

**Correlation of zeta potential and contact angle of oxygen and fluorine terminated nitrogen
incorporated ultrananocrystalline diamond (N-UNCD) thin films**

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Abstract

The surface chemistry of nitrogen incorporated ultrananocrystalline diamond (N-UNCD) films was altered by plasma treatment utilizing oxygen and fluorine plasma chemistries; the modified N-UNCD surfaces were characterized using contact angle and zeta potential measurements to give a more complete understanding of the interactions between the solid surface and the aqueous solution. The bonding character, surface composition, and morphology of the N-UNCD films before and after surface treatment were also monitored using X-ray photoelectron spectroscopy, atomic force microscopy, and Raman spectroscopy to ensure the grafting of functional groups; the contributing factor to the results was purely from the surface termination.

Keywords: zeta potential, contact angle, diamond, surface termination

1. Introduction

The hydrophilicity/hydrophobicity of a diamond surface could affect cellular adhesion, cellular proliferation, and the structure of the electric double layer.¹ Zeta potential measurements not only probe surface charge but also provide information on the isoelectric point (IEP) (the pH value of the solution in which the surface carries no net charge) and additional insight regarding the surface acidity or basicity. The goal of this study is to investigate the zeta potential, contact angle, bonding character, surface composition, and morphology of O- and F-terminated nitrogen incorporated UNCD coatings.

2. Material and methods

Nitrogen incorporated UNCD (N-UNCD) coatings were deposited on silicon wafers using 915 MHz microwave plasma chemical vapor deposition (Lambda Technologies, Morrisville, NC) with seeding pretreatment. The deposition was carried out at a substrate temperature of 850 °C with a gas mixture of methane, argon, and nitrogen gases (CH₄: 3 sccm, Ar: 160 sccm, N₂: 40 sccm) at a chamber pressure of 56 Torr and a microwave power of 2300 Watts. The resulting coating was composed of sp³ carbon with grain sizes of 5 to 10 nm and sp² carbon at grain boundaries as previously described.² Plasma treatment was performed using a reactive ion etcher (RIE, Oxford Plasmalab 80 Plus) to render oxygen (O-terminated) or fluorine (F-terminated) surface termination. The parameters for oxygen plasma treatment were as follows: 50 sccm O₂, working pressure of 35 mtorr and power of 100 W with a duration of 20 s. For fluorine plasma treatment, parameters were as follows: 25 sccm Ar, 25 sccm CHF₃, working pressure of 35 mTorr and power of 50 W with a duration of 30 s.

The hydrophilicity of the coatings was characterized by optical contact angle measurements (DataPhysics OCA200), which were carried out with distilled water using 0.2 mL droplets. Images were analyzed and calculated for contact angle with ellipse fitting of the droplet profile.

Zeta potential was measured using the streaming current method (SurPASS 3 Electrokinetic Analyzer), during which streaming current was evaluated as a function of pressure drop across the sample cell. The sample surfaces were probed with either aqueous 1 mM KCl solution, 0.05 M KOH solution to raise the pH, or 0.05 M HCl to decrease the pH to 3.

The zeta potential ζ is determined by the Helmholtz-Smoluchowski equation:

$$\zeta = \frac{dI}{dP} \frac{\eta}{\epsilon_r \epsilon_0} \frac{L}{A}$$

where dI is the differential streaming current, dP is the differential pressure drop, η is the solution viscosity, ϵ_r is the solution relative permittivity, ϵ_0 is the vacuum permittivity, L is the length of the streaming channel, and A is the cross-section of the streaming channel.^{3,4}

Raman spectroscopy measurements (Horiba Jobin Yvon LabRAM HR Evolution confocal micro-spectrometer) were performed utilizing laser excitation at a wavelength of 633 nm. Surface roughness was determined using atomic force microscopy (AFM, MFP-3D-Bio instrument); studies were tapping mode at a resonant frequency of 300 kHz under ambient conditions. X-ray photoelectron spectroscopy (XPS, SPECS FlexMod XPS) data were collected using Mg K α excitation (1254 eV) with a hemispherical analyzer (PHOIBIS 150). Energy calibration was established by referencing to adventitious carbon.

3. Results and discussion

XPS results from unmodified N-UNCD (Figure 1) showed 2.76 atomic percentage (at%) oxygen, which could be attributed to adsorption of oxygen from the air; O-terminated N-UNCD exhibited a much higher oxygen content of 16.21 at%. With fluorine termination, a distinct feature of 34.07 at% fluorine content was evident.

After confirmation of surface treatment using XPS, the surfaces were subject to contact angle measurements in which water drops at the age 5 s were reported for five replicate measurements for each sample. Figure 2 (a-c) show contact angle measurements of $87.2 \pm 0.3^\circ$ for unmodified N-UNCD, $27.8 \pm 2.3^\circ$ for O-terminated N-UNCD, and $100.4 \pm 1.2^\circ$ for F-terminated N-UNCD. Oxygen plasma treatment rendered the surface hydrophilic while fluorine plasma treatment rendered the surface more hydrophobic; these results are consistent with the literature.^{5,6}

Since plasma treatment may affect the surface conductivity, streaming current measurements were adopted, which is more appropriate than the streaming potential method for conductive surfaces.^{3,4} However, streaming current measurements are dependent on the sample surface area, and hence surface roughness is an important factor to consider. Herein, the use of N-UNCD with low surface roughness could alleviate the concern. A chart showing zeta potential versus pH value was shown in Figure 2 (d). At pH 10, O-terminated N-UNCD exhibited less negative zeta potential (-61.6 mV) than unmodified N-UNCD (-71.0 mV) while F-terminated exhibited most negative value (-98.4 mV). On the other end, the zeta potential of unmodified N-UNCD turned positive (0.3 mV) while both F-terminated (-4.2 mV) and O-terminated (-21.3 mV) N-UNCD were still negative at pH 3. The negative zeta potentials indicated that electron transfer occurred from aqueous solution to N-UNCD or ionization of oxygen-containing groups on the surface.⁷ Although IEP was not reached for O-terminated and F-terminated N-UNCD at pH 3, the trend of the curve suggested that the IEP in the sequence of unmodified, F-terminated, and O-terminated with unmodified N-UNCD the highest.

As demonstrated in Figure 3 (a-c), the Raman spectra of all N-UNCD samples exhibited major D and G bands centered at 1350 cm^{-1} and 1580 cm^{-1} , respectively, which represent a breathing mode of A_{1g} symmetry and in-plane bond-stretching motion of pairs of C sp^2 atoms with E_{2g} symmetry.⁸ The ratio of intensity (I_D/I_G) ranged from 1.35 to 1.37. A minor peak was observed at 1144 cm^{-1} , associated with

trans-polyacetylene at grain boundaries.⁹ The diamond T_{2g} peak at 1332 cm⁻¹ was not observed due to the low scattering cross-section of sp³ bonding under visible laser excitation compared to sp² bonding, which resulted in screening of the diamond T_{2g} peak by D band.¹⁰ The results were consistent with our previous studies on N-UNCD films.¹¹ The similarity between the three samples also indicated that the observed change in zeta potential originated from the surface chemistry instead of the contribution from the bulk material.

Since zeta potential is an interfacial property of the solid-liquid interface, surface roughness is considered to play a role in solid-liquid interactions, which can affect the water contact angle and subsequent surface charge-counterion interactions. Representative AFM images are shown in Figure 3 (d-f); root-mean-square (RMS) values of the surface roughness based on 10 μm x 10 μm scans were 3.94 nm for unmodified N-UNCD, 6.22 nm for O-terminated N-UNCD, and 5.55 nm for F-terminated N-UNCD. This minor change in roughness was attributed to plasma-induced etching of UNCD. The results suggested a similarity in morphology; as such, a fair comparison of zeta potential can be made.

Considering the zeta potential values of the three surface terminations, a more negative zeta potential throughout most of the pH range was observed for O-termination and F-termination compared with unmodified N-UNCD; this result could be due to the higher electron affinity of the two modified surfaces and deprotonation of carboxyl and hydroxyl groups.¹² However, the zeta potential of O-terminated N-UNCD plateaued and became less negative than the unmodified N-UNCD at around pH 8; F-terminated N-UNCD still exhibited the most negative zeta potential. When investigating the zeta potential of chemically modified low-density polyethylene, Temmel *et al.* observed that an increased magnitude of zeta potential at high pH values correlated with increased hydrophobicity; they suggested that hydrophobic surfaces increased anion (e.g., hydroxide) adsorption in aqueous solution, which was

preferential to water or cation (e.g., hydronium) adsorption¹³. Kudin and Car investigated the mechanism of preferential hydroxide adsorption onto hydrophobic surfaces with molecular dynamics simulations¹⁴. These results were consistent with our observations of zeta potential at different pH values (Figure 3), in which the relative zeta potential ordering at high pH values indicates that O-terminated N-UNCD was the most hydrophilic surface and F-terminated UNCD was the most hydrophobic surface. XPS was not able to reflect the phenomenon of preferential adsorption because the measurements were conducted under ultra-high vacuum conditions.

4. Conclusions

The surface morphologies of the N-UNCD coatings with various surface chemistries were similar before and after plasma treatment. O-termination rendered the surface hydrophilic and more negatively charged due to an increase in oxygen-containing groups but shifted the zeta potential to less negative values at high pH; it was less sensitive to changes in pH. F-termination rendered the surface more hydrophobic; it shifted zeta potential to more negative values because of preferred hydroxide adsorption as opposed to unmodified N-UNCD, and experienced a more significant change of zeta potential across the pH range.

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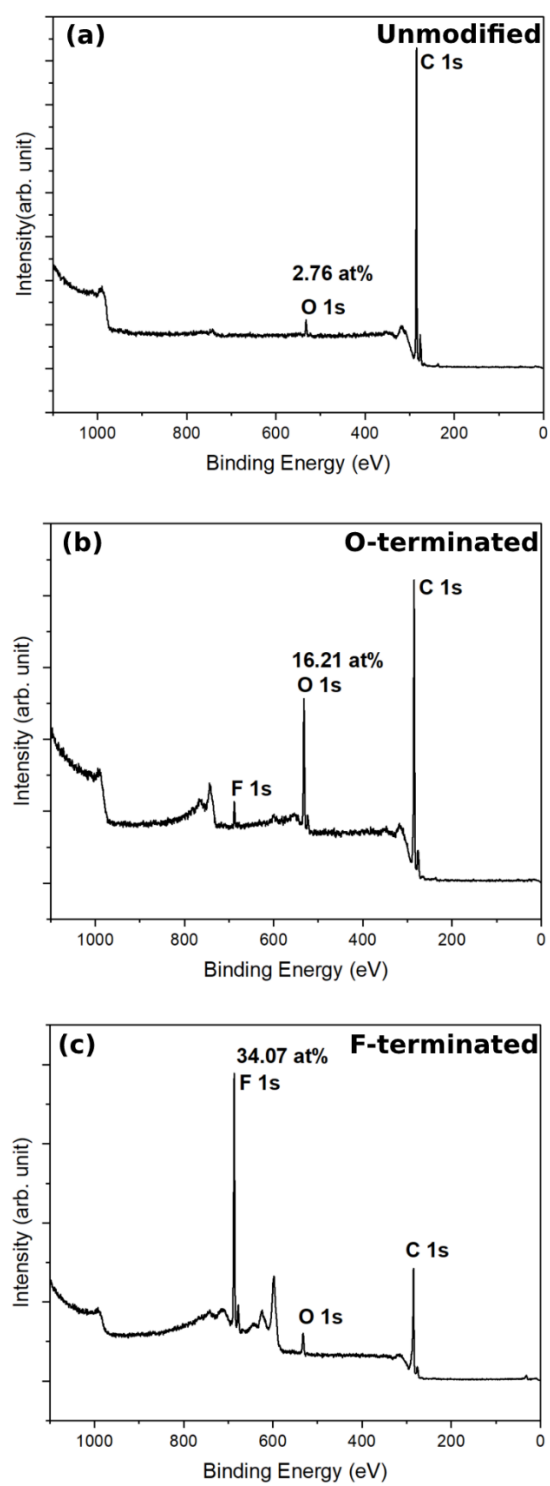


Figure 1. XPS of (a) unmodified, (b) O-terminated and (c) F-terminated N-UNCD surface.

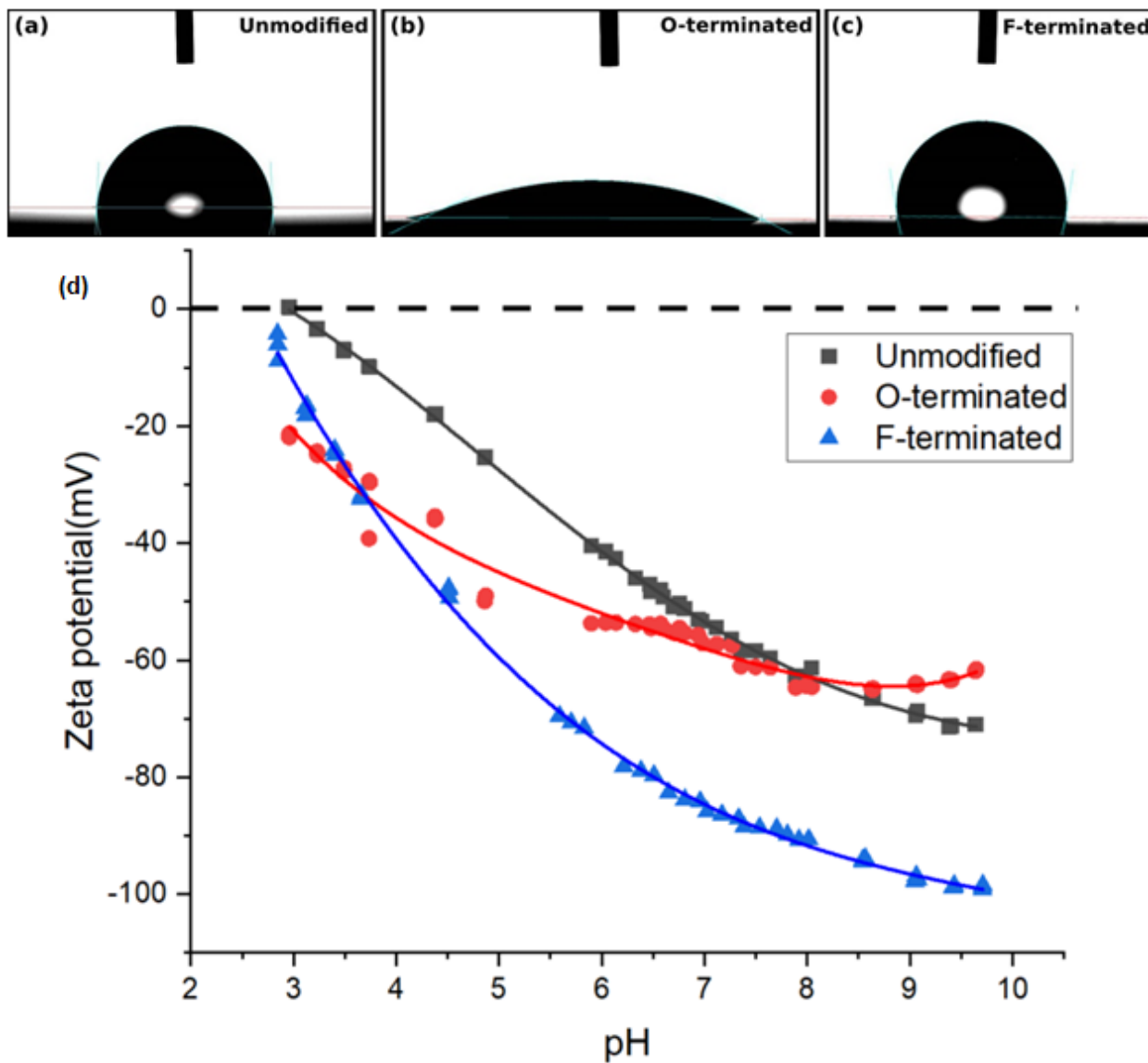


Figure 2. Water contact angle of (a) unmodified, (b) O-terminated, and (c) F-terminated N-UNCD surface.

(d) Zeta potential of unmodified, O-terminated, and F-terminated N-UNCD sample from pH 10 to pH 3 by streaming current method.

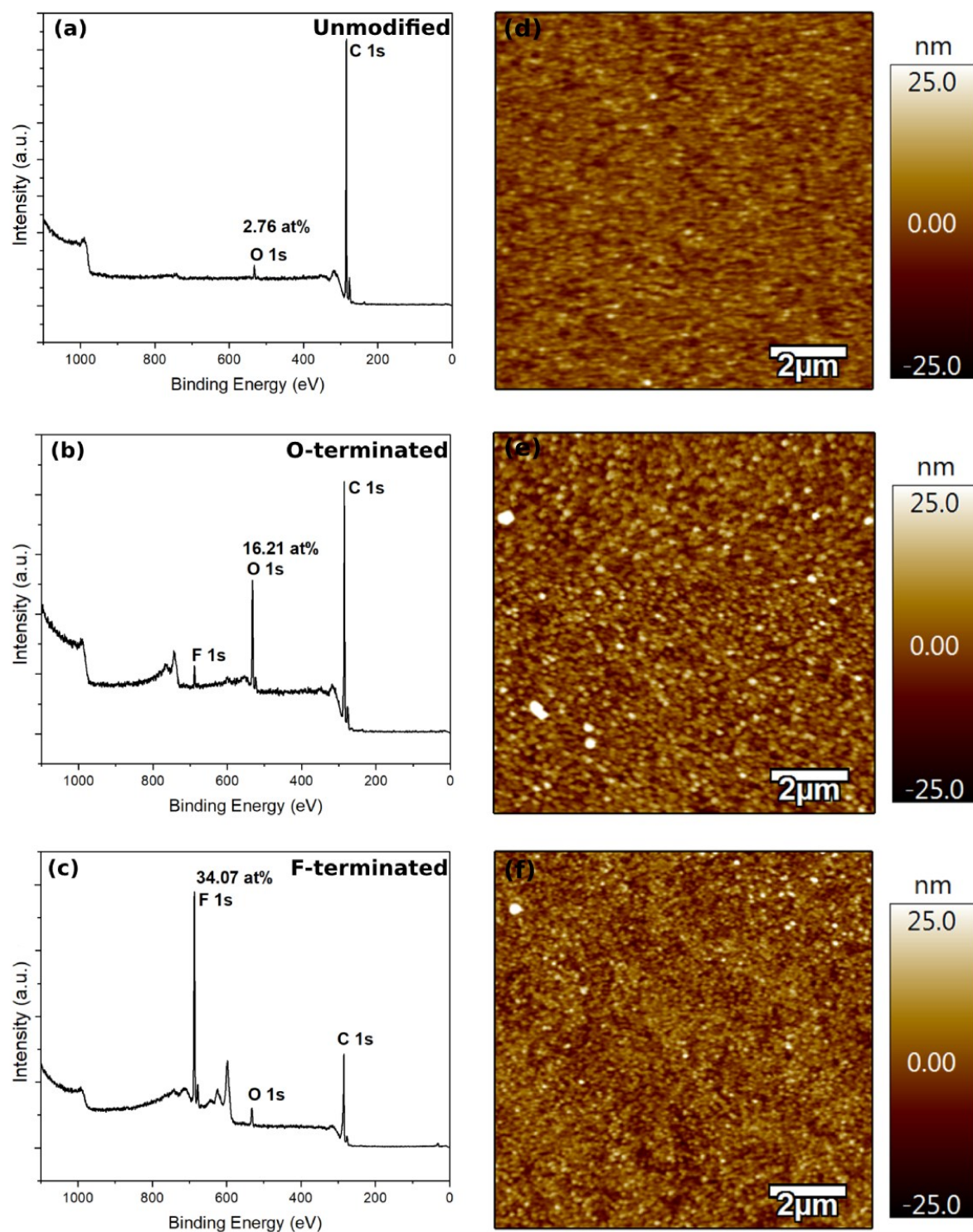


Figure 3. Raman spectra of (a) unmodified, (b) O-terminated, and (c) F-terminated N-UNCD and AFM images of (d) unmodified, (e) O-terminated, and (f) F-terminated N-UNCD.