Plasma magnetic multipole confinement used in PECVD a-C:H films deposition

1. Why and What?

Amorphous hydrogenated carbon (a-C:H) films have been studied in the last decades because of their hardness, chemical inertness, wear resistance and infrared transparency. These films deposited under certain conditions are semiconducting which extends their area of application. Plasma-enhanced chemical vapor deposition (PECVD) - one of the most widely used techniques for the deposition of a-C:H - is a versatile process and by varying the deposition conditions a variety of a-C:H films of different properties can be produced. Carbon atoms can form sp^3, sp^2 and sp^1 sites[1] and the chemical and physical properties of the a-C:H films are determined by the fractions of these sites.
Interest has been on so-called `diamond like' carbon because of its mechanical and tribological properties. But recent studies have also shown photoluminescence (PL) and electron field emission[2] (FE) from a-C:H layers with various sp^3/sp^2 ratios.

Magnetic confinement of the radio frequency (rf) plasma in a PECVD chamber has been used to increase the plasma ionization and this confinement has an effect on the structure of the films. In this paper we report on an investigation of a magnetic- multipole system to confine the plasma. The magnetic field effect on both plasma parameters and film properties has been measured.
The results are compared with those obtained on films deposited by conventional PECVD.

2. How?

The powered electrode of the PECVD system is surrounded by permanent magnets aligned in an alternating north pole, south pole configuration. In Fig. 1(a) the arrangement is shown schematically.
Using this, a line-cusp surface magnetic field layer is obtained around the plasma volume.

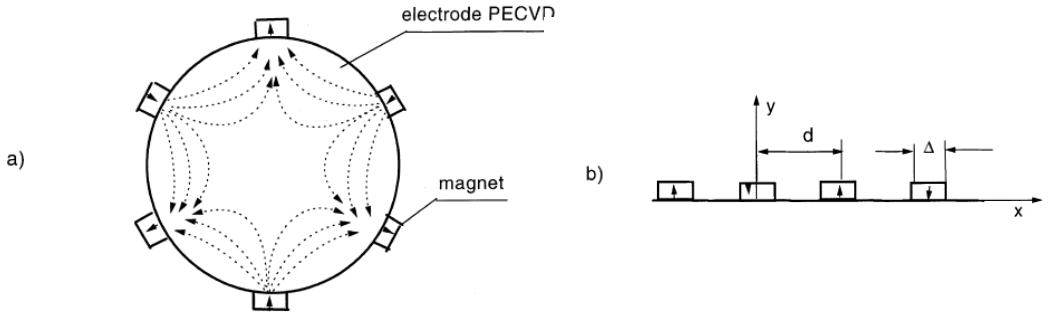

Figure 1. (a) Scheme of the multipole magnetic arrangement; (b) linear model for theoretical calculus. Eq. (1) was obtained for this arrangement of the magnets with $\Delta << d$.

[1] B. Dischler, A. Bubenzer, P. Koidl, Appl. Phys. Lett. 42 (1983) 636.
[2] G.A.J. Amaratunga, S.R.P. Silva, Appl. Phys. Lett. 68 (1996) 2529.

The magnetic field strength, B, has a maximum near the magnets and decays with distance into the reactor chamber. Its magnitude at an arbitrary point (x, y) at z= constant, in the PECVD reactor, can be calculated. For this we assume: (i) the magnet width, Δ, is much less than the separation of the magnets, d, (i.e. $\Delta << d$); (ii) the magnets' number is very big, practically infinity. Under these conditions the magnets' circle arrangement could be studied using a linear model of the magnets' system as in Fig. 1(b). The magnetic field strength of the multipole configuration can be calculated with [9]

$$B_y(x,0) = B_0 \cdot \Delta \cdot \sum_{i=0}^{\infty} (-1)^i \, \delta\left(x - id - \frac{d}{2}\right) \tag{1}$$

where B_0 is the magnetic field strength of a single magnet.

Using the Fourier transform and Laplace's equation, it can be shown that the fundamental Fourier mode is described by

$$B_{y1}(x,y) = \frac{2B_0\Delta}{d} \cdot sin\left(\frac{\pi x}{d}\right) \cdot exp\left(-\frac{\pi y}{d}\right) \quad \text{and} \quad B_{x1}(x,y) = -\frac{2B_0\Delta}{d} \cdot cos\left(\frac{\pi x}{d}\right) \cdot exp\left(-\frac{\pi y}{d}\right)$$

which leads to an independent exponential decay of magnetic field strength into the plasma column:

$$B_1(x,y) = \frac{2B_0\Delta}{d} \cdot exp\left(-\frac{\pi y}{d}\right) \tag{2}$$

In the experimental configuration (see Fig. 1(a)), the axis Oy corresponds to the radial direction. The diameter of the electrode is 18.5 cm and the magnets are sintered Ni- Fe- Ba bars with D.2.75 cm. Three configurations were formed: with 6, 8 and 10 magnets.

3. Results

1.1 Magnetic line configuration

The magnetic field strength, B, was measured across the diameter line in the multipole magnetic field configuration presented in Fig. 1, with a Hall probe. The experimental results are shown in Fig. 2(a) indicate the variation of the magnetic field into the chamber as a function of the number of magnets used. We can observe that by increasing the number of the magnets, the magnetic field strength at the same point is increased. This increase means that the plasma volume is more confined. For all configurations, the B values decrease exponentially from the wall towards the middle of the chamber. Fig. 2(b) shows on a semilogarithmic scale, the variation for the system with 6 magnets and 10 magnets; the slope depends on the configuration of the magnetic system but is not dependent on the magnetic field strength of the magnets used. In the insert in Fig. 2(b) the B values measured using 6 magnets formed by either single or double magnet per site, are plotted. The slope of both plots is the same, -0.28 ±0.01 G/cm. Therefore, we can assume an exponential dependence of the magnetic field strength defined by

$$B_1(x,y) = B_{max} \cdot exp\left(-\gamma \cdot \frac{\pi y}{d}\right) \quad (3)$$

where B_{max} is measured at the edge of the powered electrode and γ is a geometrical factor. Eq. (3), which fits the experimental data, shows the variation of the magnet field strength, B, along the electrode radius. The parameter γ is different from one, as in the theoretical Eq. (2), because the condition $\Delta << d$ is not satisfied in our experiment. Here the width of the magnet, Δ=27.5mm, is almost comparable with the separation between magnets, d=94.2mm.

Experimentally, we have found that the parameter γ is a function of the magnets' separation: 0.84 for the system with 6 magnets, and 0.63 the configuration with 10 magnets. The γ parameters do not depend on the number of magnets per site. We assume that the distance between magnets gives the principal contribution to γ.

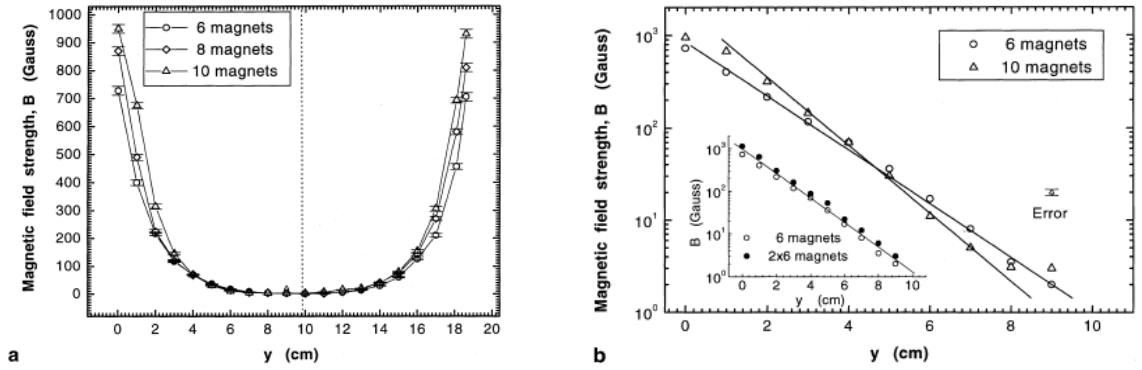

Figure 2. The magnetic field variation into the deposition chamber: (a) the experimental values of the magnetic field strength along the diameter of the deposition chamber. The lines are drawn as guides to the eye; (b) the exponential variation (Eq. (3)) of the magnetic field strength depends on the magnetic system; the insert shows that the value of the slope do not depend on the number of magnets per site.

1.2 a-C:H film properties

The deposited samples have been investigated as:

a) the film thickness was measured by ellipsometry (λ=632.8 nm) and from profilometric measurements;
b) the fraction sp^2/sp^3 bonding which define the carbon structure was determined via IR-absorption spectroscopy and electron energy loss spectra (EELS);
c) optical transmission and reflection measurements were made on the films special deposited on the glass substrates;
d) the optical bandgap of the a-C:H films was determined from the absorption coefficient spectra: the Tauc plots (E_{gT})and the photon energy at which the absorption coefficient was 10^4 cm^{-1} (E_{04}).

The EELS spectra are showed in *Figure 3*. The step at 290 eV is due to transitions from the C 1s core level to the σ^* states of the sp^2 and sp^3 sites; the peak at 285 eV is due to transitions to the π^* states of the sp^2 sites. The fraction of the sp^2 sites can be obtained from the spectrum[3] by taking the ratio of the 285 eV peak area to the area of the 290-310 eV energy window and comparing it to the similar ratio for a standard graphite sample, which has sp^2 sites only. This method gives the estimated fraction of sp^2 sites in the film assuming that there are no sp^1 sites, which also have π^* states. In this way it was found that the films deposited using magnetic field confinement (10 magnets) have sp^3/sp^2 =8.09, while the films deposited under standard PECVD conditions have sp^3/sp^2 =4.55. Therefore the samples deposited under magnetic confinement contain more diamond like sites.

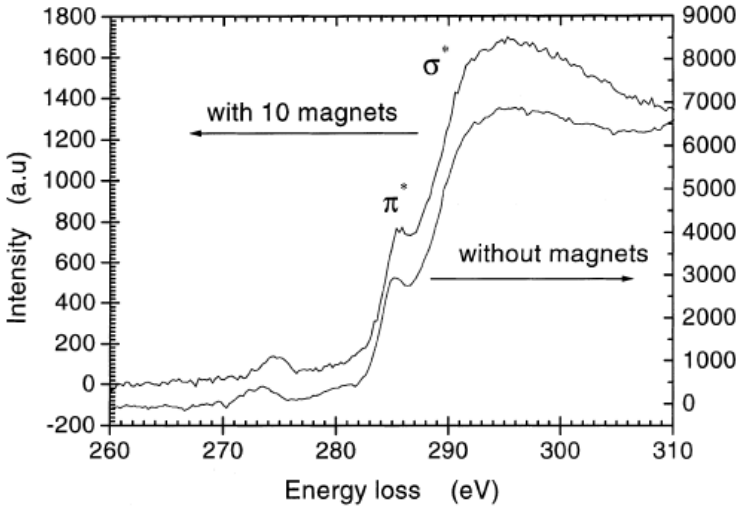

Figure 3. Electron energy loss spectroscopy (EELS) spectra for samples deposited with and without magnetic field. There are huge differences between the two samples;

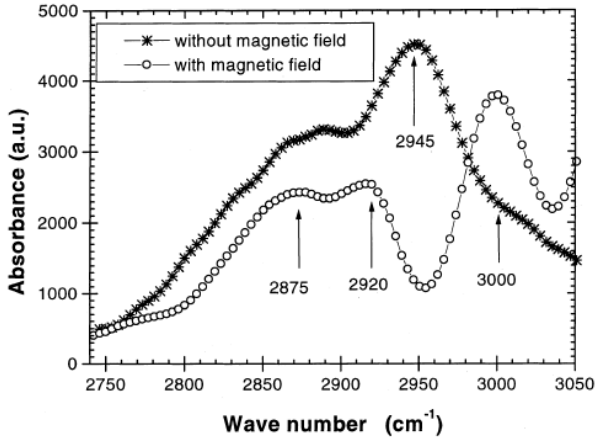

Figure 4. IR spectra show the increasing of the sp^3/sp^2 ratio for samples deposited with magnetic field. Both the plots are drawn using `line + symbol'.

[3] S.D. Berger, D.R. Mc Kenzie, P.J. Martin, Philos. Mag. Lett. 57 (1988) 285.

From the IR spectroscopy data presented in *Figure 4* we can see that both films have a band at 2875 cm^{-1} assigned to a sp^3 bonded CH_3 group. In the film deposited in a magnetic field the amplitude of the band at 2920 cm^{-1}, which confirms the sp^2 bonded CH_2, increases and the band at 2945 cm^{-1} that corresponds to a sp^2 olefinic CH_2, decreases. There is also another band at 3000 cm^{-1} assigned to the sp^2 olefinic CH group.
Therefore the sp^3 amount is larger in to the samples deposited under magnetic field confinement.

Another proof for this is the optical bandgap:

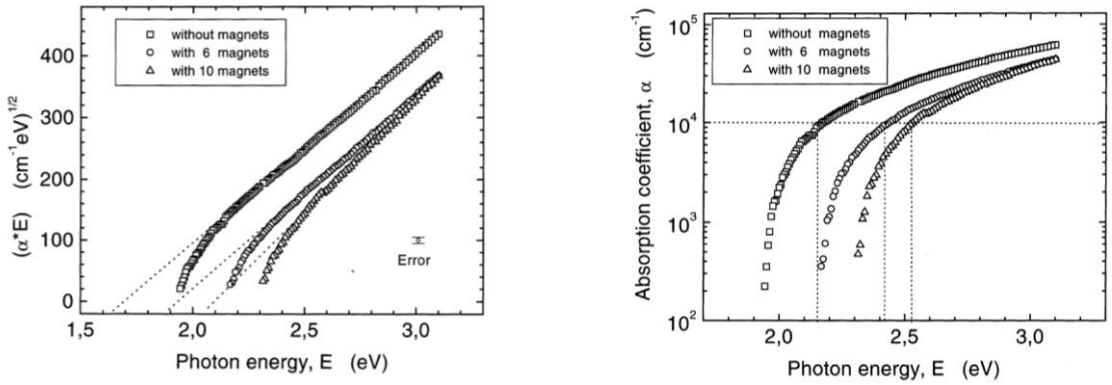

Figure 5. Tauc plots and values of the optical gap: the magnetic field increases the optical gap. With dot lines are represented the fits of the experimental data with Tauc's theory. The Ox intercept of the straight line is the Tauc gap, E_{gT} (left plot); The photon energy at which the absorption coefficient is equal to 10^4 cm^{-1} defines the optical bandgap, E_{04} (right plot).

Higher optical bandgap is specific to more diamond like sites into the carbon film.

4. Wrap-up

The findings revealed by this study are:

i) the magnetic field decreases the dc bias voltage of the plasma sheath;
ii) the deposition rate is decreased by the magnetic field strength;
iii) concerning the films' properties, the EELS and IR spectral analyses have shown that films deposited with magnetic field confinement have a larger sp^3/sp^2 ratio and a larger mass density;
iv) the optical properties of the films were also modified by the magnetic field: the optical gap increased.