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## Development of a novel hydrogen probe for plasma characterisation and control during diamond film deposition

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# Quantitative measurements of atomic hydrogen during the deposition of diamond-like carbon films

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## Abstract

Measurements of the level of atomic hydrogen in a 13.56 MHz rf plasma have been obtained during the deposition of DLC films. Two techniques were used, firstly a multi-photon laser induced fluorescence (MPLIF) system and secondly a novel combination of Langmuir probe and emission spectroscopy. In the latter technique the data obtained from electron energy distribution functions (EEDF's) and hydrogen emission line intensities are combined using a computer modelling technique to give the atomic hydrogen concentration. This system can potentiality be used as a portable atomic hydrogen probe. The results obtained were compared with those obtained using the MPLIF technique which in turn can be calibrated using a hydrogen transfer standard which is calibrated by a titration technique.

The two techniques have been used to measure atomic hydrogen, initially in a hydrogen plasma and subsequently in acetylene/hydrogen containing plasmas during the deposition of DLC films. In conjunction with these measurements *in-situ* ellipsometry was used to obtain film thickness, refractive indices and extinction coefficients. A correlation has been obtained relating the concentration of atomic hydrogen with the in-situ ellipsometry data for films with reflective index between1.6 and 2.1 (at 675 nm).

## 1. Introduction

The concentration of' atomic hydrogen in plasmas used to deposit diamond and diamond like carbon (DLC) coatings has been shown to have an important influence on film quality [1, 2]. One feature of atomic hydrogen is that it preferentially etches graphitic as opposed to diamond like layers. Thus control of the atomic hydrogen concentration would facilitate optimisation of coating performance. The first step in atomic hydrogen concentration control is to determine the degree of hydrogen dissociation in a plasma. Hydrogen dissociation is determined using Multi Photon Laser Induced Fluorescence (MPLIF). In addition, an alternative method based on electrostatic probe measurements and emission spectroscopy is described,

Quantitative measurements of atomic hydrogen density are difficult to make. Density cannot be calculated from emission spectroscopic data alone, because account must be taken of the possible non-thermal electron energy distribution in the plasmas when considering excitation from the hydrogen ground state by electron bombardment. Direct resonant fluorescence measurements from the hydrogen ground state are also difficult because of the vacuum-W source and optics required. The problems associated with direct resonant fluorescence measurements may be overcome by using Multi Photon Laser Induced Fluorescence (MPLIF) which allows operation with excitation in the mid-UV, and detection in the visible and is suited to determination of atomic hydrogen densities in the deposition environment. In addition to MPLIF data results obtained from a second and novel technique combining Langmuir probe and emission spectroscopy is also reported. The Langmuir probe is used to determine the electron energy distribution function (EEDF) which is combined with the emission spectra to compensate for the non-thermal EEDF and so allow calculation of the degree of hydrogen dissociation. In this paper the project results are broadly divided into four separate sections. The first section deals with DLC film deposition and characterisation. The next two sections outline the MPLIF and Hydrogen Probe techniques for quantitative atomic hydrogen determination. The final section correlates the atomic hydrogen measurements with DLC film quality.

## 2. DLC film deposition

DLC films were deposited in a 13.56 MHz and 40 kHz rf plasmas from a range of hydrocarbon/hydrogen reactant gas mixtures as indicated in table 2.1. Deposition was monitored using *in-situ* ellipsometry which measures refractive index (n), extinction coefficient and thickness during film growth. A range of films were deposited with refractive indices ($\lambda$ = 6'75 nm) in the range 1.6 - 2.25. Refractive index is an indirect measure of DLC film quality[3]. It is not necessary to quote extinction coefficient values as they are related to refractive index as shown in figure 1 The soft pale yellow films with indices below 1.6 were not found to have a Raman band at ca. 1540 $\text{cm}^{-1}$ and were considered to be polymeric films; in contrast the higher refractive index films were dark brown in colour, exhibited both high wear resistance and hardness.

**Table 2.1** *The parameter range studied for the deposition of DLC films during the course of this project.*

| Parameter | Range |
|---|---|
| Pressure | 0.002-7 Torr |
| Power | 7-115 W |
| Rf frequency | 40 kHz & 13.56 MHz |
| Acetylene | 0-100 seem |
| Methane | 0-200 seem |
| Butadiene | 1-55 seem |
| Hydrogen | 0-900 seem |
| Other gasses | Ar |

The effect of pressure and power on refractive indices of films produced are presented in figures 2 and 3. Refractive index was observed to decrease with pressure from 0.4 to 1 Torr and to increase with rf power from 15 to 30 Watts (Figure 3). Refractive indices of up to 2.25 were obtained for films at both 40 kHz and 13.56 MHz.

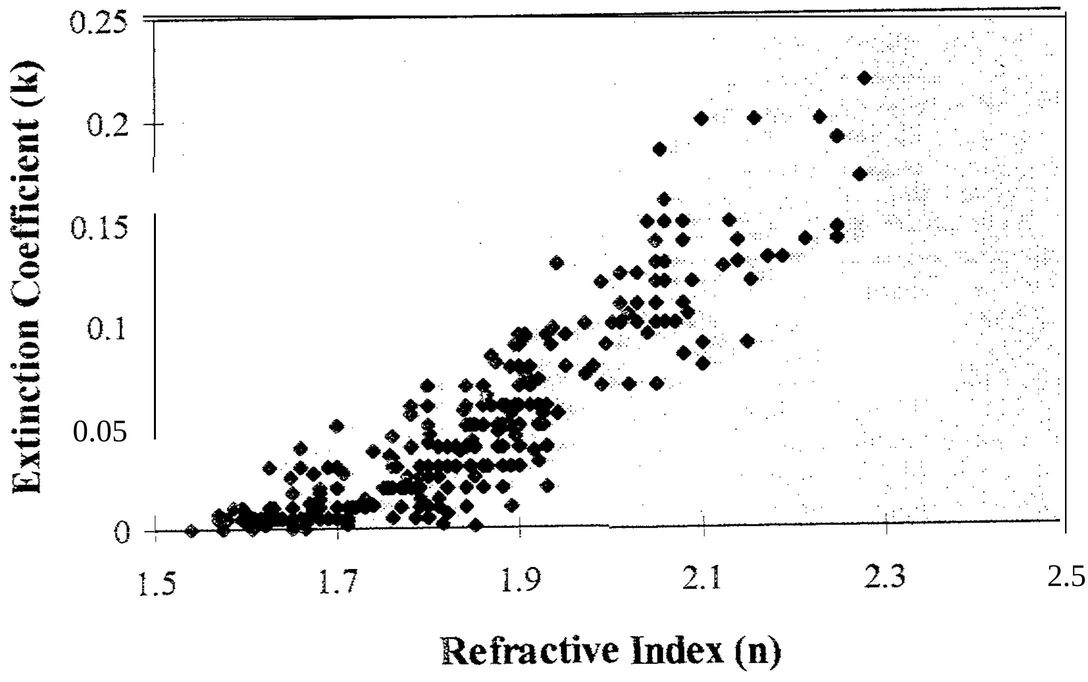


**Figure 1** *The correlation between refractive index (n) and extinction coefficient (k) for over 300 DLC films deposited in the parameter range indicated in table 3.1.*

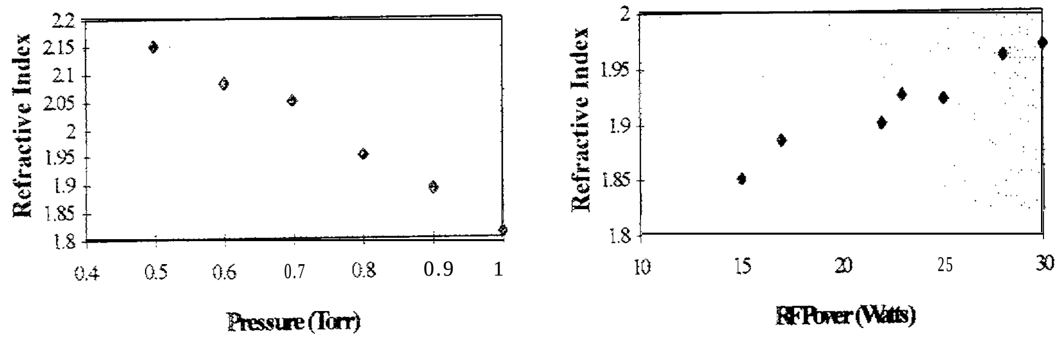


**Figure 2** *The influence of pressure and* power *on refractive index of films produced with a 40 kHz discharge in methane/hydrogen plasmas*

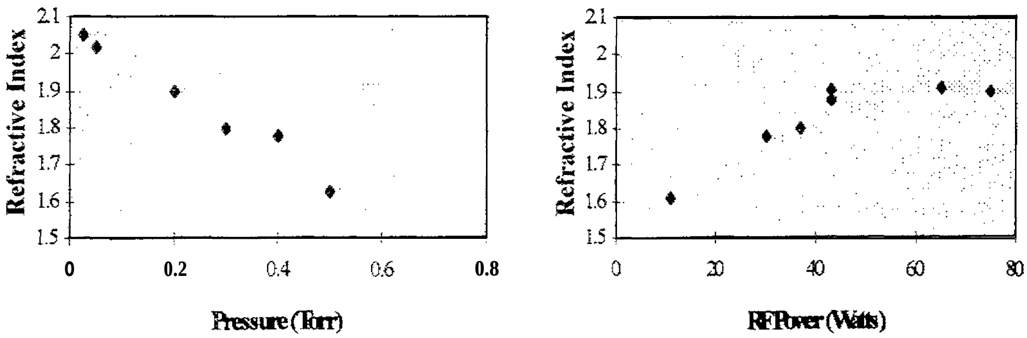


Figure 3 The *influence pressure and power on refractive index of films produced with a 1.356 MHz discharge in acetylene/hydrogen plasmas.*

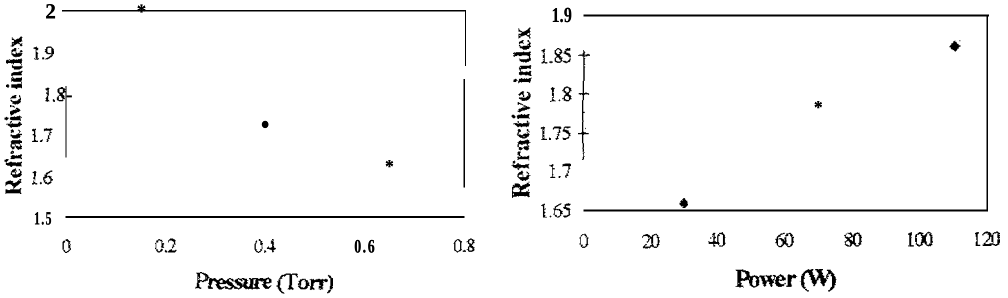


Figure 4 *The influence pressure and power on refractive index of films produced with a 13.56 MHz discharge in butadiene/hydrogen plasmas.*

Most of the deposition experiments at 13.56 MHz were performed on acetylene/hydrogen plasmas. However experiments were also performed on methane and butadiene. Some of the results of the methane experiments are given in figure 5. In this figure a comparison is made between films deposited from methane plasmas at 40 kHz and at 13.56 MHz. The refractive index decreases with pressure at both rf frequencies. However this drop occurs more rapidly and at a much earlier stage in the case of films deposited at 13.56 MHz. Good quality (n=2.15) films have been grown at 13.56 MHz but only below ≈0.05 Torr. This illustrates the large effects on film properties caused by changing the deposition parameters.

Experiments carried out with butadiene as a precursor gas for the preparation of DLC films resulted in fast growing (typically 2 μm/hr) films with a low refractive index (typically 1.8). Even higher growth rates of up to 5 μm/hour were achieved with films of refractive index 1.6.

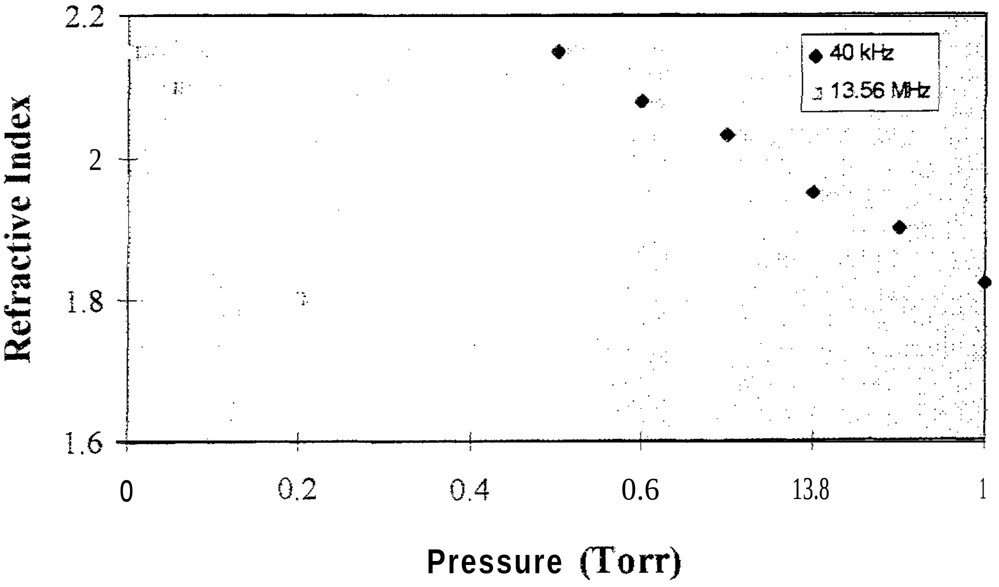


**Figure 5** *A plot of refractive index against pressure for films deposited at 40 kHz and at 13.56 MHz in methane plasmas. Note while it is possible to deposit films of good quality at 13.56 MHz (n = 2.15) deposition is at a much lower pressure.*

## 2.1 Characterisation of the DLC Films

In addition to in-situ ellipsometry amongst the techniques used to characterise the DLC films were nano hardness, AES, EPMA and SIMS. The hardness of the films was measured using a Micro Materials Nanotester. The highest hardness values obtained for films were found to be in the region of 22 GPa. A direct correlation was observed between refractive index and film hardness and is illustrated in figure 6. The films with the lowest refractive index (~1.6) were also found to have the lowest hardness of 2 to 4 GPa.

X-ray excited AES and EMPA were used to measure the $sp^3/sp^2$ ratio of the DLC films and is shown in figure 7. The hydrogen content was determined by SIMS and is shown in figure 8. The $sp^3$ content was found to decrease with refractive index but it must be noted that this is accompanied by an decrease in the amount of hydrogen incorporated into the films. This indicates that the high $sp^3/sp^2$ ratio may be realised predominantly in C-H bonds rather than in C-C ones and that simply quoting the $sp^3/sp^2$ ratio may not reflect the $sp^3/sp^2$ C-C bonding ratio.

In summary these results indicate that the degree of "diamond-likeness" (structure and properties) of the DLC films correlates with the refractive index. However care must be taken when quoting the $sp^3/sp^2$ ratio of hydrogen containing films. Refractive index on the other hand is a readily determined property that seems to be a most useful parameter with which to assess the quality of a DLC film.

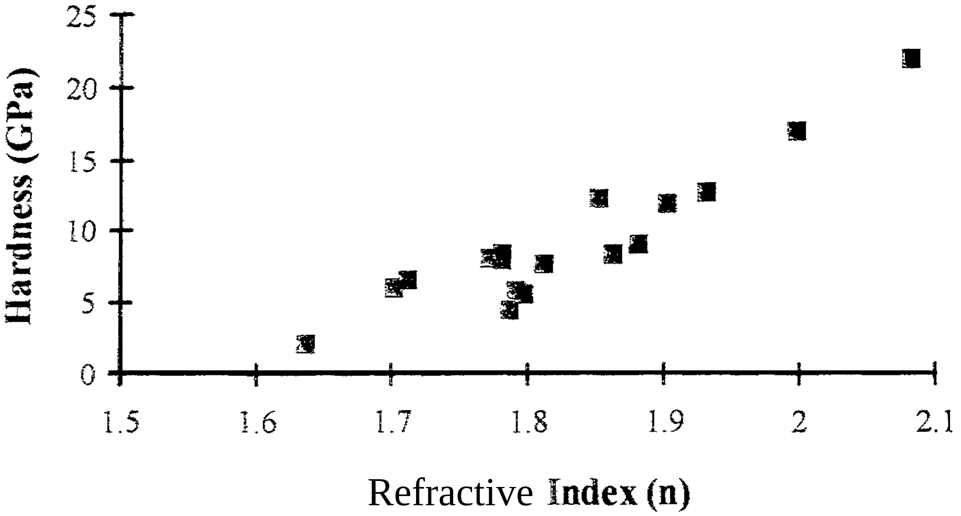
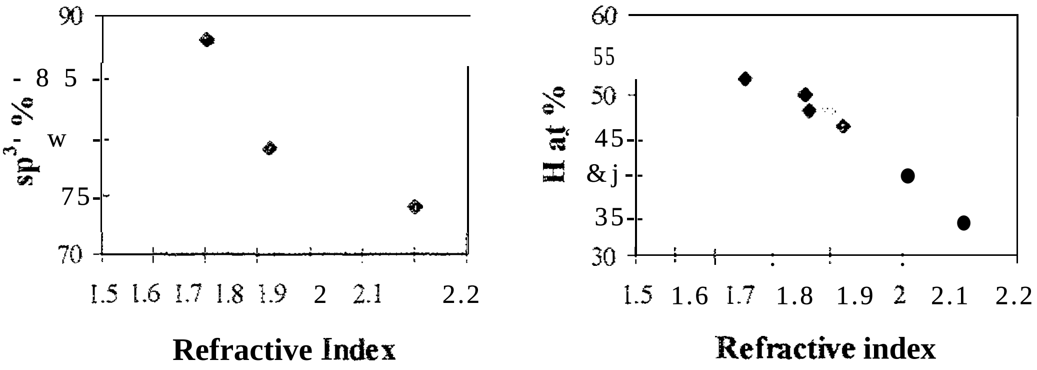


**Figure 6** ***Film hardness as a function of refractive index.***



**Figures 7 & 8** *The sp$^3$ content and the atomic percentage of hydrogen as a function of refractive index*

## 2.2 Effect of dc Electrode Voltage on Film Properties.

One plasma parameter which both pressure and power influence is the DC bias voltage ($V_{el}$) which develops on the powered electrode while the plasma is running. The electrode also acts as the substrate holder in the PECVD system at Forbairt, and so its bias can directly influence the film growth. The electrode voltage ($V_{el}$) determines how much energy positively charged particles from the plasma acquire before striking the electrode and substrate. In a relatively cold plasma such as the typical rf discharges used for deposition, the energy delivered to the substrate by ion bombardment constitutes the bulk of the energy transported from the plasma to the growing film if the self bias is large. This is the energy available to the physical and chemical processes involved in film growth.

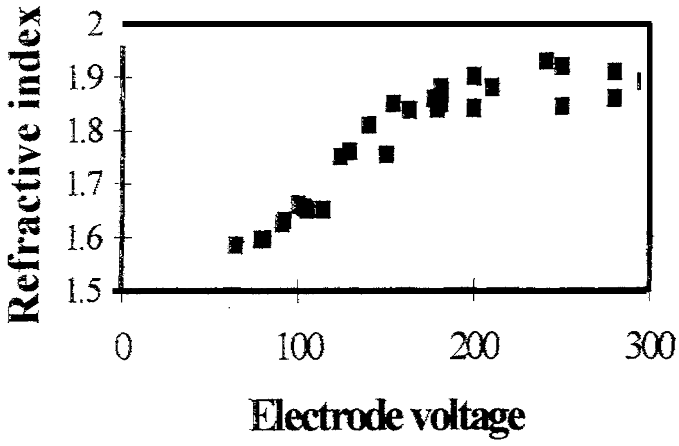


**Figure 9** ***The refractive indices of films deposited from acetylene plasmas at 13.56 MHz plotted against the electrode voltage***

The data points in figure 9 correspond to films deposited in the range of pressures from 150 mTorr to 800 mTorr, at powers from 10 Watts to 120 Watts, and with gas ratios varying from 20:1 to 60:1. Refractive index rises with bias voltage, from $n < 1.6$ at $V_{el} =$ 60 Volts to $n = 1.9$ at $V_{el} = 200$ Volts. No further increase in index is observed as $V_{el}$ increases beyond 200 Volts. Thus $V_{el}$ may be used as a measure of refractive index and hence quality but only for $V_{el} < 200$ V ($n < 1.9$). The pressure and power appear to influence refractive index solely through their effect on the electrode voltage. The deposition rate data from the films discussed above were not found to display any such simple dependence on electrode voltage. The main factor which appears to be influencing rate was found to be the hydrocarbon /'hydrogen gas ratio.

In concision the experimental results indicate a separation between the processes leading to deposition, and those influencing the final properties of the deposited films, Deposition rate is governed by processes occurring in the bulk of the plasma, specifically factors which affect the plasma density, and degree of dissociation of gas species. The strong correlation between electrode bias and film properties, indicates that the final properties of the films are largely determined by the energy of the particles which bombard the film during growth.

## 3. Determination of hydrogen dissociation - using MPLIF

During the initial part of the project several excitation schemes for LIF detection of atomic hydrogen were tested

(a): excitation with 243 nm/486 nm radiation. Two photon excitation leads to the n = 1 → n = 2 transition. After further excitation to n = 4, fluorescence radiation can be observed at the Balmer-β (486 nm) and subsequently the Balmer-α (656 nm) line.

(b): Excitation with two 205 nm photons from the ground state directly to n =3, in which case the fluorescence on the Balmer-α (656 nm) line yields the visible signal.

In both cases photo ionisation of the excited atoms leads to a reduction in the fluorescence yield. Model calculations using a simplified rate equation model have demonstrated that the (2+1) -excitation scheme produces a less favorable ratio of fluorescence to ionisation rates. For this reason the 205 nm 2-photon excitation scheme is preferred for applications in the rf discharge. The 205 nm radiation required can be generated by frequency doubling, sum-frequency mixing or stimulated Raman scattering (both Stokes and anti-Stokes are possible).

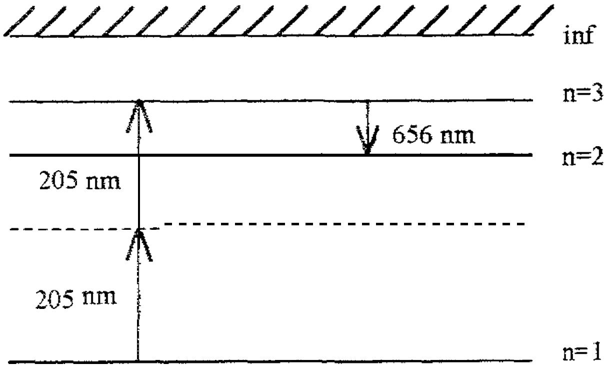


**Figure 10:** *Schematic Diagram of Two Photon Excitation Scheme for Atomic Hydrogen*

The method actually adopted is illustrated in figure 10. Excitation is via two 205 nm photons and fluorescence is on the Balmer-α line (656 rim). This system has been used by Dunlop et. al. [4] and Goldsmith [.5]. The system comprises a dye laser pumped with the second harmonic (532 nm) of a Nd:YAG laser. The dye laser is operated with Sulpho-rhodamine 640 dye which can be made to lase at 615 nrn. The dye laser output is then frequency doubled in a KDP crystal to produce 307.5 nm. Sum frequency mixing of these two wavelengths is carried out in a BBO crystal to produce 205 nm radiation. Sum frequency mixing can only occur when the incident polarisations at both wavelengths are aligned. After frequency doubling, the output wavelengths have perpendicular polarisations. A waveplate is used to rotate the plane of polarisation of the 307.5 nm by 900 while leaving the polarisation of the 615 nm beam unaffected. The required 205 nm beam is then separated from the generating beams using a Pellin-Broca prism, and is focused onto the volume under investigation. Output (205 nm) pulse energies up to 1 mJ have been obtained using this set-up. The LIF signals are collected with a 10 cm focal length lens and directed through a 656 nm interference filter onto a photomultiplier tube. The Resonantly Enhanced Multi-Photon Ionisation (REMPI) signals were also detected using a positively biased electrostatic probe. The current detected using this probe, generated a voltage puke across a monitoring resistor, which voltage could be recorded using a storage oscilloscope. The laser beam energy was monitored with a calibrated photodiode.

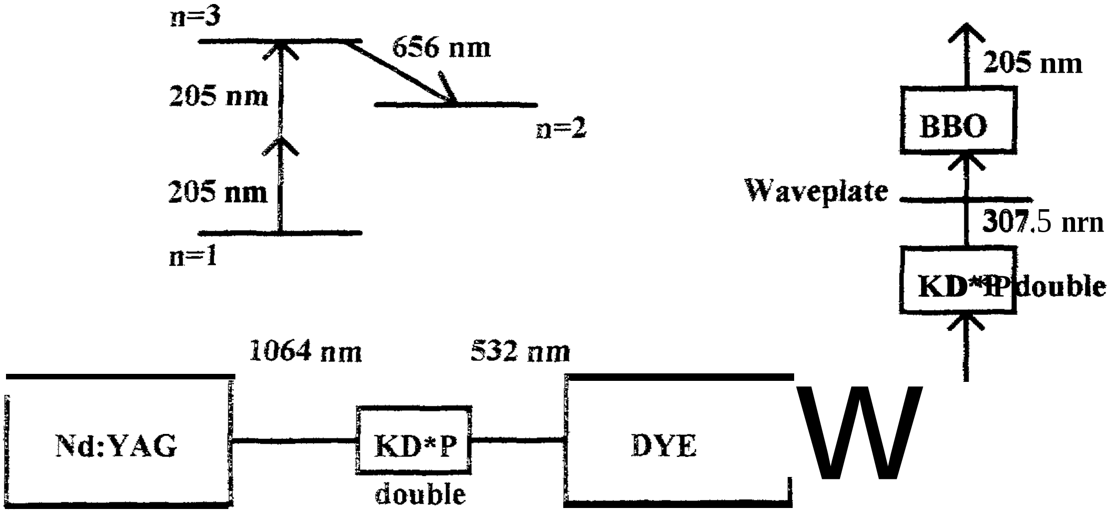


**Figure 11:** *Experimental set-up for the excitation with* $2 \times \lambda = 205$ *nm*

## 3.1 Calibration of LIF System

LIF measurements must be calibrated to determine absolute concentrations. In this case calibration was performed by comparison of the measurements with measurements performed in a 'flow reactor' [8] where the atomic hydrogen concentration can be determined independently by titration with $NO_2$. The flow reactor consists of a quartz tube into which a molecular hydrogen flow is introduced. A microwave discharge creates atomic hydrogen in the flowing gas. The radiating volume inside the reactor has the dimensions of length ≈3 mm (limited by external aperture stops) and width 200 µm (determined by beam divergence).

The gas flow and microwave power were adjusted to obtain a fluorescent signal of the desired amplitude from the atomic hydrogen present. A well controlled N02 flow is mixed and the quantity of $NO_2$ required to completely extinguish the fluorescence signal is determined. The atomic hydrogen concentration was determined from the mass of $NO_2$ titrated as follows

$$NO_2 + H \rightarrow NO + OH.$$

It is important that between the region where the $NO_2$ reacts with the atomic hydrogen and the downstream region where the atomic hydrogen is measured by fluorescence no additional losses of atomic hydrogen occurs at the walls. To this end PTFE is used in the walls as it only allows few recombination to H2 on its surface. This arrangement was checked by moving the inner tube (where $NO_2$ flows) axially by 25 mm while keeping the reaction volume fixed. No measurable signal change was found confirming that the longer path along the PTFE wall does not result in a loss of atomic hydrogen. This reactor which is used as a standard atomic hydrogen source cannot be used directly in the plasma CVD reaction chamber which would be highly desirable in order to keep the detection optics unchanged. Therefore a small transfer standard based on a heated filament was developed and calibrated against the flow reactor. For reproducibility of results, this transfer standard should have as uniform a H distribution as possible over the LIF excitation volume. The final version (Fig. 12) consists of a tungsten double loop surrounded in a cylindrical housing of stainless steel. Figure 13 shows the H concentration measured along the. axis of the two loops. The excellent homogeneity y achieved is evident.

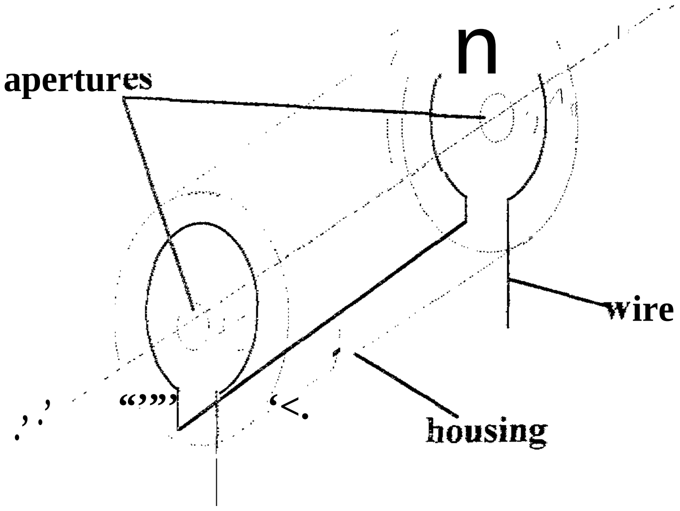


**Figure 12:** *Schematic of double-loop filament*

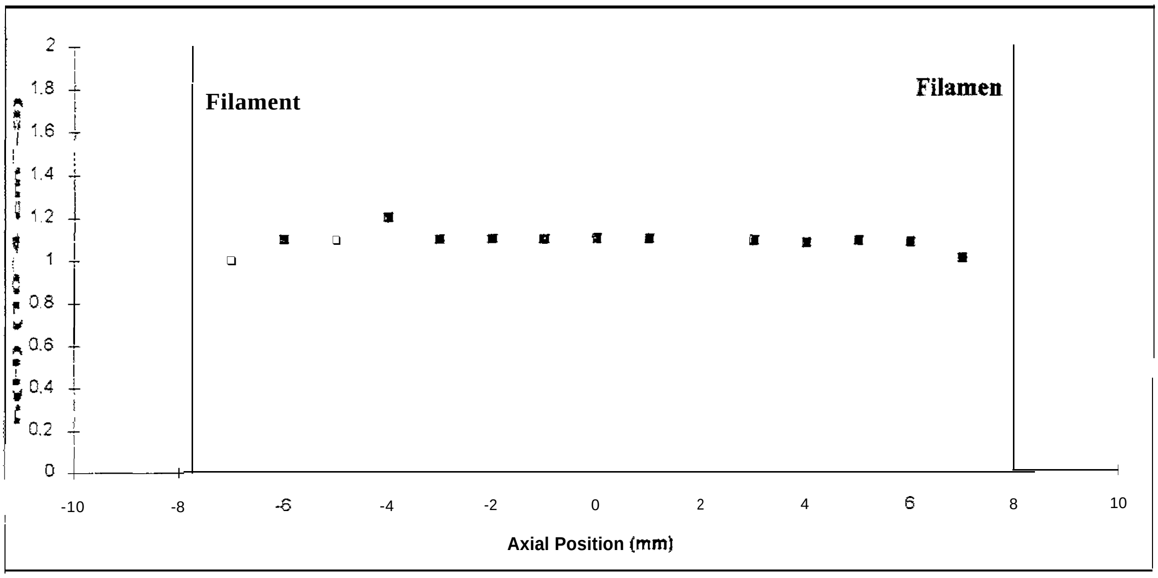


**Figure 13**: *H-density at double loop filament vs axial position*

## 4. Determination of hydrogen dissociation - using a Langmuir probe and remission spectroscopy

The novel method of hydrogen dissociation measurement described in this work involves the use of a Langmuir probe to determine the electron temperature distribution in the plasma. This information is then used to modify calculations based on the emission spectra of the same plasma. Thus the degree of dissociation may be calculated without having to assume a Maxwellian distribution in the plasma.

### 4.1. Emission spectroscopy

Emission spectra were obtained in the range $560\,\text{nm} < \lambda < 660\,\text{nm}$ using a Jobin-Yvon visible-near UV spectrometer. This region contains the molecular hydrogen Fulcher bands and the $H\alpha$ line (figure 14). The relative intensities of these lines are used to determine the degree of dissociation. A zoom lens is used to focus the radiation on the end of a quartz fibre which transfers it to the spectrometer. If the plasma were purely thermal then this measurement would be sufficient to calculate the degree of dissociation. However, the non thermal energy distribution may be compensated for if the electron energy distribution function (EEDF) is known, this is determined electrostatically by a Langmuir probe which is placed in the plasma near the area where spectroscopic data is obtained. It is important that the electrostatic probe does not interfere with the plasma sufficiently to alter the emission spectra obtained. To prevent this the 13.56 MHz rf plasma is formed over a 10 cm diameter powered electrode and is uniform in a plane parallel to the electrode as determined separately by emission spectroscopy and by Langmuir probe. Thus probe data and emission data may be obtained simultaneously in different but identical parts of the plasma.

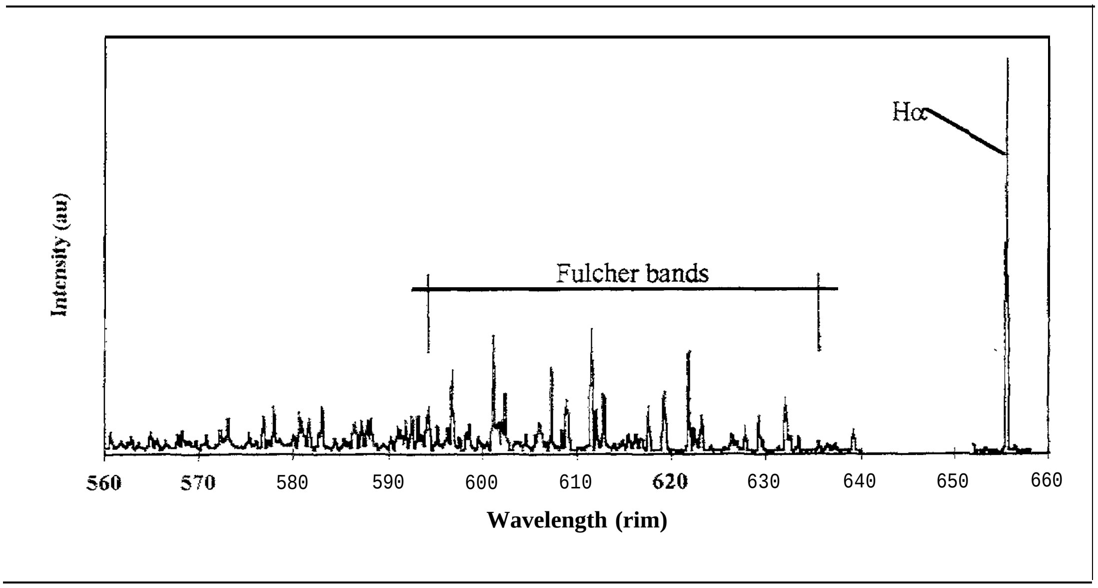


**Figure 14** *Emission spectrum from indicating the molecular hydrogen Fulcher bands and the H-alpha line.*

## 4.2. Langmuir probe

Plasma characterisation has been carried out using an rf self compensated Langmuir probe illustrated in figure 15. The probe current-voltage (I-V) characteristics are determined using a computer controlled data acquisition programme. The Langmuir probe and its associated electronics are assembled so as to minimise the effect of rf interference on the measurements. The electron energy distribution function is related directly to the second derivative of the recorded I-V curve by

$$\frac{d^2I}{dV^2} = C \exp \frac{eV}{kT} \tag{1}$$

where C is an experimentally determined constant related to the probe size and biasing voltage, e is the electronic charge, k is the Boltzmann constant and T is the electron temperature in the plasma. An electron energy distribution function (EEDF) may be obtained from the IV curves, analysis of which gives electron densities and temperatures. A typical EEDF is presented in figure 16, the feature at ≅15 eV illustrates the non thermal nature of the electrons. These data are then used in conjunction with the emission spectra (Fig. 2) to give the degree of hydrogen dissociation. One difficulty in obtaining the Langmuir probe measurements is the deposition of an insulating DLC coating onto the probe tip. To overcome this probe measurements were only made for a period of 30 seconds before the probe tip was cleaned.

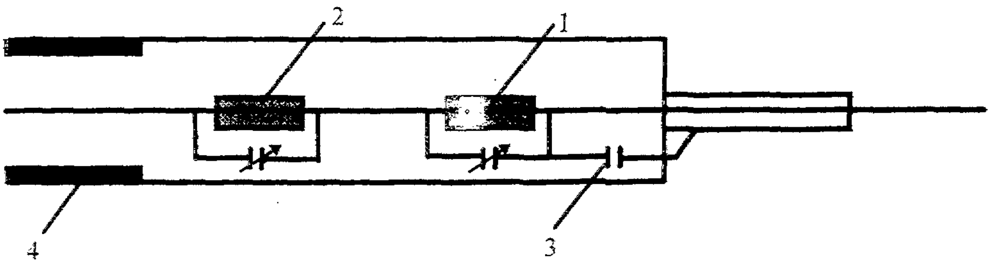


**Figure 15** *Schematic of the Langmuir probe showing 1) an rf fundamental frequency filter, 2) an rf first harmonic frequency filter, 3) a blocking capacitor for the dc signal from the compensating electrode and 4) grounded screening to protect the filtered signal from rf pick-up.*

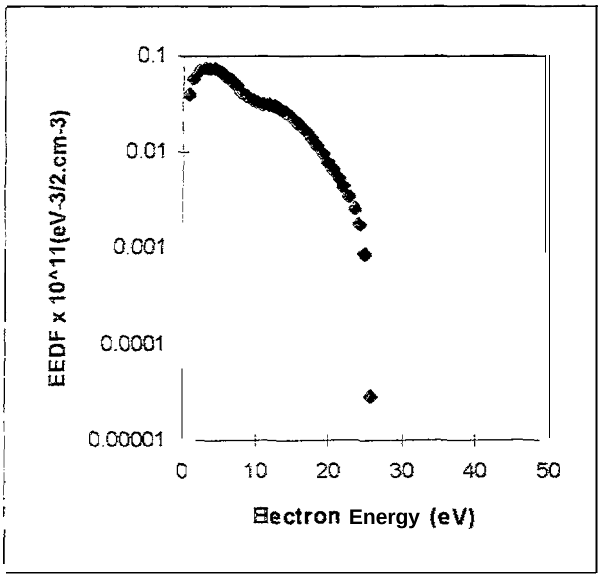


**Figure 16** *Electron energy distribution function (EEDF) of a plasma containing a 60/1 $H_2/C_2H_2$ mixture at a pressure of 0.2 Torr and rf power of 43 W.*

## 7 Correlation between molecular hydrogen dissociation and DLC film quality.

It has been shown in section 3 that the refractive index is a good measure of the quality of DLC films, the higher indices being associated with harder, more wear resistant films. Here a number of films were deposited using a range of different plasma conditions. During deposition the ground state atomic hydrogen fraction was measured using the MPLIF technique at both 1 and 13 mm from the substrate. The refractive index was measured using in-situ ellipsometry. Figure 17 shows that the refractive index of the DLC films produced is related to the atomic hydrogen fraction in the deposition plasma. The measurements were taken over a wide variety of plasma conditions with rf input powers, as determined from the measured forward and reflected powers, of between 11 and 115 Watts, and gas pressures in the range 0.03 to 0.4 Torr. The percentage acetylene in the gas mixture was varied from 1.6 to 5°/0. The higher the percentage dissociation the higher the corresponding refractive index of the film and thus the better the film quality.

As outlined earlier it has been found that the refractive index is correlated with the dc self bias which develops on the driven electrode. This has been found by other groups [6, 7]. As shown in figure 18 there is also a direct correlation between the dissociation fraction and the dc electrode bias. This is to be expected since both quantities are determined by the nature of the plasma. The partners believe that this is the first direct evidence of a correlation between the quality of DLC films and the atomic hydrogen fraction in depositing plasma. Similarly data determined by the novel Langmuir probe/emission spectra method show the same relative change in the degree of dissociation with increasing power (figure 19).

The absolute scale of the LIF measurements were considered correct within the limits set by the calibration and by the registrations of the signals. It was assumed that the difference of approximately a factor of 4 in absolute scale, have to be attributed to the probe/measurement method. The project partners consider these differences as being due to uncertainties in the electron cross sections and to the independently measured EEDF. The quality of the relative calibration of the sensitivity and the experimentally determined intensity ratios also introduce uncertainties.

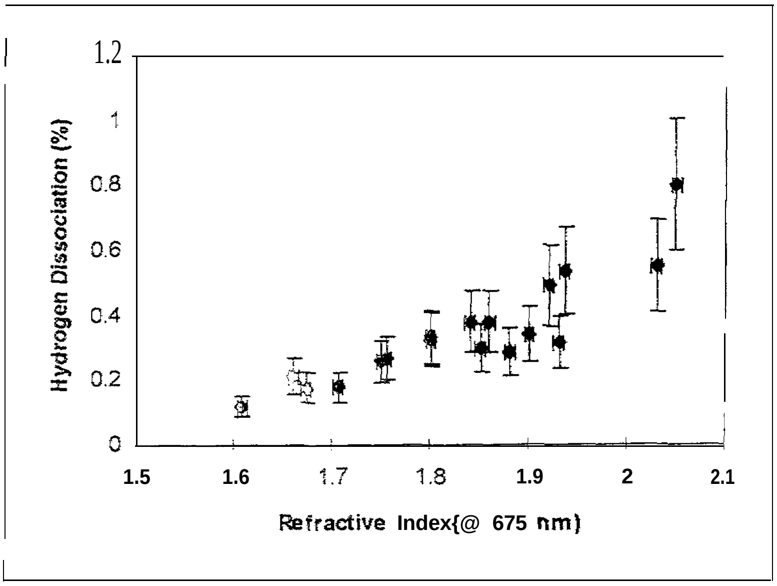


**Figure 17** *Percentage Hydrogen Dissociation as a Function of Refractive Index (@ 675 nm) as Determined by MPLIF. The Error in Dissociation Reflects a 25% Error in Calibration of the MPLIF Signal Using the Transfer Standard.*

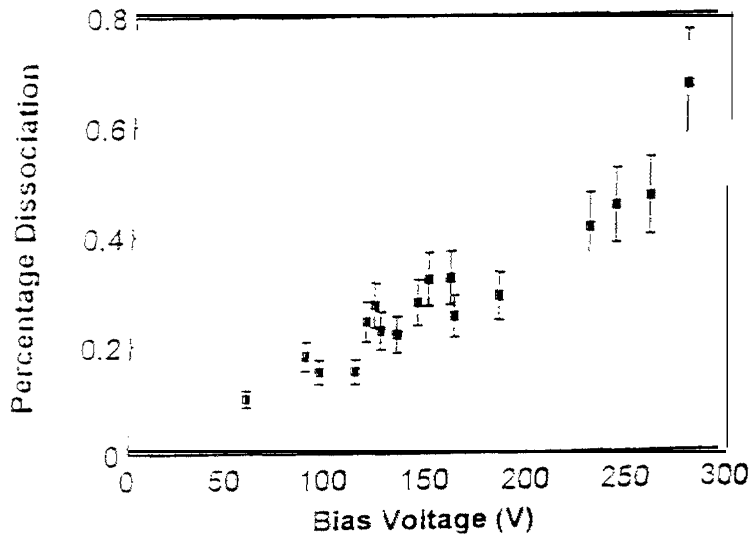


**Figure 18** *The percentage molecular hydrogen dissociation in the plasma as a function of the dc bias voltage on the electrode.*

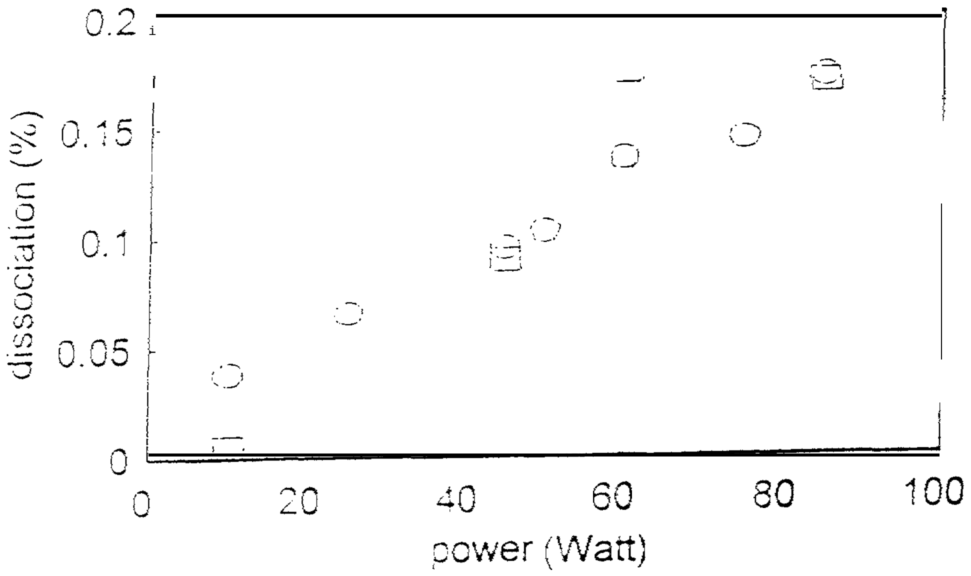


**Figure 19** *Comparison of the degree of dissociation obtained by LIF (O, absolute values) and the combined probe/emission spectroscopy method (□, relative values) as a function of rf power with pressure at 0.45 Torr.*

## 8. Conclusions

Quantitative atomic hydrogen measurements have been obtained during the deposition of DLC films, using both multi photon laser induced fluorescence (MPLIF) and the Hydrogen Probe technique based on the combination of a Langmuir Probe and emission spectroscopy. The percent age dissociation has been found to correlate with film refractive index (n). The higher the percentage dissociation the higher the corresponding n value of the film. The highest level of molecular hydrogen dissociation observed of 0.8% was obtained using the MPLIF technique, in a plasma from which a film with refractive index 2.1 was deposited. Both the MPLIF and Hydrogen Probe techniques gave similar relative increases in the concentration of atomic hydrogen with increase in deposited film refractive index. However the atomic hydrogen concentration measured using the Hydrogen Probe technique gives values which are approximately a factor of 4 higher than those obtained using MPLIF. It is anticipated that improving the spectral resolution and signal to noise ratio of the emission spectroscopy will enable the Hydrogen Probe technique to be a relatively cheap competitive alternative to laser based methods for atomic hydrogen measurements.

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