Deposition of diamondlike carbon by Magnetic Pole Enhanced inductively coupled plasma

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Abstract
A novel inductively coupled plasma source (the Magnetic Pole Enhanced ICP or MaPE-ICP) designed and characterized in our laboratory was used for depositing diamondlike carbon films. The ICP sources are particularly interesting for the deposition of amorphous carbon since they offer the possibility to control independently the ion energy from the ion flux bombarding the substrate, in contrast to capacitively coupled discharge. The MaPE-ICP uses a magnetic pole to concentrate the magnetic flux on the load (\textit{i.e.} plasma) and shows very interesting features like high plasma density, good plasma uniformity and wide pressure range.

Diamondlike carbon coatings were deposited with this source from CH\textsubscript{4} precursors and characterized by FTIR spectroscopy. Mass spectrometry including ion detection and ion energy distribution measurements have been carried out in the reactor. The sensor head was placed at the substrate holder surface in order to investigate directly the species impinging on the growing film. The plasma diagnostics were undertaken for various processing parameters and the results were related to the film properties like hardness and intrinsic stress.

Introduction
Amorphous hydrogenated carbon coatings (a-C:H) have been widely studied because of their attractive mechanical, optical, chemical, and electrical properties. Although their characteristics are quite far from diamond, diamond like carbon (DLC) coatings present the advantage to be easily synthesized by a variety of precursors and techniques. Thus, their properties can be tailored for specific applications. Among the different methods used for DLC deposition, plasma processes appear to be the most successful.

It is well known that the ion bombardment energy is a key parameter in the deposition of amorphous carbon coatings. The ion bombardment energy is controlled by adjusting the negative bias voltage on the substrate. However, in parallel plate reactor, this influences both the ion bombarding flux and the ion energy on the growing film. Inductively coupled plasma
sources offer, to a certain extent [1], the benefit of an independent control of the ion energy over the ion flux by applying a separate bias to the substrate. Moreover, the high plasma densities achieved with such sources are another appealing characteristic for obtaining higher growth rates.

In this work, a novel inductively coupled plasma source designed in our laboratory [2] has been used in order to deposit amorphous hydrogenated carbon films. This source uses a magnetic pole to concentrate the magnetic field in the plasma chamber, in order to increase plasma density and uniformity. It shows very interesting features like high plasma density (>10^{12} \text{ cm}^{-3}) with good uniformity, and wide pressure range (submillitorr pressures to 1 Torr). These characteristics makes it a versatile tool for the processing of diamondlike carbon deposition.

This paper presents a parametric study for DLC deposition by CH\textsubscript{4} decomposition with this source. The plasma phase was studied by Langmuir probe and mass spectrometry, including ion detection and ion energy distribution (IED) measurements. The sensor head was placed just under the substrate holder in order to investigate directly the different species impinging on the substrate. DLC films' structure was characterized by FTIR measurements while film properties were investigated by nanoindentation.

**Experimental Setup**

A schematic diagram of the MaPE-ICP reactor is shown in figure 1. The stainless steel plasma chamber has a cylindrical geometry with a 200-mm internal diameter and a 300-mm height. The water cooled coil is powered by a 13.56 MHz RF generator via a ‘T’ layout matching network composed of two driven air capacitors (Advanced Energy RFX II generator 1.25 kW, matching network AZ90). The magnetic pole used is a “Fluxtrol F" 200 mm diameter disc, having a 45 mm thickness. Its magnetic permeability is \mu=14 at f = 5 MHz.

This source has been characterized extensively by means of Langmuir probe, magnetic induction probe, and RF electrical probe measurements and demonstrated remarkable performances [2]. The addition of a magnetic pole improved both plasma density and plasma uniformity.

The gas is injected through a ring tube placed at the top of the chamber. Methane (CH\textsubscript{4}) was used as a source gas for the deposition of the carbon coatings. Argon was sometimes added in order to study the effect of hydrocarbon precursor dilution on mechanical properties. The substrate holder was not water cooled and its temperature was monitored with a thermocouple. Plasma phase diagnostic have been carried out by mass spectrometry (Hiden Analytical Plasma Monitor). The sensor head was placed just under the substrate holder, at approximately 3mm from the surface.

Substrates consist of 100 oriented both sides polished silicon wafers. They were cleaned chemically with acetone and alcohol, and by an Ar/H\textsubscript{2} plasma prior to deposition.
Before each deposition phase, the reactor chamber was pumped out at a pressure of $1.10^6$ mbar.

The DLC films have been characterized by FTIR measurements and their mechanical properties were investigated by nanoindentation (Nano Indenter® II). Film thickness was measured with an α-step profilometer, and stress was estimated with the Stoney equation [3] by measuring the substrate curvature radius before and after deposition.

Results and Discussion

Pressure effect

![Graph of Growth Rate vs Total Pressure in a Pure CH₄ Plasma](image)

Fig. 2 Growth rate vs total pressure in a pure CH₄ plasma ($P = 300$W, $V_b = -100$V)

Total pressure was varied in the reactor keeping a constant CH₄ flow rate of 16 sccm, a net RF power of 300W, and a bias voltage of $-100$V. In the case of a collisionless sheath (true only at low pressures, which is not the case here) the ion energy is defined as the difference between the plasma potential (around 20V) and the bias voltage. Therefore, figure 2 does not show the sole influence of increased species density but also of a slight decrease in ion energy due to collisions in the sheath.

This figure shows that the growth rate goes through a maximum with pressure. This is mainly due to the lower diffusion coefficient at higher pressures. Indeed, the substrate holder was placed quite far from the high density plasma region (140 mm from the dielectric window) because of size constraints imposed by the mass spectrometer. Another effect of the increasing pressure is the decrease of the electronic temperature that leads to a lower dissociation of the precursor molecules.

Ar content

Argon dilution showed a net variation of the mechanical properties of the DLC coatings. Figure 3 shows the evolution of hardness and Young modulus as a function of the Ar content in the gas discharge. By adding only 5% Ar in the gas mixture, the coating hardness increased from 1 GPa to almost 15 GPa. Figure 4 shows the variation of the compressive stress in the carbon films as a function of Ar content. It is found that the films are highly stressed in these conditions with values going up to 6 GPa. On the other hand, the growth rate dropped from 1.7 µm/h with pure methane to 0.6 µm/h with 5% Argon. Though it was not measured, even a significant variation of the density would not be sufficient to induce such a difference in the deposition rate.

The Ar dilution plays an important role in the mechanical properties of the deposited films not only because it modifies the plasma chemistry as revealed by mass spectrometry but also because it acts on the ratio of ion flux/reactive neutral flux reaching the surface modifying the energy deposited onto the growing surface. The atomic hydrogen content is modified in the gas phase because the Argon addition in the source gas changes the reaction pathways leading to the creation of atomic hydrogen. The atomic hydrogen content in the gas...
phase is a fundamental parameter in the deposition of DLC as it is suspected to preferentially etch the sp\textsuperscript{2} component leading to a net increase of sp\textsuperscript{3} bonded carbon [4].

No baking out of the processing chamber was performed prior to deposition. In a pure CH\textsubscript{4} discharge a peak appeared at mass 17 indicating OH\textsuperscript{-} and NH\textsubscript{3}\textsuperscript{+}. The presence of oxygen was also confirmed by the peak at m/e = 19 related to the ion H\textsubscript{2}O\textsuperscript{+}. There seems to be a small amount of oxygen in the films grown under a pure methane plasma as measured by FTIR spectroscopy. However, no oxygen have been detected with FTIR analysis in the films grown under an argon/methane plasma. As shown in figure 5, CH\textsubscript{3}\textsuperscript{+} becomes the main ion in the discharge when adding a small quantity of Argon.

**Residence time**

We investigated the effect of decreasing the residence time of the molecules in the reactor by increasing the total flow rate at constant pressure (10 mtorr). Keeping the same CH\textsubscript{4}/Ar ratio (80/20 %) but increasing the total flow rate (i.e. decreasing the residence time, and so the degree of dissociation), a higher growth rate (up to 1.2 \textmu m/h) could be obtained. It was found previously [5] that the higher deposition rates were reached at intermediate dissociation degree. In our case, a maximum in the growth rate was not reached when increasing the total flow rate from 20 to 40 sccm at a net power of 300W. Therefore the deposition rate might still be improved by optimizing the gas total flow rate.

**Net Power**

The RF power applied was varied from 200W to 500W and it showed a net effect on the growth rate that goes through a maximum at 300W. At 400W, the deposition rate dropped down from 1.2 \textmu m/h to 0.2 \textmu m/h. This may be explained by the fact that at higher powers, dissociation of the precursor gas is amplified leading to a higher concentration of hydrogen in the reactor chamber as shown by mass spectrometry measurement. Since then, an important etching of the growing film by atomic hydrogen could occur and the probability for the precursor to react with other plasma species is increased [5]. A solution to this problem might be to inject separately the hydrocarbon precursor further from the plasma source region. Moreover, since the substrate holder is not cooled, its temperature increases more rapidly at high powers due to the higher ion bombarding flux. It is generally observed [5, 6] that an
increase in processing temperature causes a decrease in the deposition rate as well as a deterioration of the mechanical properties.

**Substrate bias**

As often reported in the literature [7], one of the major parameter in DLC deposition is the ion bombardment energy on the growing film. Figure 6 shows the coatings hardness as a function of the negative bias voltage applied on the substrate holder. Hardness goes through a maximum as found before with capacitively coupled plasma sources. The films deposited with no substrate biasing were soft and showed very low stress values. Stress increased dramatically to 4.8 Gpa at −200V bias voltage with the increase in hardness. Growth rate decreases with bias because of film densification and sputtering.

The ion energy distribution function (IED) of the ions impinging on the growing surface was measured. A typical IED in a pure CH4 discharge is shown in figure 7. The single band usually found with no biasing is broadened and three main peaks appear due to the modulation of the sheath potential [8].

FTIR analyses were performed on the coated samples between 1000 and 4000 cm⁻¹. Only the broad band at 2800-3100 cm⁻¹ corresponding to the C-H stretching vibration modes was considered. The peaks at 1450 cm⁻¹ (C-H CH3 asymmetric) and 1370 cm⁻¹ (C-H CH3 symmetric) could sometimes be observed, but not the band corresponding to the C=C bonds stretching vibration at 1600 cm⁻¹.

FTIR analysis (fig. 8) suggests that at low bias voltages, i.e. low energy ion bombardment, the coating has a polymer-like structure as indicated by the well-defined peaks at 2875 cm⁻¹ (sp³ CH₃), 2925 cm⁻¹ (sp³ CH₂, sp³ CH) and 2960 cm⁻¹ (sp³ CH₃).

Increasing the ion bombardment energy the diamond like structure increases gradually from 0 to −200 V at the expense of the polymer like structure. A deconvolution of the IR absorption band shows the appearance of a peak attributed to lower hydrogen content hydrocarbon radical at 3000-3060 cm⁻¹ at high bombardment energies indicating a decrease in the coatings’ bonded hydrogen content. Thus, at higher ion energies (|V|> 50 V) the polymeric component of the deposited film was lowered.
Conclusion

Diamonlike carbon coatings were post-discharge deposited with a novel inductively coupled plasma source offering high plasma density and process flexibility. A broad scan of the processing parameters showed that the coatings structure could be tailored in a wide range from polymer-like to diamond like. Diagnostic of the plasma phase was carried out just at the substrate holder surface in order to investigate the species impinging on the growing surface. The predominant species appeared to be the methyl radicals and ions. Argon dilution, even in low concentration, induced large differences in the dissociation rate of the precursor gas and in the ion concentration modifying significantly the coatings properties. It appears that with pure CH₄, the residual gases (oxygen and nitrogen) present in the processing chamber have a significant influence on the ion composition in the discharge. However, the key parameter for the deposition of hard coatings is the ion energy as controlled by the bias voltage on the substrate holder. Increasing the ion bombardment energy on the growing film modifies its structure from polymer-like to diamond-like as shown by FTIR analysis. Clearly, the processing parameters were not yet optimized for maximizing the coatings mechanical properties and growth rate, but these preliminary results show that this novel ICP source is a promising candidate for DLC deposition. Further plasma phase diagnostics and film analysis will be performed in order to have a better understanding of the growing mechanisms.

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References