

# Surface Functionalization by RF Plasma Deposition of Ethylene Diamine, Acrylonitrile, and Acetonitrile

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**ABSTRACT:** Surface rich in covalently-bonded amine groups have wide end use applications in biomaterials. This article describes functionalization of stainless steel (SS) surface with reactive chemical groups using RF-cold-plasma polymerization of ethylene diamine (ED), acrylonitrile (AN), and acetonitrile (AcN). The effect of RF plasma power and frequency (40 kHz and 13.56 MHz) on surface chemistry was investigated by electron spectroscopy for chemical analysis (ESCA) and FTIR. It was demonstrated that all the plasma-deposited films consist of secondary and tertiary amines, imines, and amides with a small concentration of

nitrile groups present in AN plasma. Significant changes in ED, and AN plasma-induced molecular fragmentation occur as the plasma conditions are varied. However, AcN plasma polymer chemistry is observed to be independent of RF frequency. Films deposited at 13.56 MHz RF power in continuous mode have higher concentrations of C–N linkages, with maximum in ED plasma-polymerized films. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 107: 1686–1695, 2008

**Key words:** plasma polymerization; amines; surface modification; thin films

## INTRODUCTION

Advances in biological arrays, diagnostics, and tissue engineering are currently hampered by undesirable surface-related responses to biological fluids. These can be controlled by tailoring the surface characteristics of a material without detrimentally affecting the bulk properties using various surface modification techniques. The purpose of these modifications is to develop bioengineered surfaces that are able to elicit and control processes like biofilm formation, protein adsorption, enzyme immobilization, etc. A range of biological, physical, and chemical methods are used to design custom-made surfaces with end use applications in medicine and biology. Coatings rich in amine groups have been reported to improve biocompatibility, wettability, cell adhesion,<sup>1</sup> immobilization of biomolecules like enzymes,<sup>2</sup> proteins,<sup>3</sup> and polysaccharides.<sup>4</sup> They are used in biosensors,<sup>5,6</sup> microfiltration membranes,<sup>7</sup> microarrays,<sup>8</sup> or enzyme electrodes,<sup>9</sup> in which amines serve as linking agents between the substrates and the bio-active agents.

Surface functionalization has been an active area of research where biomaterials such as catheters, artifi-

cial heart valves and prosthetic devices are modified to render them biocompatible and sustainable in human body. Metallic and polymeric materials need to be surface functionalized prior to the attachment of antimicrobial compounds. These processes consist of elaborate complex wet chemistry approaches which are environmentally unfriendly and cost-ineffective. Also, the conventional wet chemistry reactions are not suitable for the modification of inert materials and usually leave residue on surfaces.

Cold plasma technologies open up novel and efficient routes for surface modification of various inorganic and organic materials. The energy levels of plasma species are comparable with bond energies of common organic compounds<sup>10</sup> (C–H = 3.5 eV; C–C = 6.3 eV; C–N = 7.8 eV) and thus, facilitating the development of structure- and functionality-controlled surfaces under selected discharge parameters without altering the bulk properties of a material. The reactive sites generated on the surface can initiate subsequent *in situ* or *ex situ* surface derivatization reactions for covalent attachment of desired molecules (low or high molecular weight).

This article describes a method using plasma functionalization to coat stainless steel (SS) surfaces with high concentrations of reactive nitrogen-containing macromolecular films. Plasma polymerization is a procedure in which gaseous monomer ionizes, dissociates, and recombines in plasma state and deposits on the substrates as densely crosslinked films.<sup>11–13</sup>

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The plasma polymer chemistry from three different gas precursors including, ethylene diamine (ED), acrylonitrile (AN), and acetonitrile (AcN) have been studied with respect to deposit crosslinked and/or three-dimensional network of macromolecular layers in applied RF power under continuous and pulsed conditions. The rationale is to use plasma processing tools and mimic structures of polymers that are commercially available and are widely used for surface functionalization. Manolache et al.<sup>14</sup> have demonstrated earlier that there is a similarity between low-energy MS-electrons- and RF plasma electrons-induced molecular fragmentation. The predominant peak in mass spectra<sup>15</sup> of ED is of molecular weight 30, with primary amine group intact. Also, ED cannot be polymerized with conventional methods. Saturated alkylamines deposited under suitable plasma conditions were used as one-step method to reactive amine groups,<sup>16,17</sup> and have been used to develop quartz crystal microbalance for immunosensors.<sup>18</sup> AN is a more complex monomer with two "polymerizable" functional groups: vinyl double bonds and nitrile. Both of these groups can form a conjugated p network readily. The MS fragmentation patterns of AN indicate that  $\sigma$  bond splitting and dehydrogenation reactions are the main electron-impact-induced processes. This opens up a possibility for the generation of conjugated carbon and nitrogen-based structures through the recombination of free radical species on the solid surfaces that confine RF-AN-plasma environment.

There is an abundant amount of literature on plasma-synthesized polyacrylonitrile,<sup>19–22</sup> but few in-depth studies of effect of frequency and pulsing on plasma polymerization exist. AcN is an unconventional monomer of choice with only one unsaturated bond and the nitrile group is not a site for conventional polymerization. The plasma-polymerized AcN films have been recently used in Pt electrodes<sup>23</sup> and in capillary electrophoresis chip.<sup>24</sup>

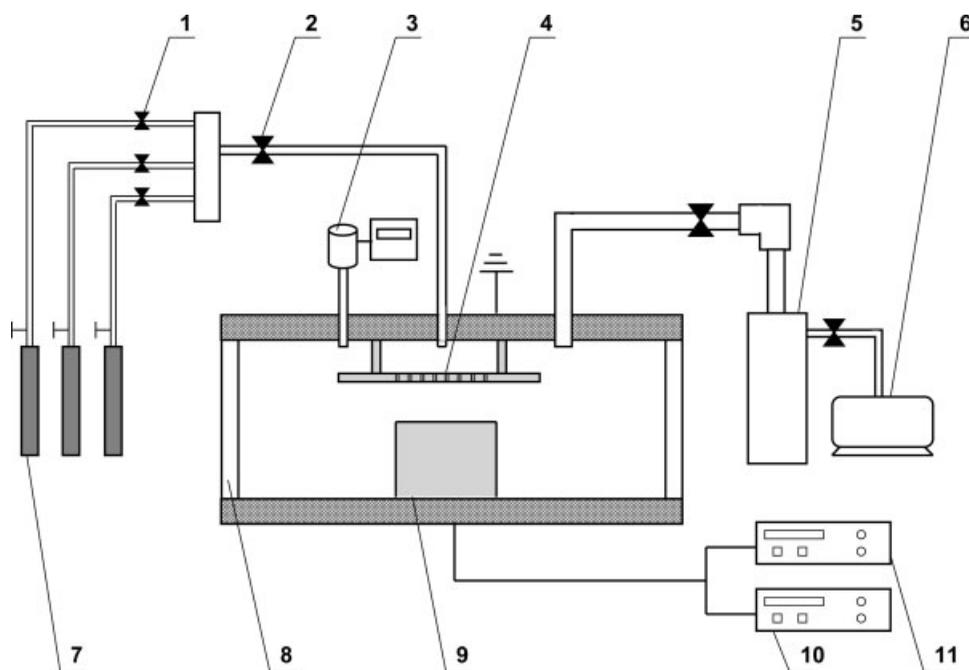
## EXPERIMENTAL

### Materials

SS sheets, type 316, no. 8 mirror finish, 0.30" thick were bought from McMaster-Carr (Chicago, IL). Circular stamps of 1" diameter were cut and washed in hot alkaline detergent (Micro; International Products, Trenton, NJ) for 30 min, rinsed several times in distilled water and air-dried at room temperature. All chemicals were purchased from Sigma-Aldrich Chemical (Milwaukee, WI) and were used without further purification. Oxygen and argon gases from Linde Gas were used for decontamination of the plasma reactor.

### Plasma treatments

All plasma treatments were carried out in a capacitively coupled, parallel plate cold plasma reactor (Fig. 1). The reactor has glass walls (8) with disk-



**Figure 1** Scheme of parallel plate cold plasma reactor: 1, metering needle valves; 2, shut-off valve; 3, Baratron<sup>®</sup> type capacitance manometer; 4, grounded stainless steel electrode; 5, liquid nitrogen trap; 6, mechanical vacuum pump; 7, chemical reservoir/gas cylinders; 8, glass reactor walls; 9, powered stainless steel electrode; 10, 40 kHz RF power generator; 11, 13.56 MHz RF power generator with matching network.

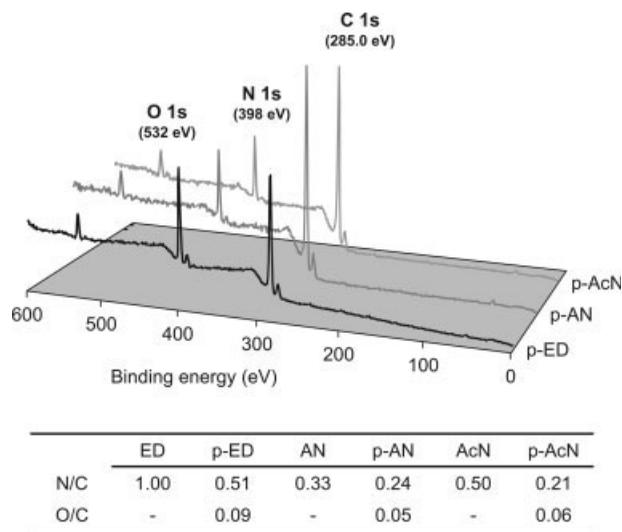
shaped SS electrodes: 9 cm diameter powered lower electrode (9) and 13 cm grounded upper electrode (4) separated by a 3 cm gap between them. The lower electrode is connected to RF power supply sources of frequencies 40 kHz (10) and 13.56 MHz (11, pulsing capabilities) with matching networks. The plasma gases and vapors from chemical feed reservoirs/gas cylinders (7) are supplied to the reactor through metering needle valves (1) and a shut-off valve (2). The valves are also used to control the pressure of feed gases in the reactor chamber, which is monitored by Baratron<sup>®</sup> type gauge (3). The mechanical vacuum pump (6) and a throttle valve ensure the quick evacuation of the system. A liquid nitrogen trap (5) between the reactor and the pump protects the contamination of the vacuum pump from plasma species and chemicals.

In a typical experiment, the reactor cleaning procedure involved rinsing with water and acetone and subsequent decontamination with oxygen plasma (300 mTorr, 300 W, 10 min). The clean SS stamps were placed symmetrically on the lower electrode and the reactor was evacuated to  $10^{-3}$  Torr. The throttle valve on the pump was slowly closed until equilibrium between pumping and leaking rate was attained. The gas pressure of 100 mTorr was established using the valves on the feed lines and the plasma was ignited and sustained at the selected power level for 5 min. The system was allowed to evacuate for 30 min followed by repressurizing it to atmospheric conditions using argon gas. The samples were removed and stored until further analysis. ED, AN, and AcN were used as precursors for plasma treatments at various power settings.

### Surface characterization

Survey and high-resolution (HR) electron spectroscopy for chemical analysis (ESCA) analyses of plasma-treated SS stamps were carried out using a Perkin-Elmer Physical Electronics Phi 5400 Small Area Spectrometer (Mg K $\alpha$  source; 15 kV; 300 W; 45° take-off angle; Perkin-Elmer, Palo Alto, CA). The pass energies of 89.45 and 35.75 eV were used for survey and HR scans respectively. HR peaks were fitted to Gaussian convolution into nonequivalent components (related to chemical states of an element) in AugerScan software version 2.4.2 (RBD Enterprises, Bend, OR). Sample charging shifts in the spectra were calibrated by sputter coating gold in a Desk II system sputter coater (Denton Vacuum, Moorestown, NJ) at 50 mTorr and sputtering current of 45 mA for 2 s.

An ATI-Mattson RS-1 IR instrument was used for FTIR measurements. All the evaluations were performed under a nitrogen blanket generated from a flow-controlled liquid nitrogen tank. Data were col-



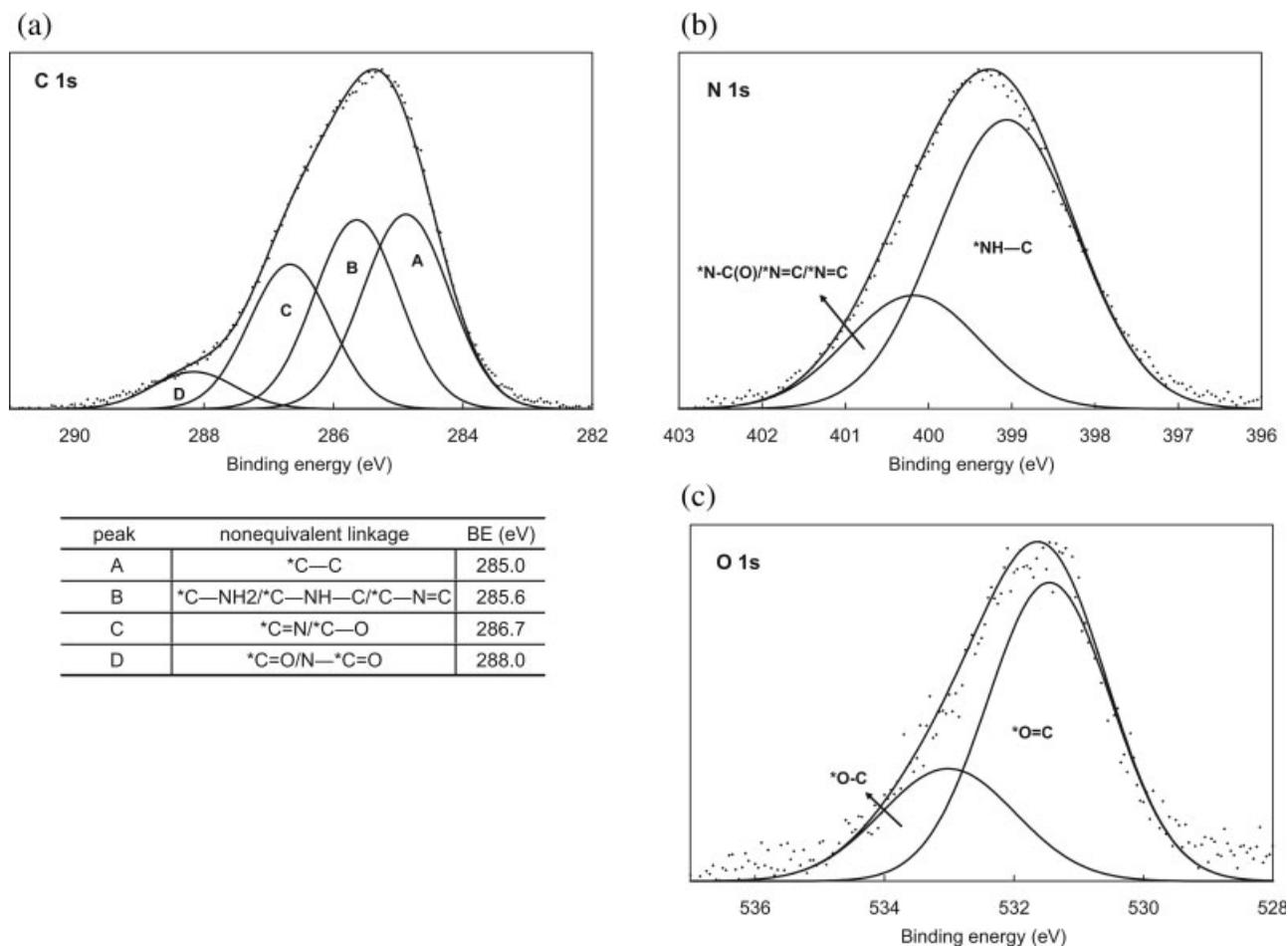
**Figure 2** Survey ESCA spectra of SS deposited with plasma-polymerized (p-) ED, AN and AcN at 100 mTorr, 30 W, 40 kHz RF for 5 min.

lected in the 600–4000  $\text{cm}^{-1}$  wavenumber region with 250 scans for each sample, with a resolution of 0.4  $\text{cm}^{-1}$ . The films were directly deposited on KBr pellets made with a die (International Crystal Laboratories, Garfield, NJ) and pressed in a Carver Laboratory Press. These pellets were grounded and mixed with plain KBr in the ratio 1 : 10 and pressed into pellets again.

## RESULTS AND DISCUSSION

### ESCA analysis

Figure 2 shows the survey spectra of ED, AN, and AcN plasma-deposited films (100 mTorr; 30 W at 40 kHz RF; 5 min) on SS stamps. The spectra indicate carbon (from core level C 1s), nitrogen (N 1s), and oxygen (O 1s) on the surface of the films. For quantitative analysis, nitrogen and oxygen peaks were normalized to carbon. The N/C ratios in all the plasma films was less than the theoretical values of the precursors, suggesting that the chemical structures deposited in the plasma environment are significantly different than conventional polymers from the monomers (eg., polyacrylonitrile from AN). The plasma-deposited film chemistry depends on RF-plasma-electron induced molecular fragmentation and subsequent recombination of these fragments into macromolecular matrix on the surface. The precursors do not contain oxygen and the oxygen incorporated in the films is primarily from the post-plasma oxidation processes initiated by plasma-generated radicals under open laboratory conditions and from the background oxygen at  $10^{-3}$  Torr base pressure. A part of oxygen in the films could also



**Figure 3** HR ESCA spectra of (a) C 1s, (b) N 1s and (c) O 1s of SS treated with ED plasma (100 mTorr, 30 W at 40 kHz RF, 5 min).

appear during the deposition process from residual outgassing of the reactor walls and the leakage from outer atmosphere. However, this possibility is remote due to the carefully cleaned plasma tool used in the process, and the vacuum-tight nature of the system. The absence of any major peak assignable to iron or chromium from SS substrates attests the complete coverage of the substrates by plasma films.

HR spectra of the elemental core levels are reconstructed with Gaussian distribution to obtain several nonequivalent components, which can be attributed to various chemical linkages on the surface. All binding energies (BE) were assigned using the database for polymeric compounds.<sup>25</sup> Amongst all the elemental peaks, C 1s is the most informative. The surface-charge-origin binding energy shifts were corrected based on Au 4f<sub>7/2</sub> and Au 4f<sub>5/2</sub> peaks at 84 and 87.7 eV respectively on gold-coated samples. Figure 3 shows HR C 1s, N 1s, and O 1s spectra for ED-plasma-treated SS fitted with possible peak assignments. The C 1s peak was deconvoluted into a quadramodal pattern with components positioned at (A) 285.0 eV, 35.3% of the total C 1s area: unfunc-

tionized hydrocarbons consisting of \*C—C and \*CH<sub>x</sub> environments; (B) 285.6 eV, 33.5%: carbon atoms singly bonded to nitrogen in linkages of type: \*C—NH<sub>2</sub>, \*C—NH—C, \*C—N=C, etc., (C) 286.7 eV, 24.7%: carbon bonded to nitrogen (\*C=N, \*C≡N, \*C=N=C, \*C—C≡N) and oxygen (\*C—OH, \*C—O—C); (D) 288.0 eV, 6.4%: carbon doubly bonded to oxygen (C—\*C=O, NH<sub>x</sub>—\*C=O). The peak (C) did not consist of C≡N linkages in ED plasma deposited films and will be further discussed in FTIR analysis.

HR spectra of N 1s and O 1s in Figure 3(b,c) have a broad pattern, however some useful information can be derived by deconvolutions. The N 1s peak is broad and can be fitted with two components. One of the peaks appears at lower BE at about 399 eV and originates from nitrogen atom in amine functional groups (primary, secondary, and tertiary). Another signal at 400.1 eV corresponds to the linkages of type \*NH<sub>x</sub>—C=O, \*N=C, and \*N≡C. There are no peaks of measurable intensity at BE positions between 403 and 408 eV, explaining the absence of nitroso, nitro or nitrate groups in the macromolecu-

**TABLE I**  
**Peak Assignments and Areas from HR C 1s ESCA**  
**Spectra of ED, AN, and AcN Plasma-Deposited Films**

Peak	Nonequivalent linkage	BE (eV)	Peak area (%)		
			p-ED	p-AN	p-AcN
A	*C—C/*C—H	285.0	35.3	38.7	34.0
B	*C—N	285.6	22.5	30.2	34.2
C	*C=N/*C≡N	286.7	24.7	25.6	24.8
D	*C=O	288.0	6.4	5.5	7.0

lar structure. This concludes that the post-plasma oxidation processes occur only at carbon moieties and not at nitrogen-containing sites. The information from N 1s spectra was not sufficient to infer the distribution of primary, secondary, and tertiary amines in the film structures. The O 1s spectrum is fitted with two peaks with one centered around 531.5 eV ascribed to oxygen doubly bonded to carbon as carbonyl group in amides or ketones. Another peak is fitted at 533 eV for oxygen atoms singly bonded to carbon (H\*O—C, C—\*O—C).

In case of AN and AcN plasma, C 1s (not shown here) consisted of earlier mentioned four peaks A, B, C, and D with concentrations represented in Table I. CN radicals were predominant in these discharges and play a crucial role in the film chemistry. The peak C in the spectrum of AN plasma was attributed to nitrile functionalities in addition to other carbon and nitrogen-based linkages. Though, the concentration of nitrile groups is low because the radicals may attack nitrile carbon more than the double bond.<sup>26</sup> The carbon in cyano groups is easily attacked by electrons, ions and nitrogen in cyano groups is sensitive to radicals. Thus, most of it recombines to form amine, imine or amide groups. AcN plasma-deposited films did not contain any intact nitrile groups from the precursor molecule and most of the cyano groups may have ejected out of the reactor as hydrogen cyanide gas. There was very less macromolecular material deposited in AcN plasma and nitrogen found on the surface was present mostly in oxidized form. It is crucial to mention that the small differences in BE values corresponding to functional groups (C—O, C=N, and C≡N) makes it difficult to predict the chemical linkages entirely by ESCA. Hence, FTIR evaluations are done in tandem to identify chemical structure and bonding configurations in plasma-deposited films.

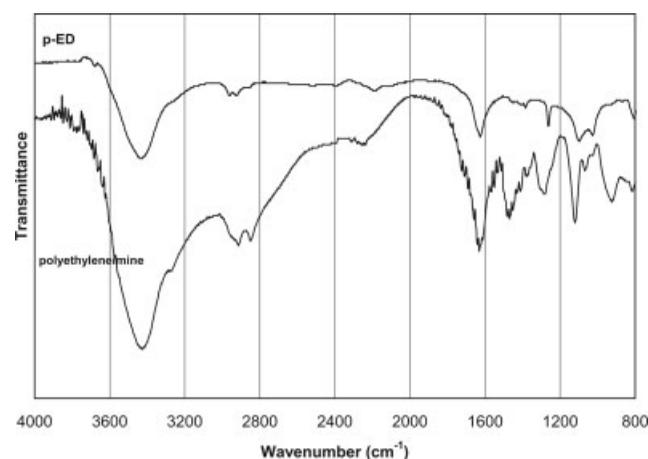
To investigate if primary amine groups are present in plasma-deposited films, two derivatization techniques were used. Chemical derivatization by 4-trifluoromethylbenzaldehyde (TFBA) provides a way of labeling the primary amine groups on the surface and evaluating their accessibility. A gas phase derivatization reaction with TFBA was carried out in a vacuum dessicator connected to a chemical reservoir. The des-

sicator was pumped after the substrate was placed inside and gas phase TFBA was introduced. The substrate was kept in TFBA atmosphere for 30 min and transferred to ESCA chamber for analysis. The fluorine concentration determined by ESCA analysis of a sample can be used to determine the concentration of reactive primary amine groups available on the surface. No fluorine was found on any of the samples deposited with ED, AN, and AcN plasma films. In another method, the samples were sprayed with 25 vol % fluorescamine solution in acetone and looked under an UV lamp (UBL 21 Black Ray UV-lamp, San Gabriel, CA). The surfaces exhibit fluorescence in presence of primary amines. In case of plasma-treated surfaces, no fluorescence was observed. Hence, the plasma treatments did not generate primary amine groups on the surface and the surface amines on plasma-deposited films are present in the form of secondary and tertiary amines.

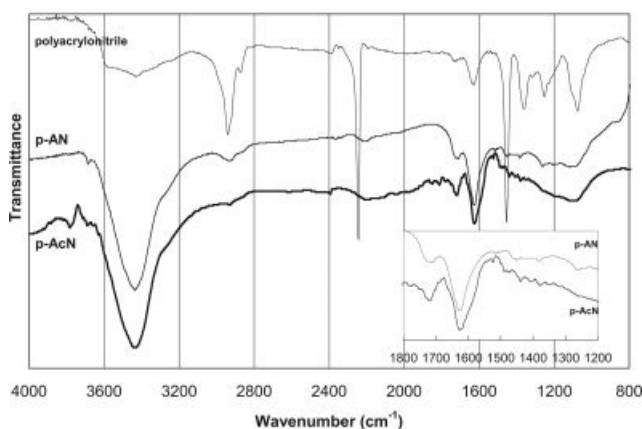
#### FTIR analysis

ESCA revealed that the plasma polymerized films have multiple functionalities dispersed in a macromolecular matrix. The surface chemistry of plasma polymerized films and conventionally synthesized polyethyleneimine and polyacrylonitrile were compared using FTIR. The absorption bands associated with several chemical linkages overlap resulting in broad and poorly resolved absorption peaks in the spectrum whereas regular polymers like polyethyleneimine and polyacrylonitrile have well-defined bands (Figs. 4 and 5). All the assignment to the peaks are done using available literature.<sup>27,28</sup> The minor differences in peaks of absorption peaks arise from crystalline structure of conventional polymers and the amorphous nature of plasma deposited films.

When comparing ED plasma polymerized (p-ED) films with linear polyethyleneimine ( $M_w = 25,000$ ,



**Figure 4** FTIR spectra of linear polyethyleneimine and plasma-polymerized ED (p-ED) film on KBr disk.



**Figure 5** FTIR of spectrum of polyacrylonitrile, AN-plasma film (p-AN) and AcN plasma film (p-AcN) on KBr disk.

Polysciences) in Figure 4, there are lot of similarities in the spectrum of the two compounds. The predominant characteristic bands for vibrations from polyethyleneimine at  $3430\text{ cm}^{-1}$  (N—H secondary amine stretching),  $1631\text{ cm}^{-1}$  (N—H secondary amine deformation),  $1122\text{ cm}^{-1}$  (C—N), and  $822\text{ cm}^{-1}$  (N—H wagging) were found in ED plasma films at  $3440$ ,  $1629$ ,  $1105$ , and  $810\text{ cm}^{-1}$ , respectively. The absence of two bands associated with primary amine groups reveal that the plasma fragmentation and recombination form amine groups only in form of secondary and tertiary amine functionalities. The band in the range of  $3300\text{--}3600\text{ cm}^{-1}$  in ED plasma was broad and can be accounted for absorption from amides in addition to amines. The presence of only one band in this region suggests the absence of primary amine groups in ED plasma films. Weak absorptions from hydrocarbons around  $2900\text{ cm}^{-1}$  were also found. However, some of the crystalline bands from polyethyleneimine powder are missing in ED plasma deposited film. The IR spectrum reveals that ED plasma films are very similar to linear polyethyleneimine structure.

The plasma-polymerized films from AN (p-AN) and AcN (p-AcN) are compared with polyacrylonitrile ( $M_w = 150,000$ , Sigma Aldrich) in Figure 5. The plasma polymers deposited from AN, and AcN are significantly different than polyacrylonitrile. The characteristic peak at  $2244\text{ cm}^{-1}$  from  $\text{C}\equiv\text{N}$  stretching vibrations in polyacrylonitrile appears as a weak band at  $2225\text{ cm}^{-1}$  in AN plasma films and is absent in AcN plasma. In the region  $1200\text{--}1800\text{ cm}^{-1}$  (inset), the peaks around  $1627\text{ cm}^{-1}$  can be attributed to combination of stretching vibrations of imine (C=N), N—H deformation frequencies of secondary amines, and C=O absorption in secondary amides. The bands around  $1520\text{ cm}^{-1}$  are characteristic of N—H deformation in secondary amides. The tertiary amine C—N stretch accounts for band at  $1260\text{ cm}^{-1}$  in AN

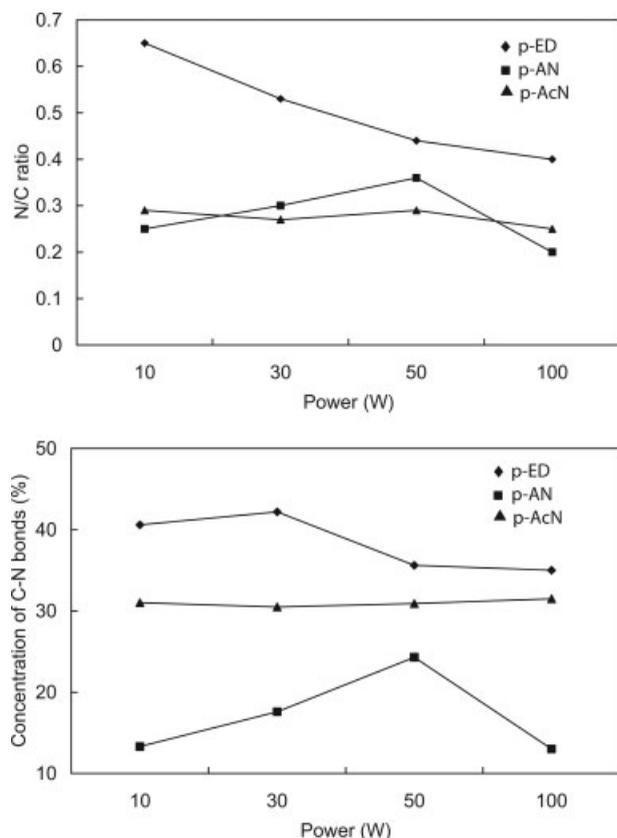
plasma polymer. The C—H deformation frequencies from methylene and methyne appear at  $1454$  and  $1367\text{ cm}^{-1}$ , respectively in all the spectra. These groups have very weak absorption bands for their stretching vibrations around  $2940$  and  $2880\text{ cm}^{-1}$  in plasma polymerized films. The peaks at  $3430\text{ cm}^{-1}$  are also very broad and result from N—H stretching of amines and amides or OH stretching in polymeric association. A shoulder at  $3650\text{ cm}^{-1}$  accounts for imine groups.<sup>29</sup> Hence, the plasma polymerized films from AN and AcN plasma are significantly different than polyacrylonitrile and have very few intact nitrile groups. Plasma-induced conversion through recombination of discharge-generated species that bear  $\text{—C}\equiv\text{N}$  functionalities into  $\text{—C=N—}$  containing structures make probably the changes in the p-AN and p-AcN structures relative to polyacrylonitrile. This process actually is significant because it opens up ways for the incorporation into the nascent plasma films of tertiary amine functionalities.

### Influence of RF power

The N/C ratios and the relative peak areas of component B relating to C—N bond in HR spectra represent the concentration of amine groups on the surface and are given in Figure 6 for ED, AN, and AcN plasma-polymerized films deposited at various discharge power. The frequency used for the power was  $13.56\text{ MHz}$  RF in continuous mode. The N/C ratio and the concentration C—N bonds in ED plasma were the highest at discharge power of  $30\text{ W}$ . The high N/C ratio but low C—N implies that ED molecules did not initiate polymerization process well at  $10\text{ W}$  and the crosslinking density of the films was low. With further increase in power, both N/C and C—N decreased because of rigorous fragmentation of ED into small molecules and possible decomposition on the surface. Hence, the optimum concentration of amine groups was in films deposited at  $30\text{ W}$ . In case of AN plasma, both N/C and C—N increase linearly with power up to  $50\text{ W}$  and decrease with further increase in discharge power. The higher powers can change the sticking factor of the films due to high substrate temperatures and resulting in compositional changes in the film. Unlike AN plasma, films deposited in AcN plasma did not show significant compositional trends with applied power. As the power was varied, the relative atomic compositions changed only slightly in AcN plasma and no trend was observed.

### Influence of RF Frequency

Low RF frequency of  $40\text{ kHz}$  in continuous mode and high RF frequency of  $13.56\text{ MHz}$  in continuous and pulsed modes were used to study the effect of



**Figure 6** Influence of RF power on N/C ratio and concentration of C–N bonds for ED (◆), AN (■), and AcN (▲) plasma-deposited films at 100 mTorr, 30 W, 13.56 MHz RF, 5 min.

RF excitation frequency of plasma power on surface chemistry. Pulsed RF plasma polymerizations have been studied for various monomers and have been reported to have improved chemistry control during film formation.<sup>30</sup> The differences in film chemistry arise because of changes in the concentrations of reactive intermediates and substrate bias potential during plasma-on and plasma-off times. To gain an idea of effects of pulsed plasma modes for all the monomers, the average power during the treatments was kept constant with continuous wave mode of plasma depositions. A power level of 30 W was chosen at 40 kHz and 13.56 MHz (continuous and pulsed) for plasma treatments. RF duty cycle (ratio of plasma-on

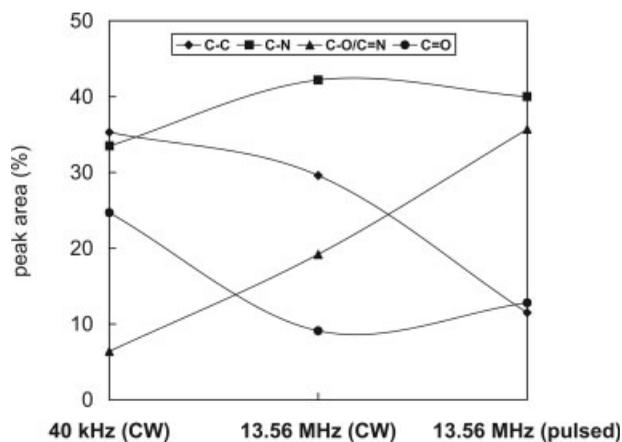
to plasma-off times) of 0.1 was used employing the peak power attained during plasma-on period to as high as 300 W. Such high powers can form free radicals in the plasma environment and initiate polymerization which can then continue during plasma-off times. From previous work<sup>31</sup> with saturated amines and cyano compounds,<sup>20,21</sup> the plasma-off times were selected to be 10 ms for ED plasma, and 50 ms for AN and AcN plasmas.

Table II represents the N/C and O/C ratios of the plasma films deposited under various conditions. It should be noted that there was significantly higher N/C and lower O/C concentrations associated with the films deposited at 13.56 MHz RF power. Figure 7 shows the composition of all carbon-related functional groups in ED plasma polymerized films as in high resolution C 1s spectra. In continuous plasma modes, there is slight increase in N/C ratio with increase in frequency. All peak area ratios corresponding to components B/A bond ratios are significantly higher in 40 kHz regime (1.0) than those of the samples treated at 13.56 MHz (1.4). This suggests that higher concentrations of amine (secondary and tertiary groups) functionalities are present on the surface of the films that are deposited at higher frequency. Also, there is decrease in concentration of carbonyl functionalities at higher frequency and thus, lower concentration of amide groups. This also indicates a more intense free radical-mediated surface oxygen uptake, under post-plasma, *ex situ* conditions at lower frequency. The increase in C–N concentration with frequency is symmetrical to the decrease in C=O and can be attributed to rigorous plasma-induced molecular fragmentation at 40 kHz. The component C in C 1s spectrum increased with frequency, though concentration of \*O–C groups in O 1s spectrum remain almost same. Therefore, the increased concentration of component C is ascribed to increase in C=N groups. Overall, there is an increase in carbon–nitrogen functionalities in the polymeric structure at higher frequency. This verifies that the plasma excitation frequency is an important parameter in plasma-assisted mechanisms. The parent molecule dehydrogenates intensely in 40 kHz regime resulting into dense populations of C–C whereas, the surface reactions are controlled by

**TABLE II**  
Relative Atomic Compositions of ED, AN, and AcN Plasma Polymerized Films at Different RF Power Conditions

Plasma gas	ED			AN			AcN		
	40 kHz cont.	13.56 MHz cont.	13.56 MHz pulsed	40 kHz cont.	13.56 MHz cont.	13.56 MHz pulsed	40 kHz cont.	13.56 MHz cont.	13.56 MHz pulsed
N/C	0.51	0.53	0.46	0.24	0.36	0.23	0.21	0.24	0.23
O/C	0.09	0.15	0.16	0.05	0.05	0.06	0.06	0.04	0.06

40 kHz cont., 13.56 MHz cont., and 13.56 MHz pulsed are the RF frequencies.



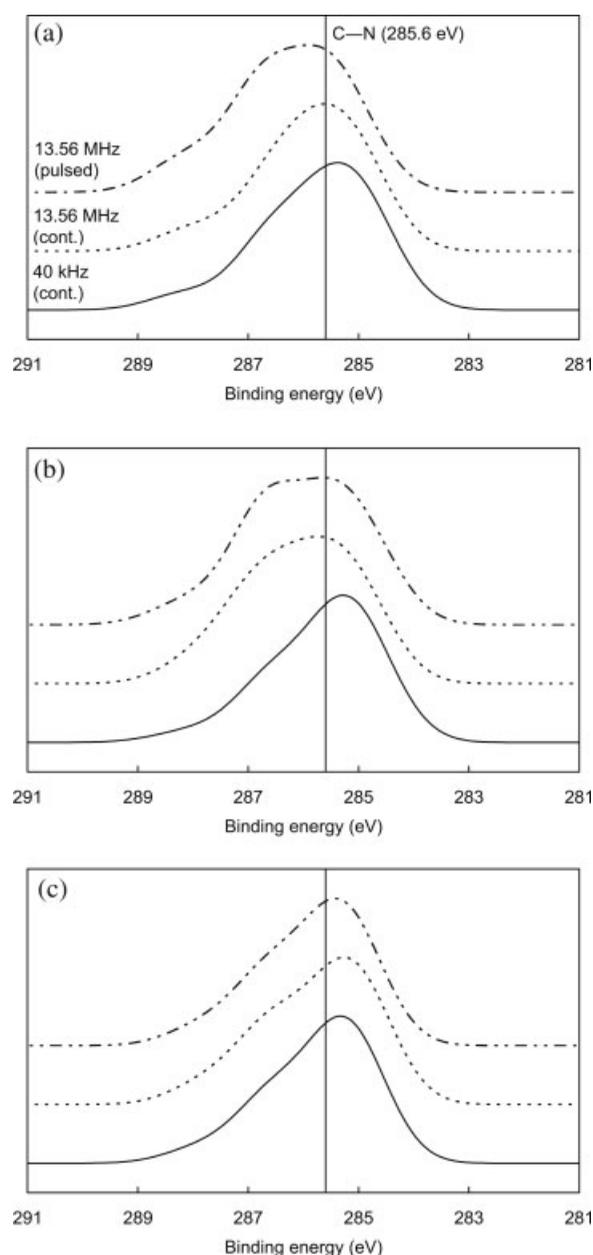
**Figure 7** Comparison of carbon-related functionalities (from C 1s ESCA peak) of ED-plasma deposited films on SS at 100 mTorr, 30 W, 40 kHz, 5 min [◆, C–C; ■, C–N; ▲, C–O/C=N; ●, C=O].

nitrogen-based free radicals in case of 13.56 MHz plasma treatments. Higher RF excitation frequency provides efficient dissociation of the gas, which forms plasma consisting of high ion flux and low ion energies.<sup>32</sup> The films so obtained by AN plasma had similar differences in compositions. But frequency had almost no effect on the plasma polymerization of AcN. So, the plasma-mediated dehydrogenation mechanisms also depend on the molecular architecture of gas forming plasma.

When comparing the continuous and pulsed plasma modes, the films deposited in ED plasma with RF frequency of 13.56 MHz at continuous and pulsed modes (duty = 10%) show similar elemental composition (N/C ratios same). There is a comparable increase in the component C in C 1s, decrease in amine functional groups in N 1s relative to other nitrogen containing groups, increase in percentage oxygen on the surface, and increase in oxygen-associated linkages (C=O). The pulsed-plasma deposition results in higher concentration of amide groups. This observation signifies that the chemistry involved in plasma polymerization process differs significantly during plasma-on and plasma-off times. There are significant higher steady state concentrations of reactive intermediates (ions, free radicals, atoms, etc.) during plasma-on periods with radical-radical type reactions being the dominant process. These reactive intermediates are consumed or quenched during plasma-off periods at either the surface of the growing film or with incoming neutral molecule changing the overall chemistry of the deposited structures.<sup>20</sup> In pulsed plasma, the fraction of low-energy ions in the ion energy distribution function increases, which leads to significant changes in the plasma chemistry. The pulsing with plasma-off periods in milliseconds range changes the sub-

strate bias and hence, competes with the impact of positive ions at high energies.<sup>30</sup> Also, the substrate heating is less pronounced in pulsed-plasma depositions than during continuous depositions under the same plasma conditions.<sup>33</sup> The films deposited in our laboratory reacted with contaminant oxygen during plasma-off periods resulting in higher concentration of oxygen-related functionalities. Thus, pulsing did not increase the retention of amine groups on the surface.

Figure 8 compares the high resolution C 1s peaks of plasma films around the peak of interest at 285.6 eV



**Figure 8** Comparison of HR C 1s ESCA spectra of SS treated with (a) ED, (b) AN and (c) AcN plasma at 40 kHz, 13.56 MHz (continuous and pulsed) RF powers.

corresponding to C—N (amine) functionalities. In case of AN-plasma-deposited films at 13.56 MHz RF power (continuous and pulsed modes); the nitrogen incorporated is more than the atomic percentage in the original monomer. The N/C ratio is 0.24, 0.34, and 0.4 in polymers deposited at 40 kHz RF, continuous 13.56 MHz RF, and pulsed 13.56 MHz RF power conditions respectively. The C 1s spectra are compared in Figure 8(b) and the peaks shift away from BE 286.5 eV. The IR spectra revealed the presence of nitrile groups. There is a decrease in C—N groups and a significant increase in C=N/C≡N functionalities. Gas phase radical attack can occur at both the vinylic carbon and the nitrile group forming imine functionalities or retaining the nitrile groups in the plasma polymerized acrylonitrile. The increase in the retention of nitrile groups in AN plasma at 13.56 MHz can possibly be explained by the chain growth polymerization taking place during the plasma-off times. The polymerization would occur at the vinylic double bond and could minimize the fragmentation of triple bond. The depositions at higher frequencies are characterized by bulky molecular fragments and are the reason for the higher concentration of nitrogen in the film. The results agree with the previous work done by Lefohn et al.<sup>20</sup> The plasma-deposited AcN films at various conditions had similar structures. When comparing the distribution of bonds in C 1s spectra (Fig. 8), the concentration of nitrogen containing moieties was same. There was only slight increase in nitrogen concentration at higher frequency and there was no effect of duty cycle (pulsing) on the structure of polymeric films. This implies that film formation proceeds under a similar mechanism in both CW and pulsed modes and that plasma-off time relaxation processes do not play a role in the deposition mechanism.

The thickness of the plasma films can play a significant role in the development of the reaction mechanisms. The absence of substrate-characteristic peaks in ESCA spectra allow to suggest that the films are thicker than 100 Å. Ellipsometric measurements for recording thickness were not performed due to the mixed nature of the film compositions and lack of required information on the films.

## CONCLUSIONS

The surfaces were successfully grafted with macromolecular thin films containing reactive amine groups. It is demonstrated that plasma polymerization of ED, AN, and AcN resulted in amine, imine, and amide groups in densely crosslinked macromolecular structures, and are significantly different than conventional polymers. The thin film depositions at 13.56 MHz resulted in higher concentrations of

C—N, and C=N bonds in ED, and AN plasma polymers. However, RF frequency or power does not significantly influence the composition of AcN plasma films. The pulsing of plasma in millisecond range led to decrease in C—N groups and increase in oxygen incorporation into the films. ED plasma polymerized films are richest in nitrogen and amine group concentrations. The results from this study can be used to coat surfaces with reactive amine groups with control on chemistry. The modified surfaces can be used to improve or modulate the interaction of a material in many systems. Further, we will use these plasma-polymerized films to synthesize quaternary ammonium groups with bactericidal properties on various metallic and polymeric surfaces. Hence, plasma surface functionalization allows for tailoring surface functionalities in a cost-effective, one-step way through dry-chemistry reaction processes.

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