Spectroscopic Characterization Of RF Hydrocarbon Plasmas For DLC Coatings

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Abstract. In previous experiments, using a RF plasma generator at low power, we have grown diamond like carbon films (DLC), using a hydrocarbon plasma, without the use of a catalyzer precursor[1]. In order to better understand the relationship between the properties of the resulting DLC films and the RF plasma parameters, we have performed detailed optical emission spectroscopy (OES) observations of RF hydrocarbon plasmas, under identical conditions to those used for DLC films growth. The experiments were performed in a low power capacitively coupled RF (13.6 MHz) plasma generator, operating at 30 W. Working gases were acetylene and hydrogen. The optical emission of the RF plasma was recorded, under different operational conditions, with a spectrometer, and an f-f light collection arrangement was used to achieve spatial resolution. The relative emission of the different molecular species was found to depend on the C\textsubscript{2}H\textsubscript{2}:H\textsubscript{2} flow ratio. Based on the OES observations, we present a description of plasma conditions in a low power RF hydrocarbon plasma reactor.

1. Introduction
Radio frequency (RF) plasmas are widely used to grow different kinds of carbon coatings with sub-micron size characteristic features and varied structural properties [2], which depend on the structural order and the micro/nanostructure of the coatings [3]. Carbon spheres can be produced with control in crystallinity and diameter [4], allowing a wide spectrum of applications. Carbon spheres have been synthesized with different methods including chemical vapour deposition (CVD), pyrolysis of hydrocarbons [5], and plasma enhanced chemical vapour deposition (PECVD). In most of the cases the studies aim to produce large amounts of carbon spheres, with low spread in sizes. As opposed to other methods [4, 5, 6], growing of carbon spheres using PECVD in RF plasmas often requires the use of a catalytic agent. Moreover, when produced in RF plasmas, carbon spheres are collected upon deposition over the chamber floor, or over a heated Si substrate. In order to overcome the use of a catalyst and to improve on the collection capability, we have investigated the formation of carbon spheres using a RF hydrocarbon plasma, produced with mixtures of acetylene and hydrogen, at different mixing ratios. In Plasma-Based Ion Implantation and Deposition (PBII&D) [7] a target sample is surrounded by a plasma and pulse biased to a high negative potential relative to the chamber.
Ions generated in the surrounding plasma are accelerated across the sheath formed around the sample and implanted normally into the surface of the targets. We have used the PBII&D technique to study the formation of micro/nanostructured a-C:H layers of sub-micron size carbon spheres on a silicon (100) substrate, without substrate heating, and in the absence of any template or catalyzer. The films have been characterized using a variety of different diagnostics, including atomic force microscopy (AFM) and scanning electron microscopy (SEM). In order to understand better the relationship between the properties of the resulting DLC films and the RF plasma parameters, we have performed detailed optical emission spectroscopy (OES) observations of RF hydrocarbon plasmas, under identical conditions to those used for DLC films growth. The identification of different molecular species in the C$_2$H$_2$ discharge plasma spectra, and their evolution as a function of the C$_2$H$_2$/H$_2$ mixing ratio is analyzed in the context of the structural and morphological properties of the DLC films.

2. Experimental details

The DLC deposition experiments were performed in a low power, capacitively coupled RF (13.6 MHz) plasma generator, operating at 30 W. The electrode assembly consists of stainless steel plates separated 7 cm. The anode, top plate, is 10 cm in diameter, and the water cooled cathode, bottom plate, is 8 cm in diameter. Working gases are acetylene and hydrogen. The flow rate of acetylene is fixed at 3 sccm, and the flow of hydrogen is varied to obtain 1:0, 1:2, 1:4, 1:8 and 1:10 C$_2$H$_2$:H$_2$ flow ratios. A schematic of the experimental set-up is shown in figure 1. Due to the high asymmetry of the electrodes, a negative dc bias is induced in the power electrode, of the same magnitude as the applied RF voltage, which results in a plasma potential of a few volts, which favours application of the PBII&D technique. These conditions reduce sputtering and surface etching, which are known to be strong at high values of the plasma potential [8]. Plasma potential, electron density and electron temperature, were measured, from the $I - V$ characteristics of a RF-compensated Langmuir, in inert gases like argon and helium, at equivalent operational conditions. Further details on the experimental arrangement have been published elsewhere [1].

![Figure 1. Schematic of the experimental setup.](image1)

![Figure 2. Characteristic substrate biasing pulse.](image2)
The plasma potential was measured to be less than 30 V, the electron temperature was between 1 and 3 eV, and the electron densities between $10^9$ and $10^{10}$ cm$^{-3}$, for RF powers below 100 W [9]. Direct measurements in the acetylene RF plasma were not reliable due to fast contamination of the probe surface. The optical emission of the RF plasma was recorded, under different operational conditions, with a SpectraPro 275 spectrometer, using a 1200 grove/mm grating, using a 30 ms integration time. The PBII&D power supply is based on two HV IGBT’s driving two transformers, which are discharged in series, to produce a negative short pulse of 30 kV, 2 s max width, at a 2 kHz rate, 400 ns rise time. These short pulses are known to improve the conformal implantation by decreasing the width of the plasma sheath. The voltage was measured with a high voltage probe and the current was measured with an optically coupled isolator phototransistor. A characteristic 4 kV voltage signal, corresponding to substrate biasing used throughout this experiments, is shown in Fig.2. The depositions were carried out on mirror-like polished silicon substrate of (100) orientation and 500 $\mu$m thickness. The substrates were positioned in an off-axis configuration, away from the main discharge plasma to reduce irradiation damage from the plasma. The deposition time was 30 min.

3. Results and discussion

Figure 3 shows SEM images of the DLC films under different C$_2$H$_2$:H$_2$ mixing ratios. The surface morphology is dominated by carbon spheres, with characteristic diameter below 1 $\mu$m. The size and size distribution is seen to depend on the C$_2$H$_2$:H$_2$ ratio. Measurements of rms roughness, made with an AFM microscope in tapping mode, showed characteristic values ranging from 170 nm up to a deep minimum of $\sim$3 nm, at a mixing ratio of C$_2$H$_2$:H$_2$=1:2 [1].

![SEM images of DLC films](image)

Figure 3. SEM images of DLC films obtained with, a) pure acetylene, b) 1:4, and c) 1:8 C$_2$H$_2$:H$_2$ mixing ratios.

Figure 4 shows OES spectra of the hydrocarbon plasma for different C$_2$H$_2$:H$_2$ mixing ratios. In addition to atomic hydrogen, prominent molecular emission from H$_2$, CH, C$_2$ and C$_4$H$_2^+$, among other active radicals, is clearly identified. This identification is noteworthy, as during the processes of DLC deposition, neutral hydrocarbon species are considered to be important precursors for film growth [10]. Additionally, C$_2$ dimer is known to play a significant role in the formation of nanodiamond films [11]. On inspecting the hydrocarbon spectra, a general and expected trend to be noticed is the increase in the intensity of atomic hydrogen emission as the hydrogen content of the hydrocarbon plasma increases. It is also observed that no molecular hydrogen emission band are observed when pure acetylene is used. In order to visualize the effect of the hydrogen content, figures 5 and 6 show the dependence of the molecular emission intensity, as a function of the C$_2$H$_2$:H$_2$ mixing ratio, for different radicals, as identified in figure 4. The rms roughness of the DLC films increases sharply as the mixing ratio becomes bigger that 1:4. On comparing with figures 5 and 6, this increase coincides with a decrease in the relative intensity of molecular emission lines. It can then be inferred that a low roughness is favored by a higher content of active hydrocarbon radicals in the RF plasma. Carbon films can be characterized in terms of the dominant C-bondings, ranging from a material with 100% sp$^2$ sites (graphite) to a material with $\sim$100% of sp$^3$ sites (defected diamond). Raman analysis of the resulting carbon films indicate that the increase in the flow of hydrogen move the sp$^3$
content to a lower values [9], which is in agreement with the literature, where the use of ion implantation cause the conversion of sp$^3$ bonds to sp$^2$ bonding [12]. Here, a combination of high content of hydrogen ions in the RF plasma, together with the negative high voltage biasing of the substrate, can explain the observed tendency to a higher graphite–like structure at higher hydrogen mixing ratios.

![Figure 4](image)

**Figure 4.** Characteristic emission spectra of the RF plasma obtained with, a) pure acetylene, b) 1:2, and c) 1:4 C$_2$H$_2$:H$_2$ mixing ratios.

![Figure 5](image)

**Figure 5.** Dependence of CH and C$_4$H$_7^+$ molecular emission intensity, as a function of the C$_2$H$_2$:H$_2$ mixing ratio.

![Figure 6](image)

**Figure 6.** Dependence of C$_2$ molecular emission intensity, at two different wavelengths, as a function of the C$_2$H$_2$:H$_2$ mixing ratio.

4. Conclusions
OES has been used to characterize a low power C$_2$H$_2$:H$_2$ RF plasma under different conditions of the flux ratio, in relation with nanostructured DLC film deposition, using PBII&D technique.
Detailed emission spectra have been obtained, which allowed several active species in the RF plasma to be identified, including neutrals, ions and active radicals. A qualitative correlation between DLC film composition and roughness with plasma composition has been established. Further analysis of the spectral information is being performed in order to establish better quantitative correlations with the resulting DLC films.

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5. References
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