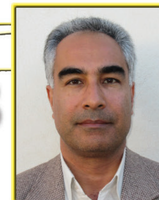
Characterization of Thin Films and Materials



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An Introduction to Silanes, their Chemical Vapor Deposition onto Si/SiO_2, and Characterization of the Resulting Monolayers

Introduction

The deposition of ultrathin coatings on various substrates is important for applications such as corrosion inhibition, adhesion promotion, and contamination control.[1-4] In addition, a large number of biosensors and bioarrays use ultrathin organic films to attach/couple biomolecules of interest to their surfaces, or alternatively to selectively resist adsorption of biomolecules.[5, 6] Accordingly, it is important to understand the various techniques for applying these coatings. The silanes are arguably the most important and diverse class of surface modification reagents. Many hundreds of different silanes are commercially available that can be used to tailor surface properties in a myriad of ways. The two most important ways for depositing silanes are by either liquid or gas phase deposition. Each of these techniques has both industrial and academic applications. The liquid approach is simple and well documented in the literature. In many cases, it only requires simple glassware, e.g., a beaker and a watch glass, some organic solvent, and perhaps another common reagent or two. The gas phase, chemical vapor deposition (CVD), approach requires vacuum equipment, which can be fairly expensive to purchase and maintain. However, the gas phase approach can be much more reproducible and is automatable – the CVD of silanes avoids some of the chemical uncertainty associated with solution deposition. For example, many of the silanes we use to modify surfaces can polymerize, and all of them can at least dimerize. This complicates a deposition if the solution from which it is occurring is changing. In addition, many liquid phase depositions of silanes are notoriously sensitive to water. There are anecdotal reports of liquid phase silane depositions working only during the summer, but not the winter (or vice versa) because of the change in the relative humidity of the laboratory! An article by van Ooij and coworkers discusses some of the complexities associated with solution phase deposition of silanes as they relate to anti-corrosion coatings.[6] In addition, the liquid phase deposition of silanes typically involves the use of organic solvents in both the deposition and subsequent rinsing of the functionalized surface. Organic solvents are generally toxic and flammable, and require special handling, so it is better when they can be avoided. In some cases, water or water-alcohol mixtures will be the main solvent, although even here other reagents are often added to the solution, e.g., acetic acid to control the solution pH, so these mixtures of say a silane and acetic acid in water will often constitute chemical waste even when no alcohol is present. Of course, the cost to dispose of chemicals can sometimes exceed their initial cost.

Some extremely careful work on silane deposition from an organic solvent (bicyclohexyl) was performed by Dave Offord and coworkers at Stanford more than 20 years ago (this is where MRL first learned about silanes),[7] and more than a decade ago the Linford lab reported the deposition of silanes from the neat, heated liquids.[8] In contrast to the liquid phase approach, the CVD of silanes generally only requires the silane itself in relatively small quantities – often less than a milliliter per run, so there is little or no waste disposal and/or environmental consequences. However, one issue with CVD is carryover between runs (the cross contamination from one deposition to another). This issue may be of minimal importance when the same silane is used run after run, which is often the case in industry. How-

ever, academic users, as well as those doing research and development who may regularly switch silanes, should be aware of this possibility. (We've recently made some nice progress in reducing carryover to extremely low levels.) One should also remember that, as is the case for the liquid phase approach, CVD recipes must be carefully developed and vetted – one should not assume that one can simply inject a silane under any conditions, e.g., volume of silane, oven temperature and pressure, surface precleaning procedure, etc., and have a viable and robust method. In this article we discuss (*i*) the chemistry of the silanes, (*ii*) their chemical vapor deposition using a piece of commercial equipment: the Yield Engineering Systems 1224P Oven (YES Oven), and (*iii*) the characterization of the resulting coatings. The three characterization tools we focus on here are contact angle goniometry, spectroscopic ellipsometry, and X-ray photoelectron spectroscopy.

The Chemistry of the Silanes

Silicon is in the same elemental family as carbon and, like carbon, prefers to form four covalent bonds. But because it is below carbon in their column of the Periodic Table, we expect it to be more electropositive than carbon, and it is. As an example of the similarities between these elements, both crystalline silicon and diamond adopt the diamond cubic structure. However, because silicon's 3p orbitals are large (more diffuse) and have a spherical node through them (this is in addition to the planar node found in all p orbitals), overlap between the orbitals is poor so silicon does its best to avoid double/multiple bonds. That is, while carbon-carbon double and triple bonds, and for that matter aromatic structures, are ubiquitous in organic chemistry, there are no commonly found analogs of these moieties in silicon chemistry. We aren't saying that researchers haven't used extreme conditions and/or means to make multiple silicon-silicon bonds; they have.[9, 10] We're just saying that typical silicon-containing chemicals like the silanes, or silicones for that matter, will generally contain only single bonds to silicon. Thus, while there are important similarities between the chemistries of carbon and silicon, there are also stark differences.

Silicon bonds strongly to oxygen. For example, consider that the melting point of crystalline SiO_2 (quartz) is 1670 – 1713 °C – obviously if the bonds weren't strong here the material wouldn't have such a high melting point. And strong bonds that form through exothermic reactions are important in chemical synthesis. Think about the difficult task of the natural products/synthetic organic chemist who is asked to make a complex drug. Clearly as one synthesizes a larger and more organized molecule one is essentially being asked to beat entropy. **Figure 1** shows an example of such a molecule (Taxol, a natural product that is also an anticancer agent) that would need to be assembled (synthesized) from many smaller pieces (molecules).[11] Here, the formation of strong bonds via exothermic reactions is an important way to make the free energy (measure of spontaneity in these reactions) work in one's favor.

In this article we discuss the formation of silicon-oxygen bonds through the attachment of silanes to surfaces that contain SiOH groups. The 'SiOH' group is called the 'silanol' group. The 'ol'

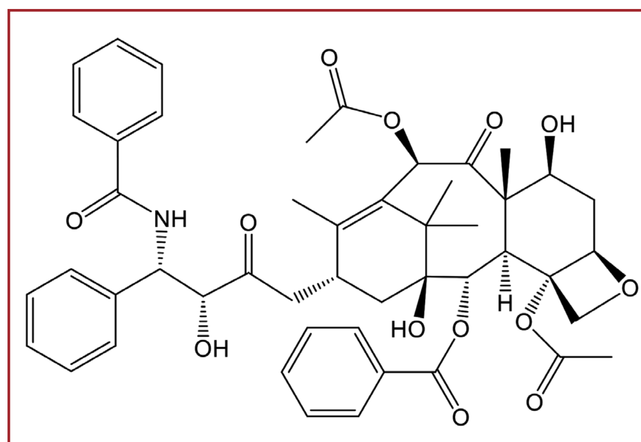

Figure 1. Taxol

ending in 'silanol' makes us think of 'alcohol', where alcohols in organic chemistry similarly contain –OH groups, i.e., C-OH groups. The classic silicon surface that is often studied and modified is the silicon wafer. It typically consists of bulk silicon that is terminated with an extremely thin layer, ca. 1.5 nm, of oxide. This coating of oxide, often referred to as the native oxide layer, will be terminated, at least to some degree, in silanol groups. Depending on its history, it will probably also have Si-O-Si groups (siloxanes) at its surface, i.e., if we heat the surface of silicon/silica we can condense the SiOH groups, driving off water to yield siloxanes.[12-14] In its clean form, the native oxide surface of silicon contaminates easily – its surface free energy is very high. This is why if you clean a piece of silicon it will initially be hydrophilic (a drop of water will spread over its surface), but if you let it sit out in the laboratory it will gradually become more and more hydrophobic (water will spread less and less over the surface and begin to bead up) as it adsorbs hydrocarbons from the air. A trick we have used over the years to store clean silicon wafers is to immerse them in ultrapure water. This tends to keep them clean for a week or two.

Before we discuss the reactions of surface SiOH groups with silanes, we need to ask: What is a silane? 'Silane' itself has the chemical formula SiH_4. The integrated circuit industry is a very large user of silane, primarily for growing epitaxial silicon on the silicon substrate. This has been the case for several decades, as the process produces highly pure and monocrystalline silicon and allows for incorporation of various dopants at different levels. Silane is highly reactive – pyrophoric in the air. Thus, the use of silane requires special handling and equipment. We don't use it in our laboratory. However, when we talk about 'a silane', we mean a derivative of SiH_4 that has had one or more of its hydrogen groups replaced with another chemical moiety. Thus, there are an enormous number of possible silanes, and, fortunately, the vast majority of these are much safer to work with than silane. However, before using any chemical, one should read and then follow its safety data sheet (SDS), complying with all governmental regulations regarding its safety, use, and disposal.

Figure 2 shows some silanes. Here we see silanes with alkyl groups (most of them), Si-Cl groups (**Figure 2a-j, p-s**), Si-OCH_3 groups (**Figure 2j-l, u**), Si-OCH_2CH_3 groups (**Figure 2m-n**), dimethylamino groups (Si-$N(CH_3)_2$, **Figure 2o**), perfluoro alkyl

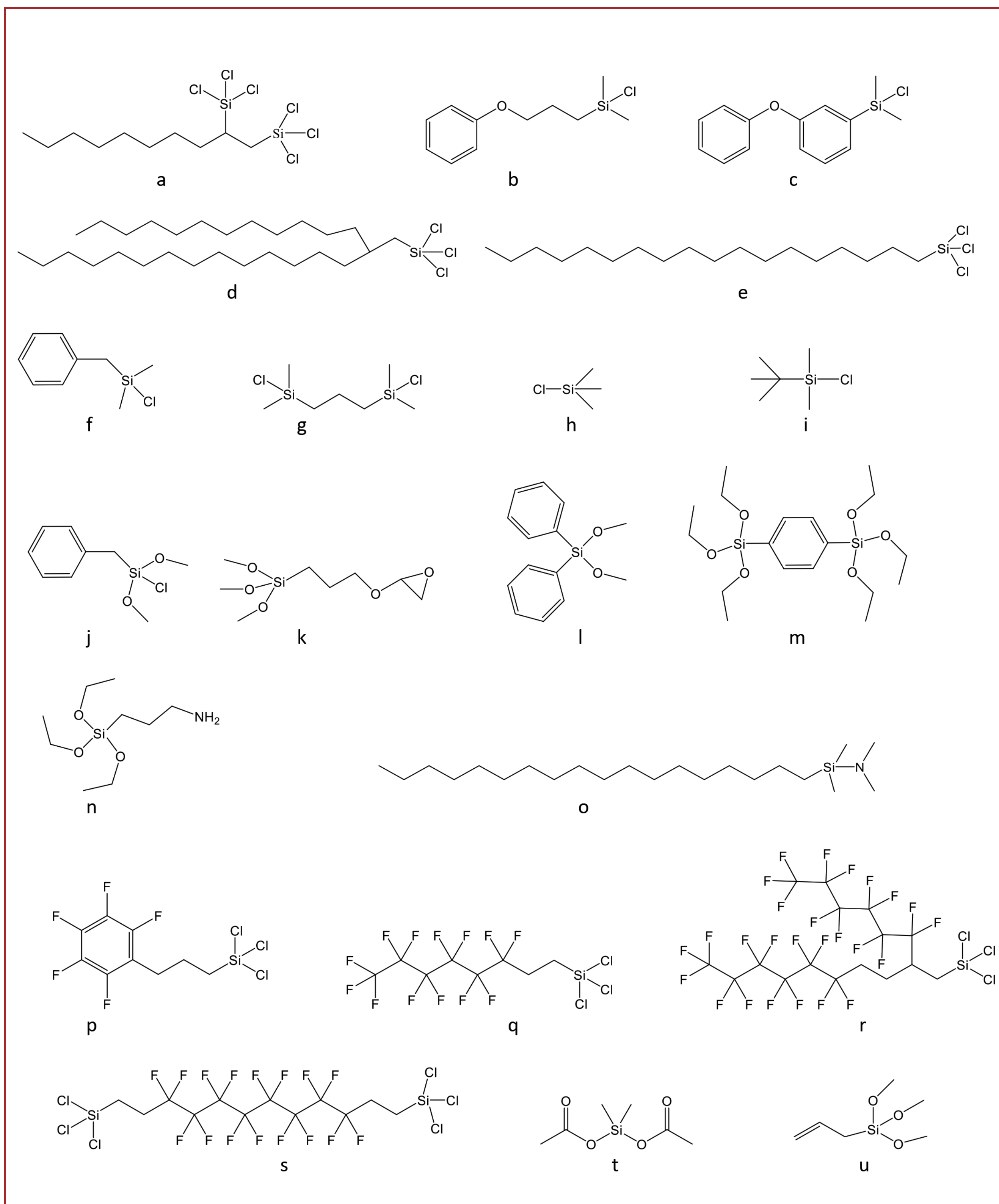

Figure 2. Silanes available on the market: **a)** decane-1,2-diylbis(trichlorosilane), **b)** chlorodimethyl(3-phenoxypropyl)silane, **c)** chlorodimethyl(3-phenoxyphenyl)silane, **d)** trichloro(2-dodecylhexadecyl)silane, **e)** trichloro(octadecyl)silane, **f)** benzylchlorodimethylsilane, **g)** 1,3-bis(chlorodimethylsilyl)propane, **h)** chlorotrimethylsilane, **i)** tert-butylchlorodimethylsilane, **j)** benzylchlorodimethoxysilane, **k)** trimethoxy(3-(oxiran-2-yloxy)propyl)silane, **l)** dimethoxydiphenylsilane, **m)** 1,4-bis(triethoxysilyl)benzene, **n)** (3-aminopropyl)triethoxysilane, **o)** n-octadecyldimethyl(dimethylamino)silane, **p)** trichloro(3-(perfluorophenyl)propyl)silane, **q)** trichloro(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)silane, **r)** trichloro(5,5,6,6,7,7,8,8,9,9,10,10,10-tridecafluoro-2-(perfluorohexyl)decyl)silane, **s)** (3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10-hexadecafluorododecane-1,12-diyl)bis(trichlorosilane), **t)** diacetoxydimethylsilane, **u)** allyltrimethoxysilane.

groups (**Figure 2p-s**) and functionalized alkyl groups (**Figures 2k** (epoxy/glycidyl), **n** (amino), **p** (pentafluorophenyl)). This figure underscores one of the points we have been trying to make: at least one key reason for the widespread use of silanes is that they exist in tremendous variety. For years we have purchased silanes from Sigma-Aldrich (www.sial.com) and Gelest (www.gelest.com). Sigma-Aldrich carries most of the more common silanes, while Gelest has a wider offering – it specializes in them.

The silanes we care about have reactive functional groups that allow them to react (condense) with surface silanol groups. Note that surface hydroxyl groups play a key role in the surface reactivity of metal-oxide surfaces, and are often the target of surface modification reactions.[13, 15-17] Examples of five of the most common reactive functional groups on silanes are provided in **Figure 2**: Si-Cl, Si-OCH_3, Si-OCH_2CH_3, Si-$N(CH_3)_2$, and Si-OC(O)CH_3. We will discuss each of these below.

First, the Si-Cl moiety reacts as follows with a silanol group:

$$R_3Si\text{-}Cl + HO\text{-}Si \rightarrow R_3Si\text{-}O\text{-}Si + HCl \quad \textbf{(1)}$$

The 'R' groups here and below could be the same or different chemical entities. This reaction, like the others we will consider, has pros and cons. The key advantage of chlorosilanes is that they are very reactive. Their main disadvantage is the production of HCl, which is a nasty byproduct. The Si-Cl group will also react with water to produce HCl, so there are safety issues associated with storing chlorosilanes. And while the production of some HCl may not be much of an issue in the liquid phase deposition of silanes in glass, HCl can be damaging to the stainless steel chamber and metal components of a CVD deposition system. This does not mean that they cannot be used for CVD, just that one should be aware of the HCl they produce. For example, it would be unwise to let transfer lines filled with a chlorosilane stand for an extended period of time. Obviously, the Si-Cl moiety is incompatible with some functional groups.

The second reactive functional group on silicon we discuss is the methoxy group (-OCH_3). Methoxy silanes react with surface silanol groups as follows:

$$R_3Si\text{-}OCH_3 + HO\text{-}Si \rightarrow R_3Si\text{-}O\text{-}Si + HOCH_3 \quad \textbf{(2)}$$

The advantage of methoxy silanes over chlorosilanes is that their byproduct (methanol, $HOCH_3$) is less toxic than HCl. This makes them easier to work with and store. Perhaps their greatest disadvantage is their lower reactivity. Ethoxy silanes are also common. Their structure and reactivity with surface silanols is illustrated in *Equation 3*, as follows:

$$R_3Si\text{-}OCH_2CH_3 + HO\text{-}Si \rightarrow R_3Si\text{-}O\text{-}Si + HOCH_2CH_3 \quad \textbf{(3)}$$

Note that the byproduct here is ethanol ($HOCH_2CH_3$), which is even less toxic than methanol. There are many important and useful ethoxy silanes, including 3-aminopropyltriethoxysilane (APTES, see **Figure 2n**), which has been very widely used to functionalize silicon surfaces with amino (-NH_2) groups.[5, 18] Ethoxy silanes are less reactive than methoxy silanes for steric reasons, i.e., the ethoxy group is larger/more bulky.

Next we consider the dimethylamino moiety. Its reaction with surface silanols is as follows:

$$R_3Si\text{-}N(CH_3)_2 + HO\text{-}Si \rightarrow R_3Si\text{-}O\text{-}Si + HN(CH_3)_2 \quad \textbf{(4)}$$

These silanes are gaining popularity as surface modification reagents. Like chlorosilanes they are extremely reactive. Unfortunately, low molecular weight amines, like $HN(CH_3)_2$, are toxic so these reagents and their byproducts should be handled with care. However, as bases these amines are not expected to be corrosive to metal components.

Finally, we note that the Si-OC(O)CH_3 group react with silanols to produce acetic acid in the following manner:

$$R_3Si\text{-}OC(O)CH_3 + HO\text{-}Si \rightarrow R_3Si\text{-}O\text{-}Si + HOC(O)CH_3 \quad \textbf{(5)}$$

Chemical Vapor Deposition of Silanes with a Commercial System

We are fortunate to have a Yield Engineering Systems (YES) 1224P chemical vapor deposition tool in our laboratory. The 'P' in the name here stands for 'plasma', i.e., the system does CVD and also has plasma capabilities – the latter is helpful for sample and system cleaning. The system allows up to three plasma gases to be attached to the system, where common ones would be argon, oxygen, and hydrogen. The flow of these gases can be controlled by mass flow controllers, which allows them to be mixed. **Figure 3** show a picture of this oven. In its upper left corner we see a screen. This touch screen allows the user to create recipes and also modify the parameters in previously stored recipes. In this way, processes/sample cleaning/depositions can be automated. The upper right part of the oven has six black/red squares. These are LED outputs that give the temperatures of the oven/door/system at different locations. The lower right part of the system is dominated by the oven. It is filled with a series of shelves. These shelves can be grounded, allowed to float, or

Figure 3. Picture of the YES 1224P chemical vapor deposition system from Yield Engineering Systems.

given an oscillating potential to generate a plasma in the tool. The system is quite convenient here in that the ground shelves have metal tabs that electrically connect them to the chamber – one would expect the chamber to be grounded! The active shelves have a plug that connects to an electrical bus running down the back of the chamber, which allows them to be biased. These shelves have ceramic tabs so that they are not in electrical contact with the chamber. As might be expected, the float shelves do not have a plug but also have ceramic tabs. The shelf configuration and position of samples determines the degree to which samples on the shelves interact with a plasma. Some time ago we showed that silicon wafers with native oxide see an increase in their oxide thickness when on either the active or ground plates, but not when they are on a float plate.[19] Thus, the float plate can be used to gently clean a sample using the downstream products of a plasma. The door to the oven is O-ring sealed. This is adequate because the YES 1224P is not a high vacuum deposition system – it is pumped by rotary vane pumps. Indeed, the vacuum seal on the face of the oven is a double O-ring seal with low pressure nitrogen trapped between the seals. If there are any leaks in the inner seal only nitrogen enters the process area. Finally, there is a door on the lower left side of the chamber (it is shut in the picture). Inside this door one finds the vials of silanes or other chemicals to be injected, transfer lines for getting these materials to the pumps, and heated flasks that vaporize the chemicals so they can enter the oven.

We have mentioned two of the capabilities of the YES 1224P Oven – CVD of silanes and plasma cleaning/treatment of samples. In addition, the oven can effectively dehydrate surfaces. That is, most oxide surfaces, like native oxide coated silicon, will have a few layers of water molecules physisorbed on them.[12] Obviously these water molecules can react with silane molecules. In the case of trifunctional silanes, a polymerization may occur. While this may be desirable in some cases, the presence of this water may also lead to uncertainties in a deposition. Accordingly, the YES oven is specifically designed to be able to remove it. It does so by introducing hot nitrogen, waiting, i.e., allowing the system to approach equilibrium so that the water physisorbed on the surfaces of the oven and samples will partition between these surfaces and the gas phase, and then pumping off the desorbed water. Obviously we want hot nitrogen instead of cold nitrogen to keep the system at temperature, and also to favor the desorption of water. This process is repeated at least three times. In this manner one can fully dehydrate a surface so that only its silanols are available for reaction. The YES oven employs a clever system for heating the incoming nitrogen. Rather than have it enter the system directly from a tank, it goes through tubing that is bent in a serpentine fashion and attached to the back of the hot oven. In this manner, the nitrogen that enters the oven is already at an elevated temperature. The other use for nitrogen in the YES oven is to control its pneumatic valves.

Here are a few other details of the YES 1224P. First, it has two pumping systems: one for plasma processes and the other for CVD. This was primarily done for safety. The concern was that pumping oxygen from an oxygen plasma might ignite hydrocarbon oil. Accordingly, the pump for the plasma has Fomblin® oil, which is fluorinated (Fomblin® oil is quite expensive). Second, the sample vials that hold the silanes are accessed through needles that pierce septa. The liquid silanes are drawn up through the needles into transfer lines and then to pumps that dispense the silanes/reagents into hot flasks that vaporize them. The temperatures of the flasks and oven are controlled independently. In general we prefer to have the flasks hotter than the oven – if we're trying to get the silane into the oven it doesn't make a lot of sense to have the flask in which it is vaporized be a cold (or perhaps we should say less hot) spot in the system. The reagent vials are protected by a low head pressure of nitrogen gas from another needle/line assembly. The purpose of this feature is to prevent a vacuum from forming in the vials when silane is removed from them. This lower pressure might then suck in air, which could lead to hydrolysis and condensation of a silane.

The YES Oven has recipes that are broken down into processes, where each recipe can run up to four processes. In general, the initial process is a plasma process employed for sample cleaning. Each process can be programmed so that a specific amount of deposition chemical is injected from one of two or three different sources at a specified base pressure. The amount of time that the deposition chemical is in contact with the substrate can also be programmed as can evacuation and dehydration purges (see above). The evacuation process at the end of a run is particularly important because it ensures that no vapors remain in the oven after the CVD.

Characterization of Monolayer Films of Silanes

Obviously, a monolayer of an adsorbate on a small shard of a planar surface isn't very much matter. Thus we need exquisitely sensitive instruments to observe their presence. And while there are very complex and expensive instruments that have monolayer (and sub-monolayer) sensitivity, e.g., X-ray photoelectron spectroscopy (XPS),[20, 21] time-of-flight secondary ion mass spectrometry (ToF-SIMS),[22] and low energy ion scattering (LEIS),[23] the first tool we will mention, the contact angle goniometer, is surprisingly simple. In its most rudimentary form, it consists of a sample stage, a syringe (dispenser) that can deliver a drop of a liquid, and a telescope or camera that can observe the droplet. A picture of the contact angle goniometer in our laboratory, which we just upgraded, is shown in **Figure 4**. This piece of equipment contains a camera and software for capturing and measuring the contact angle. We mentioned above that a clean silicon surface will gradually contaminate in the laboratory, going from hydrophilic to hydrophobic. Water contact angle goniometry easily picks up this change, which is caused by the deposition of only a few Ångstroms of hydrocarbon! Thus, in spite of its simplicity, contact angle goniometry is amazingly sensitive. It is also a rather inexpensive instrument to purchase and maintain. In particular, with this technique we find that hydrophilic (high free energy) surfaces have lower water contact angles and hydrophobic (lower free energy) surfaces have higher water contact angles. We would recommend that anyone performing silane or similar depositions have and employ a contact angle goniometer. Finally, note that, in addition to water, other probe liquids are used from time to time in contact angle goniometry, the most common

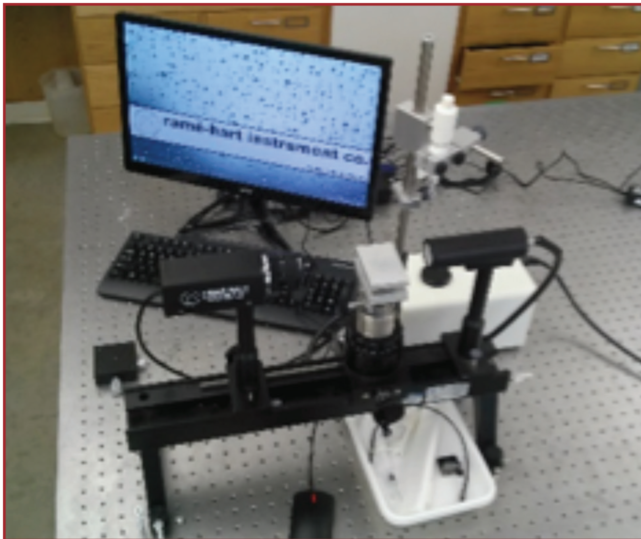

Figure 4. The water contact angle goniometer in our laboratory (from Ramé-Hart).

of which is hexadecane. However, water contact angles suffice for much of what we do. In particular, we generally try to measure both the advancing (from expanded droplets) and receding (from retracted droplets) contact angles. For more information on contact angle goniometry, the reader is referred to any of a number of papers or books on this topic.[24-26]

The next piece of equipment we will describe is the ellipsometer. We use ellipsometry to measure the thickness of silane films. Most of the ellipsometers sold today are of the spectroscopic variety, which means they probe a surface at multiple wavelengths. Spectroscopic ellipsometry offers significant advantages over the single wavelength approach. For example, by probing a material at a series of wavelengths one obtains more data to fit – more complex modeling can be undertaken. In addition, the resulting dispersion relationships that are generated for materials ($n(\lambda)$ and $k(\lambda)$) teach one much more about a material than the values of n and k at a single wavelength. Our ellipsometer operates from ca. 190 – 1690 nm, i.e., from the UV through the visible and out into the near IR regions of the electromagnetic spectrum. Ellipsometers are more complex and expensive than contact angle goniometers. Nevertheless, the type of information one can obtain from ellipsometry is indispensible for understanding thin films and their deposition. The picture of the J.A. Woollam spectroscopic ellipsometer in our laboratory is shown in **Figure 5**. We have found J.A. Woollam to be a great partner – their equipment, software, and service have all been top notch. Those that cannot afford a J.A. Woollam instrument may want to consider a cheaper alternative. For example, Film Sense sells a relatively inexpensive four-wavelength ellipsometer, with blue, green, yellow, and red LEDs as the sources of light.

Ellipsometry requires modeling of data, and ultrathin (monolayer) films of silanes on native oxide on silicon are some of the simplest systems to analyze. The most basic model for silicon and native oxide (no monolayer) is a one-layer model of the native oxide on silicon that assumes perfectly flat/planar interfaces. The optical constants for these materials (oxide and silicon) are in our software. In our model, we will give the silicon a thickness of 1 mm, i.e., it is opaque (whether we chose 1 mm or 1 mile we'll get the same answer). We guess the native oxide thickness to be about 1.5 nm. We then let the software determine the actual thickness of the oxide layer, and use this surface for CVD silane deposition. We then use the very same model for the silane film on native oxide on silicon and determine the thickness of this film by taking the difference between the thicknesses of the coated and uncoated surfaces. In his excellent book on ellipsometry, Harland Tompkins explained why this works.[27] It turns out that the thinner the film, the less the thickness determined by ellipsometry depends on its optical constants. Thus, when we consider two materials like native oxide and an organic film, which already have quite similar optical constants ($n \sim 1.5$), we see that the error associated with using the optical constants of native oxide to model the silane film should be quite small. Of course the silane contains silicon and forms a siloxane bond to the surface, so in this regard it already looks a little bit like SiO_2.

The third tool we regularly use to analyze silane monolayers on silicon wafers is XPS. It would be hard to overstate the importance of XPS in modern thin film analysis. As a quick review, in XPS soft X-rays (energies around 1.5 keV) are directed onto a sample surface. These photons eject core electrons from the elements present in the sample. And while the X-rays can penetrate fairly deeply into the sample, the electrons they produce can only travel 5 – 10 nm without being attenuated. This makes XPS surface sensitive. The kinetic energies of the expelled electrons are characteristic of the elements from which they come. XPS is great for both qualitative and quantitative analysis – in general signals are proportional to concentrations. We have discussed various aspects of XPS in some of our previous ***VT&C*** articles.[28-30]

For now, here are a few thoughts on XPS that pertain directly to the analysis of silanes on silicon wafers. First, because the native oxide layer on silicon is so thin and because we work with doped silicon wafers, we do not, in general, need to employ any charge compensation during our XPS analyses. Of course the use of an electron flood gun in XPS is not a big deal – it is done all the time. However, the fact that we don't need it means that we simplify our experimental procedure (we don't need to turn it on or adjust its settings), we eliminate any peak shifting that may occur, and we also eliminate any possible sample damage

Figure 5. The spectroscopic ellipsometer in our laboratory (from the J.A. Woollam company).

from the electrons. In general these issues are not of great significance for most analyses. However, the fact that we don't need the flood gun gives us one thing less to worry about. Second, almost all samples contain at least a little adventitious carbon (carbon from the environment). That is, unless we are very careful, even a freshly cleaned silicon wafer will show at least a little carbon, in addition to strong signals from silicon and oxygen. Thus, if we react a silane like $ClSi(CH_3)_3$ to a native oxide surface to form tethered $–OSi(CH_3)_3$ groups, it may hard to figure out from XPS what is going on – there's already a lot of silicon in the sample, and, again, we always expect some carbon. For this reason, what we call heteroatoms can be really helpful. By 'heteroatom' (we borrow this term from organic chemistry) we mean an atom that would not be expected to be at the surface, i.e., not C, Si, or O. The presence of a heteroatom can be a solid confirmation of a silane deposition. For example, the presence of chemisorbed 3-aminopropyltriethoxysilane is indicated by an N 1s signal, and the presence of 3-mercaptopropyltrimethoxysilane is similarly indicated by the S 2s and/or 2p signals.[31] Finally, the results from XPS, ellipsometry, and wetting can and should be used to confirm one another. For example, if one is depositing a silane with a long alkyl chain as a monolayer on a silicon wafer, and a high degree of surface coverage is expected, one had better see a significant rise in the water contact angle, *and* a noticeable increase in the film thickness by ellipsometry, *and* a rather significant C 1s signal by XPS. Otherwise something is wrong. Perhaps we have said it so often that it is basically a cliché now, but multi-instrument characterization is essential for understanding surfaces because of the complimentary information they provide.[22]

Conclusions

Silanes are among the most important surface functionalization reagents. There are many commercially available silanes with different reactive groups and different functional groups. Silanes can be deposited from solution or in the vapor phase (CVD). Vapor phase deposition offers a number of advantages, especially for processes that need to be automated/put into production. Three important techniques for characterizing silane thin films are contact angle goniometry, spectroscopic ellipsometry, and X-ray photoelectron spectroscopy.

References

1. Van Ooij, W.; Zhu, D.; Stacy, M.; Seth, A.; Mugada, T.; Gandhi, J.; Puomi, P. Corrosion protection properties of organofunctional silanes—an overview. *Tsinghua Science & Technology* **2005**, *10* (6), 639-664.
2. Wang, H.; Xue, Y.; Ding, J.; Feng, L.; Wang, X.; Lin, T. Durable, Self-Healing Superhydrophobic and Superoleophobic Surfaces from Fluorinated-Decyl Polyhedral Oligomeric Silsesquioxane and Hydrolyzed Fluorinated Alkyl Silane. *Angewandte Chemie International Edition* **2011**, *50* (48), 11433-11436.
3. Bikiaris, D.; Matzinos, P.; Larena, A.; Flaris, V.; Panayiotou, C. Use of silane agents and poly (propylene-g-maleic anhydride) copolymer as adhesion promoters in glass fiber/polypropylene composites. *Journal of Applied Polymer Science* **2001**, *81* (3), 701-709.
4. Gupta, V.; Diwan, A.; Evans, D.; Telford, C.; Linford, M. R. Self-termination in the gas-phase layer-by-layer growth of an aza silane and water on planar silicon and nylon substrates. *Journal of Vacuum Science & Technology B* **2014**, *32* (6), 061803.
5. Zhang, F.; Gates, R. J.; Smentkowski, V. S.; Natarajan, S.; Gale, B. K.; Watt, R. K.; Asplund, M. C.; Linford, M. R. Direct adsorption and detection of proteins, including ferritin, onto microlens array patterned bioarrays. *Journal of the American Chemical Society* **2007**, *129* (30), 9252-9253.
6. Carroll, G. T.; Wang, D.; Turro, N. J.; Koberstein, J. T. Photons to illuminate the universe of sugar diversity through bioarrays. *Glycoconjugate Journal* **2008**, *25* (1), 5-10.
7. Offord, D. A.; Griffin, J. H. Kinetic control in the formation of self-assembled mixed monolayers on planar silica substrates. *Langmuir* **1993**, *9* (11), 3015-3025.
8. Husseini, G. A.; Peacock, J.; Sathyapalan, A.; Zilch, L. W.; Asplund, M. C.; Sevy, E. T.; Linford, M. R. Alkyl monolayers on silica surfaces prepared using neat, heated dimethylmonochlorosilanes with low vapor pressures. *Langmuir* **2003**, *19* (12), 5169-5171.
9. Luppia, M.; Ossicini, S. Multiple SiBO bonds at the silicon cluster surface. *Journal of Applied Physics* **2003**, *94* (3).
10. West, R. Multiple bonds to silicon: 20 years later. *Polyhedron* **2002**, *21* (5), 467-472.
11. Nicolaou, K.; Yang, Z.; Liu, J.; Ueno, H.; Nantermet, P.; Guy, R.; Claiborne, C.; Renaud, J.; Couladouros, E.; Paulvannan, K. Total synthesis of taxol. *Nature* **1994**, *367* (6464), 630-634.
12. Zhuravlev, L. Concentration of hydroxyl groups on the surface of amorphous silicas. *Langmuir* **1987**, 3 (3), 316-318.
13. Hair, M. L. Hydroxyl groups on silica surface. *Journal of Non-Crystalline Solids* **1975**, *19*, 299-309.
14. D'Souza, A. S.; Pantano, C. G. Mechanisms for silanol formation on amorphous silica fracture surfaces. *Journal of the American Ceramic Society* **1999**, *82* (5), 1289-1293.
15. Takeda, S.; Fukawa, M. Surface OH groups governing surface chemical properties of SiO_2 thin films deposited by RF magnetron sputtering. *Thin Solid Films* **2003**, *444* (1), 153-157.
16. Takeda, S.; Fukawa, M. Role of surface OH groups in surface chemical properties of metal oxide films. *Materials Science and Engineering: B* **2005**, 1*19* (3), 265-267.
17. Takeda, S.; Yamamoto, K.; Hayasaka, Y.; Matsumoto, K. Surface OH group governing wettability of commercial glasses. *Journal of Non-Crystalline Solids* **1999**, *249* (1), 41-46.
18. Zhang, F.; Sautter, K.; Larsen, A. M.; Findley, D. A.; Davis, R. C.; Samha, H.; Linford, M. R. Chemical vapor deposition of three aminosilanes on silicon dioxide: surface characterization, stability, effects of silane concentration, and cyanine dye adsorption. *Langmuir* **2010**, *26* (18), 14648-14654.
19. Zhang, F.; Sautter, K.; Davis, R. C.; Linford, M. R. Subsurface Oxidation for Micropatterning Silicon (SOMS). *Langmuir* **2009**, *25* (3), 1289-1291.
20. Gupta, V.; Ganegoda, H.; Engelhard, M. H.; Terry, J.; Linford, M. R. Assigning oxidation states to organic compounds via predictions from x-ray photoelectron spectroscopy: a discussion of approaches and recommended improvements. *Journal of Chemical Education* **2014**, *91* (2), 232-238.
21. Singh, B.; Velázquez, D.; Terry, J.; Linford, M. R. Comparison of the equivalent width, the autocorrelation width, and the variance as figures of merit for XPS narrow scans. *Journal of Electron Spectroscopy and Related Phenomena* **2014**, *197*, 112-117.
22. Jensen, D. S.; Kanyal, S. S.; Madaan, N.; Hancock, J. M.; Dadson, A. E.; Vail, M. A.; Vanfleet, R.; Shutthanandan, V.; Zhu, Z.; Engelhard, M. H. Multi-instrument characterization of the surfaces and

materials in microfabricated, carbon nanotube-templated thin layer chromatography plates. An analogy to 'The Blind Men and the Elephant'. *Surface and Interface Analysis* **2013**, *45* (8), 1273-1282.
23. Cushman, C. V.; Brüner, P.; Zakel, J.; Major, G. H.; Lunt, B. M.; Smith, N. J.; Grehl, T.; Linford, M. R. Low energy ion scattering (LEIS). A practical introduction to its theory, instrumentation, and applications. *Analytical Methods* **2016**, *8* (17), 3419-3439.
24. Clegg, C., Contact Angle Made Easy. Carl Clegg: 2013.
25. Balkenende, A.; Van de Boogaard, H.; Scholten, M.; Willard, N. Evaluation of different approaches to assess the surface tension of low-energy solids by means of contact angle measurements. *Langmuir* **1998**, *14* (20), 5907-5912.
26. Extrand, C. Model for contact angles and hysteresis on rough and ultraphobic surfaces. *Langmuir* **2002**, *18* (21), 7991-7999.
27. Tompkins, H. G., *A User's Guide to Ellipsometry.* Academic Press: 2012.
28. Linford, M. R. Understanding One of the Governing Equations of XPS and Highlights from a Recent Paper by Akagawa and Fujiwara. *Vacuum Technology & Coating March* **2014**.
29. Linford, M. R. The Gaussian-Lorentzian Sum, Product, and Convolution (Voigt) Functions Used in Peak Fitting XPS Narrow Scans, and an Introduction to the Impulse Function. *Vacuum Technology & Coating July* **2014**, 27-34.
30. Linford, M. R. Introduction to Surface and Material Analysis and to Various Analytical Techniques. *Vacuum Technology & Coating* **2014**, 27-32.
31. Quast, A. D.; Zhang, F.; Linford, M. R.; Patterson, J. E. Back-Surface Gold Mirrors for Vibrationally Resonant Sum-Frequency (VR-SFG) Spectroscopy Using 3-Mercaptopropyltrimethoxysilane as an Adhesion Promoter. *Applied Spectroscopy* **2011**, *65* (6), 634-641.