If sufficient strain is induced, the silicon atom may insert beyond the topmost layer into the substrate bulk, but the organic substituent is lost.
(6) The silylene reacts with oxygen on exposure to air, forming silsesquioxanes or, in the metallic bulk, oxides.

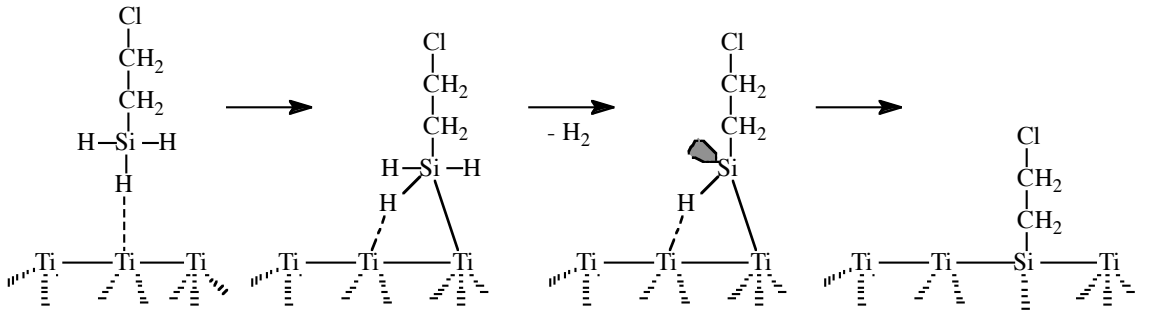
The dissociative-adsorption and silicon atom insertion is depicted for titanium in scheme 1.



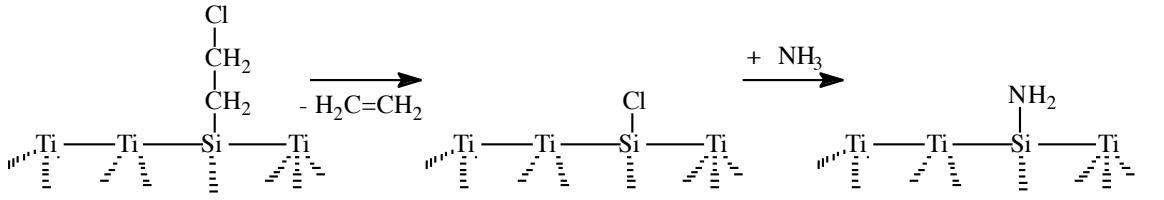
Scheme 1. Dissociative-adsorption and silicon atom insertion for titanium

ALD with trihydridosilane derived SAMs (SiN and SiO_2 on Ti)

The conversion of a silane species containing a strong electron withdrawing group has been reported previously for the formation of high density silicon dioxide films [4] and later for CVD of silicon nitride [5]. The process involves the migration of electronegative atoms to silicon and is sometimes referred to as the beta-effect. In the experiments presented here, the first step is the dissociative adsorption and insertion of 2-chloroethylsilane depicted in scheme 2, followed at relatively low temperatures to form a substrate activated for conventional ALD. Scheme 3 shows the case for an ammonia pulse reaction with the formation of a hydrogenated SiN. Similarly, water-vapor pulse reaction results in the formation of SiO_2.



Scheme 2. Chloroethylsilane SAM formation



Scheme 3. Conversion to a reactive site and ALD deposition

The SAM surface functionalization step was performed by maintaining both the oxide-free substrate and reactor temperature of 100-110° C. The precursor was maintained at room temperature and the carrier/purge gas was nitrogen in all experiments. Exposure time was 5 minutes in all cases tested but hold time and temperature were varied before the next reactant: ammonia or ammonia/water pulse. Samples were exposed to air before analysis. Results shown in Table 1 are for the ammonia pulse. RBS and AES

were utilized to evaluate films. The substrate metal contribution varied from 2-25 atom % (except for the control) and are not included in the tabulated values. The control experiment is indicative of the oxidation of the SAM to an oxidized silsesquioxane film. When the hold times were short (5 minutes) examination of surfaces showed no indications of film deposition suggesting that the dissociative-adsorption had probably not occurred and presumably the reaction products were volatile and not bound to the substrate. Conversion to Si:N films required a minimum of 200° C under the conditions tested, but did not reach acceptable Si:N ratios until temperatures of 300° C under the limited conditions tested. Conversion to SiO_2 was more facile than conversion to SiN, with essentially complete conversion after pulsed exposure to water vapor/ammonia at all temperatures above 200°C following a 30 minutes hold.

Table 1. SiN from 2-chloroethylsilane NH_3 on gold			
Run #	Hold Time (min)	Temperature (°C)	Si:N:O:C
1	30 (control-no NH_3)	110	32:0:12:54
2	5	110	no deposition
3	30	200	35:28:16:21
4	30	300	33:51:4:12
5	60	350	34:55:3:8

Conclusion

Alkyltrihydridosilanes interact with a variety of oxide-free metal surfaces to form SAMs. The adsorption of alkyltrihydridosilanes on metal appears more likely when a metal has the ability to adsorb or coordinate with hydrogen. It is proposed that the key step in chemisorption of trihydridosilanes involves dissociative-adsorption of the alkyltrihydridosilane with either the release of hydrogen or hydrogen absorption by the metal substrate. Initial results suggest that SAMs formed from selected alkyltrihydridosilanes, demonstrated by the example of 2-chloroethylsilane, can modify substrates as a first step in ALD, potentially opening a pathway for the precise formation of functional structures on metal substrates.

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