Modification of Inert Surfaces by PECVD and Their Characterization by Surface Analysis Techniques

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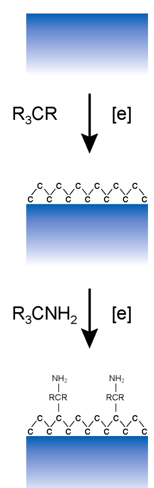
INTRODUCTION

- Biomedical applications often require tailoring of material surfaces to impart specific properties such as hemocompatibility, lubricity, or drug incorporation.
- Plasma processes can be used to functionalize surfaces of polymers, metals, and ceramics.
- Plasma treatment offers a number of advantages over liquid and gaseous chemical treatments: the plasma can be used to clean off organic contaminants from the initial surface; three dimensional surfaces and interstices of porous materials are readily accessible to the plasma gas; and a thin, pinhole-free coating will protect smooth, continuous surfaces without bridging and blocking porous media.
- Surface modification requires analytical techniques that can accurately characterize materials before and after processing.
- XPS (X-ray Photoelectron Spectroscopy) provides quantitative elemental information as well as chemical bonding information from the top 50-100 Å on both conductive and insulating materials.
- TOF-SIMS (Time of Flight Secondary Ion Mass Spectrometry) provides mass spectra and images of organic and inorganic species present on the top 30 Å of a material surface. Molecular identification of species can be made and detection limits are typically in the ppm range.
- In this presentation, an inert metal surface (gold) has been functionalized using various plasma processes. These modified surfaces have then been characterized using XPS and TOF-SIMS. Surface treatments were carried out by 4th State. Surface characterization was performed by Charles Evans & Associates.

EXPERIMENTAL

- Plasma processes are routinely used to functionalize polymer surfaces. Functionalization of inert surfaces such as metals and ceramics using plasma is less common and not as well understood. Such inert surfaces often require the formation of a transition layer to create binding sites for the desired functional groups.
- 4th State has used plasma enhanced chemical vapor deposition (PECVD) to treat inert materials with a thin, tenaciously adhered hydrocarbon transition layer. The transition layer is then amine-functionalized by subsequent plasma processing. For certain applications further modifications can be made using wet chemistry techniques. Alternatively, an amine coating can be applied directly to the inert surface, without a transition layer.
- Method 1 (Transition Layer/Amination). The samples were: (1) an untreated Au control; (2) Au with PECVD hydrocarbon thin film; (3) Sample 2 after ultrasonic washing in hexane then methanol; (4) sample 3 with amine functionalization; and (5) sample 4 after ultrasonic washing.
- Method 2 (Direct Amination). The samples were (6) an untreated Au control; (7) amine film directly deposited onto Au surface; (8) amine film after oxygen plasma pre-clean of Au, trial 1; (9) amine film after oxygen plasma pre-clean of Au, trial 2; (10) amine film after oxygen plasma pre-clean of Au and after chamber pre-conditioning with amine to minimize chamber wall reactions with amine; (11) sample 7 after ultrasonic washing in hexane then methanol; (12) sample 8 after ultrasonic wash; (13) sample 9 after ultrasonic wash; and (14) sample 10 after ultrasonic wash.



Method 1

RESULTS

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 (2)	85.0	-	4.8	-	-	-	-	-	10.3	-
Hydrocarbon + Wash (3)	76.6	-	10.9	-	1.9	-	-	-	10.1	0.6
Hydrocarbon + Amine (4)	74.5	17.8	7.6	0.1	-	-	<0.1	-	0.1	-
Hydrocarbon + Amine + Wash (5)	64.7	13.3	15.1	-	6.5	-	-	-	0.2	0.2

Table 1: XPS Atomic Concentrations of PECVD-treated Gold (at%)

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 (2)	94.8	5.2	-	-
Hydrocarbon + Wash (3)	96.6	3.4	-	-
Hydrocarbon + Amine (4)	62.0	29.5	8.6	-
Hydrocarbon + Amine + Wash (5)	70.7	22.4	6.8	-

Table 2: XPS Carbon Chemical States for PECVD-treated Gold (%)

Sample	C	N	O	F	Si	Cl	S	Cu	Zn	Au
Control (6)	46.5	-	10.8	-	-	0.7	0.8	1.6	-	39.7
Amine (7)	72.9	16.5	8.1	-	-	0.2	-	0.1	-	2.2
Amine Pre-cleaned, Lot 1 (8)	68.9	15.8	7.4	-	-	-	-	<0.1	-	7.8
Amine Pre-cleaned, Lot 2 (9)	75.3	19.8	4.5	-	0.1	-	-	0.2	-	0.1
Amine Pre-cleaned Pre-conditioned (10)	73.1	18.9	7.6	-	-	-	-	-	-	0.3
Amine Washed (11)	73.6	15.7	10.0	0.1	-	-	-	-	0.4	0.2
Amine, Pre-cleaned Washed, Lot 1 (12)	72.6	16.6	9.6	-	-	-	-	-	0.3	1.0
Amine, Pre-cleaned Washed, Lot 2 (13)	73.0	16.8	6.3	0.8	-	0.3	-	-	0.3	2.5
Amine, Pre-cleaned Pre-conditioned, Washed (14)	70.7	16.0	9.6	-	-	0.1	-	-	0.6	3.0

Table 3: XPS Direct Amination, Atomic Concentrations (at%)

RESULTS

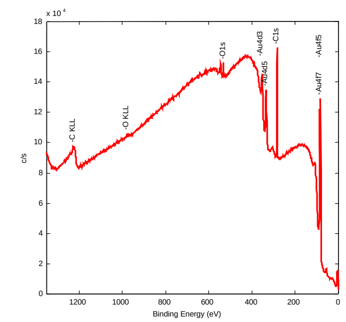


Figure 1: XPS Survey Spectrum of Hydrocarbon Film (Sample 2)

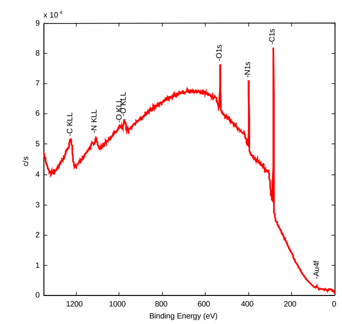


Figure 2: XPS Survey Spectrum of Amine Film (Sample 4)

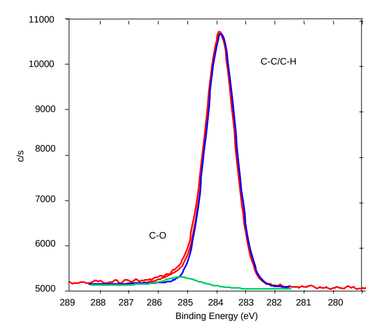


Figure 3: XPS Carbon 1s Curve-fit of Hydrocarbon Film (Sample 2)

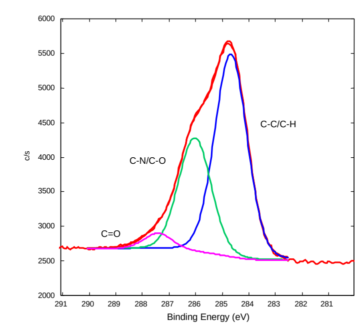


Figure 4: XPS Carbon 1s Curve-fit of Amine Film (Sample 4)

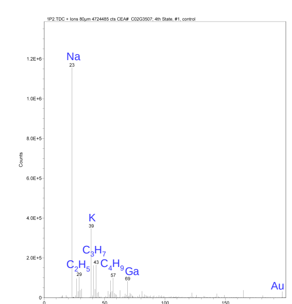


Figure 5a: TOF-SIMS of Control, Sample 1 (+ ions, mass 0 – 200)

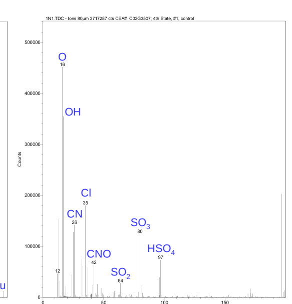


Figure 5b: TOF-SIMS of Control, Sample 1 (- ions, mass 0 – 200)

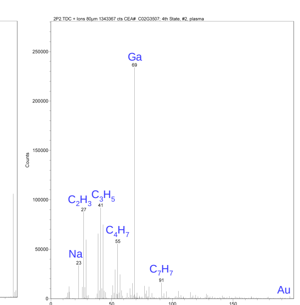


Figure 6a: TOF-SIMS of Hydrocarbon Film, Sample 2 (+ ions, mass 0 – 200)

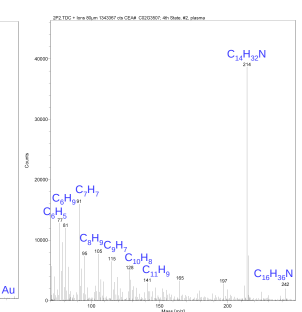


Figure 6b: TOF-SIMS of Hydrocarbon Film, Sample 2 (+ ions, mass 70 – 250)

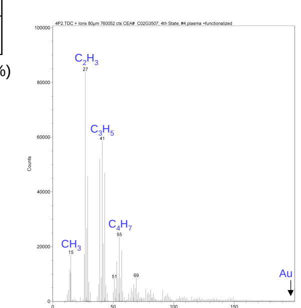


Figure 7a: TOF-SIMS of Hydrocarbon + Amine, Sample 4 (+ ions, mass 0 – 200)

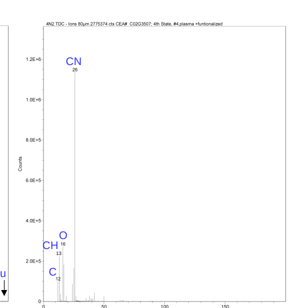


Figure 7b: TOF-SIMS of Hydrocarbon + Amine, Sample 4 (- ions, mass 0 – 200)

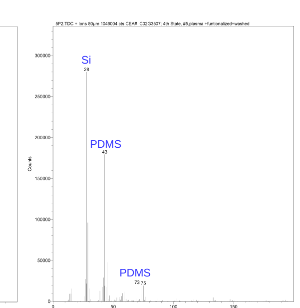


Figure 8a: TOF-SIMS of Hydrocarbon + Amine + Wash, Sample 5 (+ ions, mass 0 – 200)

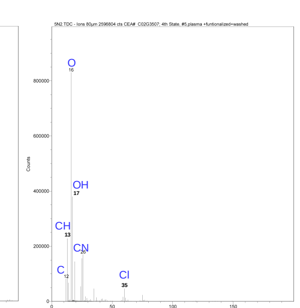


Figure 8b: TOF-SIMS of Hydrocarbon + Amine + Wash, Sample 5 (- ions, mass 0 – 200)

DISCUSSION

Control (Sample 1)

- XPS In addition to Au, the Control shows a number of contaminants, typical for a Au surface. Carbon and O are commonly observed on surfaces analyzed by XPS, much of it probably originating from contaminants in the atmosphere (Table 1).
- TOF-SIMS This sample shows the highest intensity of Au of all the samples, indicating it has the thinnest organic over-layer. Contaminants are observed, some which may have been part of the gold and some which may have been deposited. Relatively high levels of Na and K (Figure 5a) and Cl, Br, I, S and various SO_x ions (Figure 5b) are detected. CN and CNO are observed; CN is commonly observed on Au surfaces (Figure 5b).

Hydrocarbon Transition Layer Deposition (Sample 2)

- XPS There is a significant increase in the carbon level and a corresponding decrease in Au upon deposition of the hydrocarbon film, indicating successful deposition (Table 1 and Figure 2). A curve-fit of the C1s region shows almost exclusively C-C/C-H; very little oxidized C species are present (Table 2 and Figure 3).
- TOF-SIMS This sample shows high levels of low mass hydrocarbon species, many of which are typical of aromatic functionality; e.g., C_6H_5, C_7H_7, C_8H_9, C_9H_7, and $C_{10}H_8$(Figure 6a and 6b). An ion at m/z 214 due to $C_{14}H_{32}N$ is observed (Figure 6b). Other N species are also observed: $AuC_{14}H_{31}N$ and $AuCH_2N$. However, the overall level of N species is low, since N is not detected by XPS on the hydrocarbon film sample.

Hydrocarbon Layer Washing (Sample 3)

- XPS Upon ultrasonic washing, Si appeared, O increased, and the apparent C concentration decreased. However, this decrease of C is due to dilution by the presence of Si- and O-containing contaminants, not due to removal of film. Thus, the hydrocarbon film appears to be adherent under ultrasonic treatment with organic solvent.
- TOF-SIMS This sample shows the presence of ions due to a silicone, such as PDMS (polydimethylsiloxane). The level of PDMS is in the submonolayer range since substrate Au as well as hydrocarbon species are still observed (data not shown but similar to that of Sample 5).
- The source of silicone was found to be a silicone fixture used to hold samples in the washing step.

Amine Deposition (Sample 4)

- XPS The nitrogen concentration increased significantly on the sample with an amine film deposited on top of the hydrocarbon film (Table 1 and Figure 3). The organic nature of the N is indicated by the increase in C-N bonding in the C1s curve-fit results (Table 2 and Figure 4).
- TOF-SIMS Au levels are very low, indicating nearly complete coverage of the sample with other species (Figure 7a). Negative ion data is dominated by CN (an order of magnitude more intense than other samples in which N is observed) and accompanied by other N species such as CNO, C_3N, and C_3NO (Figure 7b). The exact form of N present is not known since CN is the most common fragment from almost all N-rich surfaces. In addition to N, low mass hydrocarbon signals were intense, indicating high organic levels on the surface (Figure 7a).

Amine Film Washing (Sample 5)

- XPS Silicon is observed at a significant level upon washing the amine film (see Table 1). Along with the appearance of Si, C and N levels are decreased. However, this decrease of C and N is due to dilution by the presence of Si-containing contaminants, not due to removal of film. Thus, the amine film appears to be adherent under ultrasonic treatment with organic solvent.
- TOF-SIMS Au levels are very low, indicating high surface coverage by other species. The most intense ions are due to PDMS (Figure 8a). PDMS levels are about 3 monolayers since almost no other ions are detected. CN is observed in the negative ion mode but at a much lower level than for Sample 4 (Figure 8b).
- The source of silicone was found to be a silicone fixture used to hold samples in the washing step.

Direct Amination Results by XPS

- Amine Sample (Sample 7). Increased levels of N and C and decreased levels of Au are observed relative to the Control, indicating deposition of an amine layer (Table 3).
- Amine, Pre-cleaned, Lot 1 (Sample 8) and Lot 2 (Sample 9). Slight variations in deposition thickness are observed from lot to lot. As indicated by the lower concentration of Au, a thicker deposition of amine film occurred on the Lot 2 sample. Pre-cleaning of the sample with oxygen plasma does not appear to enhance significantly the amount of amine deposited, since the results for Samples 8 and 10 are similar to that of Sample 7 (Table 3).
- Amine, Pre-cleaned, Pre-conditioned (Sample 10). Comparing Sample 10 with Sample 7, it appears that pre-conditioning the chamber with amine prior to processing the Au sample does not affect the level of amine deposition under the processing conditions used (Table 3).
- Washed Amine Samples (Samples 11, 12, 13, and 14). A comparison of the unwashed samples with the ultrasonically washed aminated samples (hexane and methanol) shows little change in composition, indicating that the direct amination procedure produces an adherent film (Table 3).

CONCLUSIONS

- Plasma enhanced chemical vapor deposition is an effective method for producing thin, adherent, amine-coated films on inert surfaces. The amine film can be applied directly to the gold surface. Alternatively, a transition layer of hydrocarbon can be applied first and the amine layer deposited in a subsequent step. Such functionalized films are important for enhancing the biocompatibility of medical devices.
- XPS and TOF-SIMS are powerful tools for the chemical characterization of surface-modified materials.