The Best Kept Secret in Industry

By: **Stephen L. Kaplan**[*]
Plasma Technology Systems
276 Harbor Blvd.
Belmont, CA 94002

Abstract:

Five decades ago there were only a few green choices to modify polymer surfaces, corona and flame. In the 1960s cold gas plasma was introduced as a work place and environmentally safe and particularly effective method to modify polymers to enhance adhesion. Plasma's superiority quickly became obvious and corona and flame manufacturers adopted the term "plasma" for their processes, then confusion reigned. While it is true that corona and flame are "plasmas", the energetic species present in them are significantly less than in cold gas plasma, aka low pressure plasma. Thus they are very limited in the chemical changes they can effect. Trade publications and often even scientific journals fail to adequately discern between the various plasma processes in their published articles. Material engineers often miss the subtle differences in such learned papers and assume the limitations discussed for coronas, atmospheric plasma and flames are not necessarily applicable to cold gas plasma.

The very significant difference between the capabilities of low pressure plasma and other plasma has inadvertently been obfuscated and perhaps intentionally kept secret. One of the best kept secrets is the utility of cold gas plasma to successfully graft silanes to the surfaces of metals, ceramics and polymers.

Background:

Generally silanizations are carried out in liquid-phase over an extended time where the silane of interest is dissolved in a solvent [1], possibly in the presence of a catalyst [2], and cleaned substrates are added to the solution. Liquid phase silanization is however not easy to control, mainly due to difficulties in controlling the amount of water present in the solution. Absence of water results in incomplete monolayers and excess water results in extensive polymerization and formation of polysiloxane aggregates which can be deposited onto the surface of substrates [3].

Gas-phase depositions have the advantage in that the moisture level can easily be controlled and thus eliminate extensive polymerization and formation of aggregates on

---

[*] Presented at the "Ninth International Symposium on Polymer Surface Modification: Relevance to Adhesion" in collaboration with the Center for Polymer Science and Engineering, Lehigh University,Bethlehem, Pennsylvania, USA. June 17-18, 2013.

the surface. A further advantage with gas-phase deposition is the high permeability of gas molecules which allows functionalization of nano-scale devices where the access of liquid is limited by capillary forces. Various methods for gas phase depositions have been proposed and depositions can be made either at elevated temperature, in the presence of a gas flow, or with the help of cold gas plasma, here referred to as plasma-enhanced chemical vapor deposition (PECVD) [4]. Such depositions are achieved through a vacuum process where substrates are placed in a chamber; air is removed through a vacuum pump to a pressure often less than 100 mTorr. Process gases are then fed into the chamber and radio-frequency energy is supplied to electrodes within the chamber. A highly reactive gas mixture of electrons, ions and other meta-stable species is thus produced. These species have sufficient energy to react with the substrate and by carefully choosing the gas mixture and process parameters surface properties can be tailored to a desired application.

Discussion:
As indicated, cold gas plasma is effective on all materials. One such application involved the alteration of quartz nano-pipettes as a method for electrical detection of DNA-functionalized nanoparticles [4]. The ability to tailor surface properties of such nano-scale devices are essential to avoid undesired adsorption of biological material onto the walls of a nano channel since it can alter flow properties as well as electrical properties of the channel. Another important aspect is to find a convenient method for functionalizing nano-pipettes while maintaining desired wetting properties. Silanization employing solvent methods provided poor yield as globules from homopolymerization would plug the pipette tip. Plasma-enhanced chemical vapor deposition (PECVD) of mercaptopropyltrimethoxysilane was investigated as an alternative method to silanize the internal surfaces of these nano-pipettes. The mercaptosilane in a subsequent step was coupled to bovine SA.

Elemental composition as determined by XPS for both plasma deposited and liquid-phase deposited mercaptotrimethoxysilane is shown in Table 1.

Table 1
Deposition Characterization

| Deposition method	Contact Angle [0]	Thickness [A]	XPS [atomic%]			
			Si	O	c	s
Plasma deposition	69	410±25	15.2	36.2	41.7	6.8
Liquid-phase	64	15± 5	31.7	30.3	27.1	10.8

Contact angle measurements showed little differences between the two deposition methods since batches prepared in liquid-phase generally give variation of contact angles in the range of 60 -70 °. However ellipsometry measurements show a significantly thicker silane layer was achieved with plasma deposition compared to liquid-phase deposition. This was also verified by XPS measurements indicating a thicker organic layer despite the order or magnitude difference in treatment time. The lower silicon content found on plasma deposited samples can easily be explained by the thicker organosilicon layer. Generally more than 90% of the XPS signal comes from the outermost 100 Angstrom of the sample hence for the plasma deposited silane layer the silicon detected originates mainly from the deposited silane film. This is in contrast to the liquid-phase deposition where the detected silicon originates from the deposited silane film, silicon from the native silicon oxide layer as well as from elemental silicon in the underlying substrate. Furthermore a significant increase in carbon content is found in the PECVD film as expected for a thicker silane layer. However an expected increase in sulfur content was not found.

For a perfect mercaptopropylsilane monolayer the sulfur functionality is expected to be oriented as the terminal group at the interface. The theoretical film thickness of a monolayer can be estimated to approximately 9 Angstroms using standard bond length and bond angles as well as van der Waals radii according to the literature. This is short enough that inelastic scattering of underlying carbon atoms can be considered insignificant and therefore a carbon-to-sulfur ratio of 3 is expected. A reasonable C/S ratio is also found in samples made from liquid-phase deposition (C/S=2.5). However the carbon-to-sulfur ratio deviates significantly from the expected ratio for samples made with the PECVD method *(*C/S= 6.1). It is well known that high RF-powers can lead to extensive molecular fragmentation and reduced deposition of precursor molecules. This can possibly explain fragmentation of the C - S bond during the plasma process resulting in the formation of partly methyl-terminated silane layers and a higher C/S ratio.

The discrepancy in the desired carbon to sulfur content of the plasma deposited silane layers compared to the solvent silanization process motivated further investigation into the relation between silane layer characteristics and plasma power. Figure 1 shows the film thickness as

function of plasma power exhibiting a clear correlation between film thickness and plasma power.

Figure 1
Influence of Power on Deposition
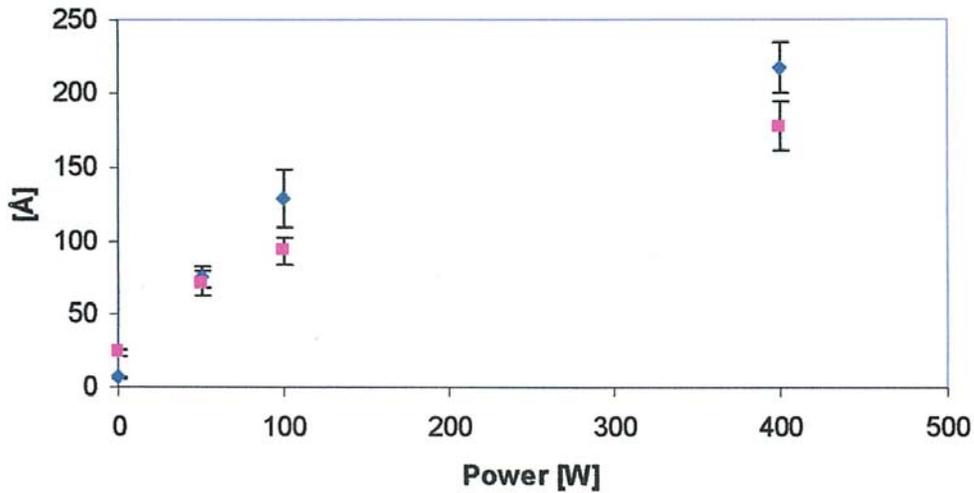
The variation in elemental composition to plasma power is shown in Figure 2. An interesting feature is observed. Sulfur content appears to reach its maximum relative composition at a power of 50 Watts (W). A minimum in C:S ratio of 3.3 is found at 50 W and increases with power suggesting that higher plasma power lead to extensive fragmentation of the carbon-sulfur bond in mercaptopropyltrimethoxysilane.

Figure 2
Elemental Composition determined by XPS as a function of power
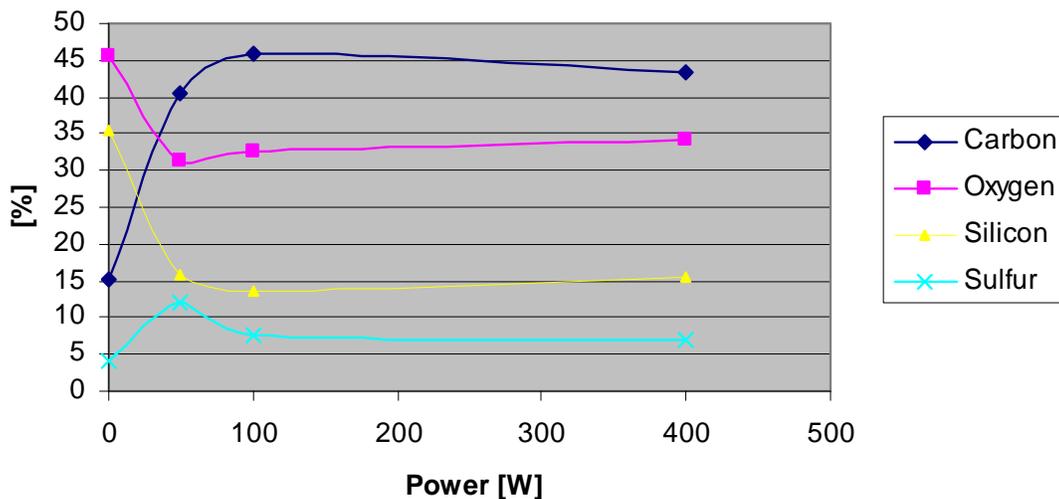
Little variation in elemental composition is found in films produced at plasma powers of 100 W and higher. Such films have a thickness of at least 100 Angstroms suggesting that signal contributions from the underlying substrates are depleted. It is also indicative of a possible equilibrium fragmentation at 100 W and that further increase in plasma power does not alter the composition of reactive species produced by the RF-plasma.

AFM analysis of these films was also conducted which indicates that smooth silane films are accomplished. In contrast there are pre-polymerized agglomerates found on liquid-phase deposited silane layers not present in the layers produced by plasma deposition. This is important in micro-fluidic devices since such agglomerates are generally on the size of tens of nanometers and can alter the properties of nano-scale devices. Essentially the roughness of plasma deposited silane layers is comparable to the roughness of bare silicon dioxide and significantly smoother than liquid-deposited silane layers of comparable nominal thickness.

Ultimately the plasma parameters were optimized to provide a thinner silanized layer (approximately 150 Angstroms) for the nano-pipette. The process which included a plasma cleaning step totaled 15 minutes compared to a 12 hours solvent silanization. In addition the solvent process also greatly suffered from homopolymerization which created large agglomerates that plugged many of the devices.

Coupling or grafting by the chemical reaction of silanes to glass via wet chemistry is well established. Globules of silane homopolymerization products that occur in solution application methods has been a serious problem in the manufacture of nano-fluidic devices. The preceding study shows the effectiveness of the PECVD process to graft silanes to the surface of glass. Plasma silane grafting (aka plasma silanization) extends the utility of silanes to nano-fluidic devices.

Silanes are also commonly used with metals to enhance adhesion strength. A dry and environmentally-clean "green" process is desirable especially when the metal is part of a composite that could be deteriorated by exposure to harsh metal etchants. In the following metal bonding studies the processes have not been optimized. The studies were conducted as proof of concepts. Several amine functional silanes were examined and found in some cases to have significant influence on the bond strength as reported in Table 2.

Table 2
Lap Shear Adhesive Tests
Stainless Steel

Stainless Steel & Epoxy Film Adhesive								
Treatment	Specimen 1	Specimen 2	Specimen 3	Specimen 4	Specimen 5	Specimen 6	AVG PSI	Treatment
Baseline (Untreated)	***	***	***	938	882	1004	**941**	Baseline (Untreated)
Plasma silanization	1752	1670	1828	1578	1648	1790	**1711**	Amine functional silane
All values in pounds per square inch								

*** Indicates a dis-bond in fixture or during machining, before a test value was attained

Very noteworthy with stainless steel is not only the nearly 100% increase in bond strength but a change in the failure mechanism from adhesive to cohesive within the adhesive.

Table 3
Lap Shear Adhesive Tests
Titanium

Titanium & Epoxy Adhesive								
Treatment	Specimen 1	Specimen 2	Specimen 3	Specimen 4	Specimen 5	Specimen 6	AVG PSI	Treatment
Baseline (Untreated)	4052	3998	4446	4230	4382	4006	4186	Baseline (Untreated)
Baseline (Primed)	5434	4744	5366	4800	5648	4638	5105	Baseline (Primed)
Plasma Silanization	4812	4774	4252	4752	4318	4840	4625	Amine functional Silane

While the case of the bonding enhancement for plasma silanized Titanium is not as compelling, failing to provide equivalent performance to the normal chemically primed methodology. However, in these very preliminary trials plasma silanization does show at least a 10% bond improvement versus untreated Titanium and a significantly increased percentage of cohesive failure within the mixed failure mode. Additional studies are being conducted and progress is being made to achieve a "green"

technology without any compromise to the attainable bond strength, with a goal of achieving a failure mechanism totally cohesive within the adhesive.

Plasma silanization chemistry is also an important tool for the modification of polymer surfaces. One commercial application requires the bonding of an addition cured silicone resin to a composite to protect the composite from environmental attack during its use. The substrate is a somewhat resin poor composite, thus solvents and chemicals present in solvent based priming systems could infiltrate and damage the composite.

Table 4
Adhesive Pull Strength using PosiTest Tester
Tensile Strength (psi)

	Untreated	Plasma Treated
	58	119
	91	109
	46	115
	58	124
Average Strength	61	117
Failure Mode	Adhesive to composite	Interply within composite

In this application the plasma process employed vinyltrimethoxysilane, $(CH_3O)_3SiCH=CH_2$ as the silane. The vinyl group participates in the addition cure mechanism becoming chemically cross-linked with the pendant vinyl groups of the silicone resin. The obvious challenge is grafting the silane to the composite without polymerizing or fragmenting the very reactive vinyl group. In a prior study an alkyl silane, ethyltrimethoxysilane [$CH_3O)_3Si-CH_2CH_3$] was used as a control and proved to provide no adhesion benefit with addition cured silicones providing empirical proof that the vinyl reactivity of the vinyl silane is essential and has been maintained in the plasma grafting process. A 90+% adhesion improvement was realized with a reduction of the standard deviation by 70% providing a very desirable product improvement.

Conclusion:
Silanes are available in almost and perhaps all known functionalities and structures. In our laboratories we have successfully grafted via the PECVD process a wide variety of silanes to provide reactive sites such as: amine, amino, aldehyde, vinyl, allyl, glycidyl and mercapto. The processes and knowledge developed have proved to be applicable to an extremely wide variety of materials. In addition to establishing functional sites on materials we have also employed silanization to alter the surface chemistry of materials by populating the surface with long chain alkyl groups to render the surface anti-fouling, fluoroalkyls to impart hydrophobicity and silicone oligomers to impart lubricity.

The information presented in this paper demonstrates the ability to employ plasma enhanced chemical vapor deposition process techniques to covalently graft reactive silane to almost any material. Optimization of the plasma parameters is essential to control grafting or deposition thickness as well as to maintain the functionality that led to the selection of a specific silane. The variety of silanes available provides the potential for an almost limitless possibility of modification of an almost limitless list of materials. Harnessing the power of plasma with the potential variants of silanes provides an environmental and work-place clean "green" technology.

References:
1. Halliwell, C.M. and Cass, A.E.G., "A Factorial Analysis of Silanization Conditions for the Immobilization of Oligonucleotides on Glass Surfaces", Analytical Chemistry, 2001, 73(11) p. 2476-2483
2. Fadeev, A.Y. and McCarthy, T.J., "Self-Assembly Is Not the Only Reaction Possible Between Alkyltrichlorosilanes and Surfaces: Monomeric and Oligomeric Covalently Attached Layers of Dichloro- and Trichloroalkylsilanes on Silicon", Langmuir, 2000, 16 (18), p. 7268 -7274
3. Ulman, A., "Formation and Structure of Self-Assembled Monolayers", Chem. Rev. 1996, 96 (4), p. 1533-1554
4. Persson, H.J., Kaplan, S.L., Larner, M., Kam, R., Davis, R., and Pourmand, N., "Plasma Enhanced Deposition of Silane Coupling Agents for Biological Applications", Fifth International Symposium on Silanes and Other Coupling Agents", Toronto, Canada, June 2005.