

# Confirming the Hydrogenation of Diamond Films Using X-ray Photoelectron Spectroscopy (XPS)

## Introduction

Diamond films have been utilized in the fields of biosensors, ion-sensitive field effect transistors and electrochemical sensors.<sup>1</sup>

The surface termination of a diamond influences its properties; hydrogen-terminated and oxygen-terminated diamond surfaces behave as p-type conductors, and electrical insulators, respectively. This transition between hydrogen termination and oxygen termination at the surface is both manageable and reversible.

Oxygen-terminated diamond surfaces are produced using techniques including, but not limited to, contact with oxygen plasma or boiling oxidizing acid, cathodic treatment or UV/ozone treatment.<sup>2</sup>

Hydrogen-terminated surfaces have conventionally been produced using monatomic hydrogen, with one of the following:<sup>3</sup>

- Plasma techniques, which can lead to unwanted etching of the diamond film.
- Hot filament techniques, which can lead to contamination of the diamond film through deposition of material from the filament.
- Electrochemical techniques, however this can only be used to achieve hydrogenation of electrically conductive diamond films.

Diamond film hydrogenation has also been achieved using molecular hydrogen, through the exposure of diamond surfaces to H<sub>2</sub> at elevated temperatures (>500°C) under vacuum conditions.<sup>4</sup> However the operational constraints of high vacuum limit the degree to which hydrogenated diamond surfaces can be produced on an industrial scale using this technique.

Recently, the hydrogenation of chemical vapour deposited (CVD) diamond films at atmospheric pressures using H<sub>2</sub> has been achieved at the Delft University of Technology in collaboration with Hasselt University,<sup>5</sup> increasing the feasibility of producing hydrogenated-diamond films on an industrial scale. X-ray Photoelectron Spectroscopy (XPS), performed with the Thermo Scientific™ K-Alpha™ XPS system, has been used to compare the surface chemical composition of the diamond film hydrogenated using molecular hydrogen (H<sub>2</sub>-treated) with diamond film hydrogenated using a more conventional monatomic hydrogen plasma technique (H plasma-treated). Spectra from a diamond film oxidized using UV/ozone (UV/ozone-treated) were also acquired for reference purposes.

## Experimental

Oxidation of the diamond films was achieved by UV/ozone treatment, performed under ambient conditions for approximately 4 hours. Diamond film hydrogenation by H-plasma treatment occurred in a plasma reactor at  $\sim 700^{\circ}\text{C}$  and 3500W for 5 minutes, hydrogenation by exposure to a flow of  $\text{H}_2$  was performed in a non-plasma quartz tube, reactor heated at  $\sim 850^{\circ}\text{C}$  for 20 minutes at ambient pressure and cooled to room temperature whilst maintaining a flow of  $\text{H}_2$ .

C 1s core level and valence band spectra of undoped nanocrystalline diamond films, grown on quartz by CVD method and exposed to ambient conditions for several days, were acquired using Al K $\alpha$  X-rays with a spot size of  $400\mu\text{m}$ , in conjunction with the patented K-Alpha charge compensation that was utilized during the acquisition of all spectra. C 1s core level spectra were acquired at a pass energy (PE) of 50 eV, with a step size of 0.1 eV and 10 repeat scans used. Additionally, valence band spectra were acquired from undoped nanocrystalline diamond films after oxidation by UV/ozone treatment and hydrogenation by exposure to  $\text{H}_2$ .

## Results

Processing and analysis of acquired XPS spectra was performed using Thermo Scientific™ Avantage™ software. Background correction of the C 1s core level spectra used the “Smart” base line subtraction function and the corrected profiles fitted to 70/30 Gaussian/Lorentzian convolution peak(s). Qualitative comparison of the fitted C 1s spectra shows a marked similarity between the hydrogenated diamond films prepared by H-plasma treatment (Figure 2) and  $\text{H}_2$ -treatment (Figure 3), whereas the UV/ozone treated film spectrum (Figure 1) differs in appearance with fitted components that can be attributed to oxidized carbon at  $\sim 286.5$  and  $\sim 288$  eV, most likely C-O and C=O respectively. Fitted peaks at 284 and 285 eV, indicative of C-C bonding and referred to as “Peak A” and “Peak B,” were observed in all three samples. Differing ratios of Peak A to Peak B between the oxidized diamond film (UV/ozone-treated, Figure 1) and hydrogenated diamond films (H plasma-treated and  $\text{H}_2$ -treated, Figure 2 and Figure 3) were attributed to an increase in the energy barrier for electron emission in the oxidized sample, by the researchers who created the  $\text{H}_2$ -treated films.<sup>5</sup>

A small oxidized component is still present in the C 1s spectra of the hydrogenated films, which could be attributed to partial oxidation of the diamond on exposure of the films to ambient conditions. Additionally, the presence of a small Peak A component in the spectrum of the oxidized film indicates that full oxidation does not occur, possibly due to roughened areas that are not fully exposed to ozone during treatment, whereas the inverse is true for the hydrogenated films.

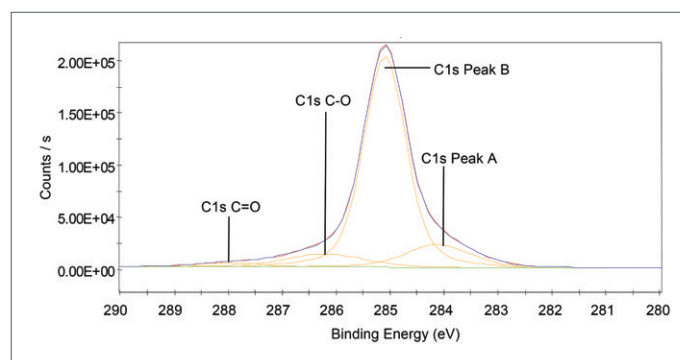


Figure 1: UV/ozone-treatment C 1s scan. 10 scans, 1 m 35.5 s,  $400\mu\text{m}$ , CAE 50, 0.10 eV.

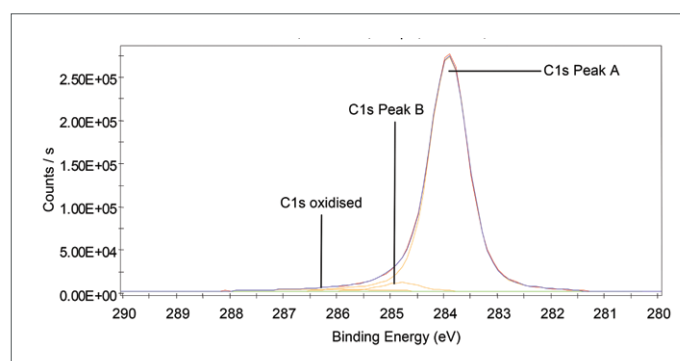


Figure 2: H-plasma treatment C 1s scan. 10 scans, 1 m 35.5 s,  $400\mu\text{m}$ , CAE 50, 0.10 eV.

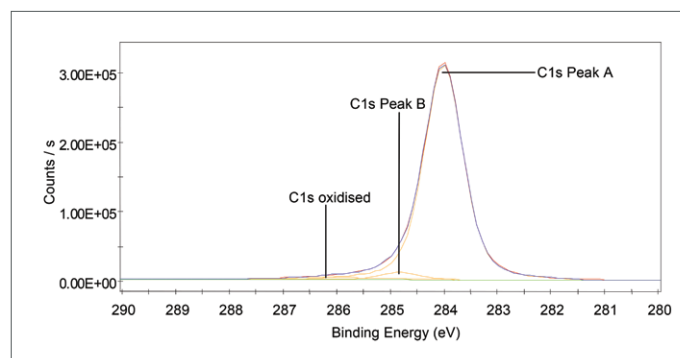


Figure 3:  $\text{H}_2$ -plasma treatment C 1s scan. 10 scans, 1 m 35.5 s,  $400\mu\text{m}$ , CAE 50, 0.10 eV.

Valence band spectra of oxidized and hydrogenated films, undoped nanocrystalline diamond films, as shown in Figure 4 and Figure 5 were also acquired and compared qualitatively. It is observed that spectra from the hydrogenated films are shifted to a lower binding energy by approximately 1.0-1.5 eV in comparison with the oxidized films. Additionally a decrease in the intensity of the peak at ~25 eV, assigned as photoemission signal from the Oxygen 2s orbital by the researchers who performed this work,<sup>6</sup> is observed in the hydrogenated films.

## Summary

The surface chemical composition of diamond films hydrogenated using a novel, ambient pressure, treatment involving H<sub>2</sub> gas has been investigated using XPS and comparisons with a hydrogenated film prepared using a conventional H-plasma treatment made. Comparison with UV/ozone treated diamond films indicates that oxidized carbon species are removed and/or reduced during H<sub>2</sub>-treatment. No discrepancies in the C 1s core level spectra of these films were observed, demonstrating the validity of H<sub>2</sub>-treatment as a technique for diamond surface hydrogenation that can be performed at ambient pressure. The effect of band bending was also observed within the valence band spectra.

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## References

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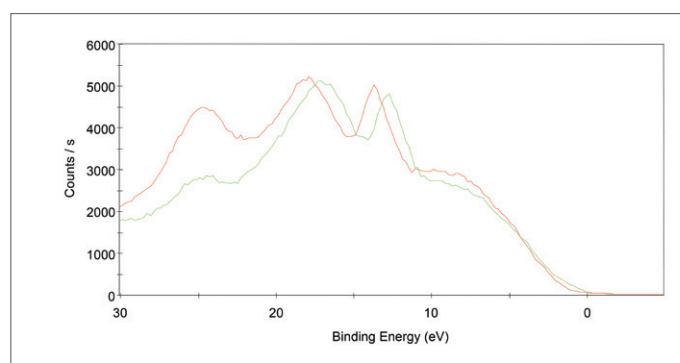


Figure 4: Valence band spectra of UV-treatment (red) H-plasma treated (green) 175nm thick diamond films. 50 scans, 70 m 20.0 s, 400  $\mu$ m, CAE 100, 0.20 eV.

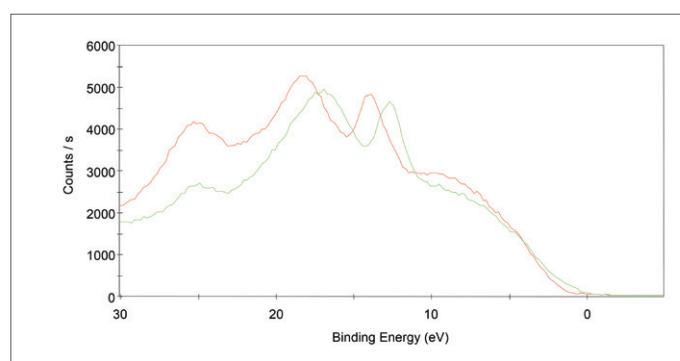


Figure 5: Valence band spectra of UV-treatment (red) H-plasma treated (green) 115nm thick diamond films. 50 scans, 70 m 20.0 s, 400  $\mu$ m, CAE 100, 0.20 eV.

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