Functional Sites on Non-polymeric Materials: Gas Plasma Treatment and Surface Analysis

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Biomedical and other life science applications present intriguing and demanding requirements for materials. In the case of biomedical devices, the primary challenge is to ensure that a material is biocompatible - the body must not reject or react adversely to a device. A second challenge is to engineer surfaces that impart specific functionality, such as cell adhesion, lubricity, or drug attachment. The surface characteristics of a material, and the ability to tailor surface chemistry, are critical to address both of these issues. In turn, understanding changes made to surfaces during processing requires analytical techniques that can accurately characterize materials before and after modification.

Plasma processing is routinely used to functionalize polymeric surfaces. Functionalizing inert materials such as metals, glasses, and ceramics, however, is more difficult and often requires formation of a transition layer to create binding sites for the desired functional groups. Using plasma enhanced chemical vapor deposition (PECVD), 4th State Inc. is able to treat inert materials with a thin, tenaciously adhered, polymeric transition layer. This transition layer can be readily functionalized by subsequent plasma processing and, for certain applications, further modified using wet chemistry techniques (Figure 1).

PECVD offers a number of advantages over conventional surface treatment methods involving liquid and gaseous chemical reactions. A major advantage of plasma is that parts can be cleaned (a critical first step for successful surface modifications) and polymer-coated in the same plasma reaction chamber. In addition, because the reactive material is a gas, three-dimensional surfaces and interstices of porous materials are readily and uniformly modified. PECVD produces a thin (~300 Å) pinhole-free coating that will protect smooth continuous surfaces but not bridge and block porous media, something most liquid chemical treatments cannot do.

Polymer-coating and functionalization of a metal surface using plasma processes and the characterization of these modified surfaces are demonstrated in this technical note. A series of five gold samples was prepared by 4th State and analyzed at Charles Evans & Associates (CEA). The samples were: (1) an untreated Au control; (2) Au with PECVD hydrocarbon thin film; (3) sample 2 after washing; (4) sample 3 with amine functionalization; (5) sample 4 after washing.

The surface analysis was performed using X-ray photoelectron spectroscopy (XPS, also known as Electron Spectroscopy for Chemical Analysis or ESCA) and Time-of-Flight Secondary Ion Mass Spectrometry (TOF-SIMS). XPS provides elemental quantification and chemical state information of the top 50 to 100 Å of a surface, while TOF-SIMS provides highly specific molecular and elemental information from the top several monolayers (<30 Å) of a surface. The capabilities of XPS and TOF-SIMS make them ideal for the analysis of plasma-treated, surface-modified biomaterials.

Table 1 lists the atomic concentrations of various elements on the five samples as determined by XPS, while Figure 2 shows portions of the TOF-SIMS spectra from three of the samples. Changes in surface composition that correspond to each plasma treatment are identified by both techniques. From the control (sample 1) to the hydrocarbon treated sample 2, the XPS data show a significant increase in the carbon levels and a corresponding decrease in gold. A similar increase in molecular hydrocarbon species after plasma treatment is seen in the TOF-SIMS data. Following the second plasma treatment to deposit amine (sample 4), the XPS data indicate that the atomic concentration of nitrogen increased significantly, while the presence of organic amines is confirmed in the carbon bonding results shown in Table 2.

In addition to the expected Au, a number of other elements are detected on the control sample (see Table 1). Much of the C and O is likely caused by adventitious materials, i.e. contamination resulting from exposure to the atmosphere. Organic contaminants will be readily removed upon plasma exposure, while removal of inorganic contaminants requires an aqueous or solvent wash.

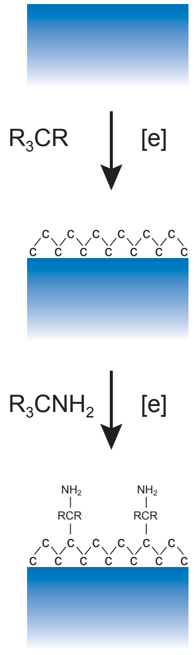

Figure 1. Representation of functional coating on metal

After each plasma treatment step, the gold chips were washed to demonstrate the stability of the transition coating and the amine-functionalized surface. In practice the two plasma steps would be conducted in sequence without exposing the product to the atmosphere between steps. XPS and TOF-SIMS results show that the washing steps introduce significant levels of a silicon-containing contaminant (see Table 1 and the Washed Amine TOF-SIMS spectrum in Figure 2). From the TOF-SIMS data, the contaminant can be more specifically identified as a silicone polymer. 4th State has disclosed that the samples were fixtured in a silicone tube during the washing step, and it is likely that this tube is the source of the unintentional contamination.

The introduction of silicone during washing would be expected to increase Si and O levels to the same degree, given the 1 to 1 ratio of Si to O in silicones. However, the washing steps introduced more O than Si (see Table 1), indicating an additional source of O contamination, possibly due to residual washing solvent.

Note that the decrease in N concentration on the washed amine sample is not due to removal of amine (compare samples 4 and 5 in Table 1); rather, this decrease in N is due to dilution of amine by the presence of contaminants. Similarly, the decrease in relative C concentration upon washing the hydrocarbon transition is due to the addition of contaminants (compare samples 2 and 3 in Table 1).

In summary, plasma is an effective tool for creating functional sites on non-polymeric materials and XPS and TOF-SIMS are useful techniques for characterizing the modified materials.

Table 1: XPS survey data (atomic concentrations, in %)

Sample	C	N	O	Na	Si	S	Cl	K	Au	F
Control (1)	33.5	4.4	18.3	5.1	-	3.5	0.3	0.1	34.7	-
Hydrocarbon transition (2)	85.0	-	4.8	-	-	-	-	-	10.3	-
Washed transition (3)	76.6	-	10.9	-	1.9	-	-	-	10.1	0.6
Amine treated (4)	74.5	17.8	7.6	0.1	-	-	<0.1	-	0.1	-
Washed amine (5)	64.7	13.3	15.1	-	6.5	-	-	-	0.2	0.2

Table 2: Carbon chemical states (in %)

Sample	C-C/C-H	C-O/C-N	C=O	O-C=O/N-C=O
Control (1)	55.0	29.6	9.2	6.2
Hydrocarbon transition (2)	94.8	5.2	-	-
Washed transition (3)	96.6	3.4	-	-
Amine treated (4)	62.0	29.5	8.6	-
Washed amine (5)	70.7	22.4	6.8	-

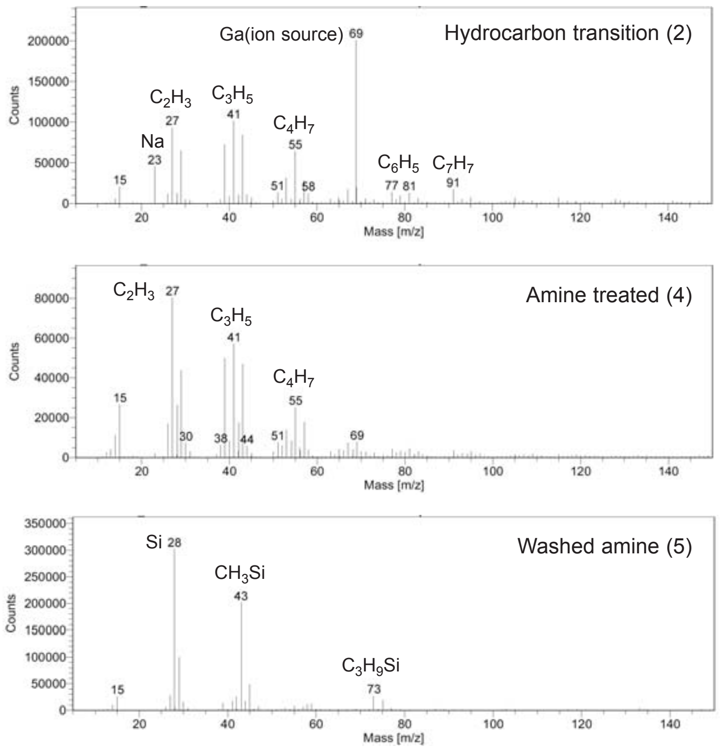

Figure 2. Positive ion TOF-SIMS spectra

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