Peak voltage variation in a bipolar pulsed-DC methane discharge aimed to the deposition of DLC films

C. Corbella, M. Rubio-Roy, M.C. Polo, E. Pascual, E. Bertran, J.L. Andújar

FEMAN Group, IN2UB, Departament de Física Aplicada i Óptica, Universitat de Barcelona
c/ Martí i Franquès 1, E-08028 Barcelona, Spain

Abstract: Plasma diagnostics of a pulsed-DC CH\textsubscript{4} discharge was performed by means of a fast Langmuir probe. The variation of the measured I-V characteristics within a pulse cycle has provided valuable information concerning the evolution of the discharge parameters. Such variables have a direct impact on the growth characteristics of diamond-like carbon (DLC) films prepared by plasma-enhanced chemical vapour deposition (PECVD). The influence of peak voltage on the plasma parameters and the deposition rate has been analyzed.

Keywords: DLC; PECVD; Pulsed-DC power; Fast Langmuir probe; Plasma parameters.

1. Introduction

Plasma techniques are of maximal importance in the processing and deposition of materials. Among the different growth techniques of coatings and thin films, magnetron sputtering and PECVD are the most used nowadays in the hard coating industry, being the latter a necessary method to prepare materials that require gas precursors. The development of pulsed power supplies has provided several advantages for the mentioned techniques, namely a better control of particle formation, the up-scaling of plasma processes to industrial reactors, and the enhancement of the ion energy through an intense peak voltage. Hard coating industry is benefited by the adoption of bipolar pulsed-DC discharges, since their characteristics improve the surface properties of the material [1,2]. DLC is an amorphous allotropic of carbon exhibiting intermediate features between those of graphite and diamond, and shows mechanical and tribological properties that can be optimized by selecting the adequate technological parameters of deposition [3,4]. In the framework of PECVD processes fed by pulse supplies, the relatively large peak voltages driven to the substrate-holder (cathode) yield an intense ion bombardment which promotes cross-linking of the amorphous carbon network, providing hard films. At the same time, intrinsic stress is reduced and, thus, the substrate adhesion of thicker films is improved [2].

Plasma diagnostics by Langmuir probe consists in a reliable method to monitor the discharge parameters, which can be complemented by further techniques such as optical emission spectroscopy (OES) and quadrupole mass spectrometry (QMS). On the other hand, the time-resolved acquisition of plasma parameters provides valuable information about the kinetics of rapidly-varying discharges [5,6]. In this paper, we report the study of the plasma parameters (electron temperature, electron and ion densities, and plasma and floating potentials) recorded by a fast Langmuir probe in a pulsed-DC CH\textsubscript{4} discharge aimed to the deposition of DLC coatings. The roles played by the peak voltage and input power are discussed, in order to shed some light in the physical processes responsible of DLC growth by pulsed-DC PECVD.

2. Experimental details

DLC films between 300 nm and 1 µm thick have been prepared at room temperature by PECVD. All the processes were carried out in a 10 Pa-atmosphere of CH\textsubscript{4}. The substrates (c-Si wafers) were placed onto the cathode, which was biased by a pulse supply (ENI-RPG-50) working in power regulation mode. The pulse frequency was set to 100 kHz, with a duty cycle of 2 µs and peak voltages between -600 and -1400 V. In order to perform a time-resolved tracking of the plasma parameters, a Langmuir probe (SmartProbe, Scientific Systems) acquisition system was modified with a time-delay circuit. Hence, the acquisition of the I-V characteristics was externally triggered by the periodic signal driven from the pulse supply, which had to be chopped by a frequency divider in order to be measurable by the system electronics. The I-V curves corresponded to different times within the pulse (time resolution = 1 µs). Fig. 1 depicts the signal of the bipolar pulse waveform. There, the ON and OFF phases, pulse frequency and peak voltage are defined, as well as the range of variation of the peak voltage (dashed line).

Fig. 1 Asymmetric bipolar pulsed-DC signal waveform, which is divided into the regions of positive (OFF) and negative (ON) voltages.

The film thickness was measured by means of a Dektak...
3030 surface profilometer. To assess the diamond-like properties of the coatings, a systematic study of the structure, morphology and surface characteristics was performed: X-ray reflectivity (XRR), atomic force microscopy (AFM), contact angle (sessile drop), hardness (nanoindenter), friction coefficient (nanotribometer) and abrasive wear rate (Calotest) \[6,7\]. Table 1 shows the results of such characterizations.

Table 1. Properties of the deposited films

<table>
<thead>
<tr>
<th>Hardness (nanoindenter)</th>
<th>Roughness (AFM)</th>
<th>Friction coeff. (nanotribometer)</th>
<th>Wear rate (Calotest)</th>
</tr>
</thead>
<tbody>
<tr>
<td>17-24 GPa</td>
<td>0.1-1 nm</td>
<td>0.15-0.20</td>
<td>0.5-1·1·10^\text{-3}</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>mm\text{m}^{-3} N^\text{i}^\text{-1}</td>
</tr>
</tbody>
</table>

3. Results and discussion

3.1. Plasma diagnostics in time-resolved mode

Fig. 2 plots the different I-V characteristics registered by the fast Langmuir probe every 1 \(\mu\)s within the ON phase of the pulse. The curves corresponding to the OFF phase were Maxwellian and had a low intensity, which strongly increased as soon as the ON phase started. In the ON interval, the experimental data pointed to a non-Maxwellian electron distribution, which indicates that the processes from the ON phase took place further from equilibrium in comparison with the OFF phase.

![Fig.2 I-V curves recorded in time-resolved mode. The inset shows the analyzed region of the pulse waveform.](image)

The fitting of the I-V curves to the following model has provided the plasma parameters of the pulsed discharges along one pulse cycle:

\[
i_e = C\sqrt{V_p - V} + i_e^{\text{cold}} \exp \left[ \frac{e(V - V_p)}{kT_e^{\text{cold}}} \right] + i_e^{\text{hot}} \exp \left[ \frac{e(V - V_p)}{kT_e^{\text{hot}}} \right]
\]

where \(V\) is the probe voltage, \(V_p\) is the plasma potential, \(e\) is the elemental charge (1.6·10^{-19} C), \(k\) is the Boltzmann’s constant (1.38·10^{-23} J/K), \(T_e^{\text{cold}}\) and \(T_e^{\text{hot}}\) are the respective cold and hot electron populations, which correspond to the respective intensities at \(V_p\), \(i_e^{\text{cold}}\) and \(i_e^{\text{hot}}\).

\[
i_e^{\text{cold}} = n_e^{\text{cold}} \frac{e}{2m} \left( \frac{kT_e^{\text{cold}}}{2\pi m} \right)^{1/2}
\]

\[
i_e^{\text{hot}} = n_e^{\text{hot}} \frac{e}{2m} \left( \frac{kT_e^{\text{hot}}}{2\pi m} \right)^{1/2}
\]

where \(m\) is the electron mass (9.109·10^{-31} kg) and \(A\) is the probe area. The total electron density is the sum of the cold \((n_e^{\text{cold}})\) and hot \((n_e^{\text{hot}})\) electron densities. Hence, the second and third terms are the respective contributions of cold and hot populations to the electron current. The first term accounts for the saturation ion current, where the constant \(C\) has been estimated according to the orbit motion limit (OML) theory:

\[
C = \frac{n_i A \left( \frac{2e^2}{M_i} \right)^{1/2}}{\pi}
\]

where \(n_i\) is the ion density and \(M_i\) is the ion mass.

Fig. 3 shows the time evolution of the plasma parameters within cycles corresponding to peak voltages of -700, -900 and -1100 V. A single electron population was detected in the OFF phase. There, the identities \(T_e^{\text{cold}} = T_e^{\text{hot}}\) and \(n_e^{\text{cold}} = n_e^{\text{hot}}\) are fulfilled. This Maxwellian distribution changes rapidly to bi-Maxwellian at the beginning of the ON phase, where the cold group remains at around 1 eV and the hot electrons reach 10 eV. As the pulse advances, the cold group remains in the range of 1 eV, whereas the hot electrons undergo a smooth cooling down. The origin of the hot electrons is discussed in section 3.2.

![Fig.3 Evolution of the (a) electron temperature, (b) electron and ion densities (full symbols: hot electrons; open symbols: cold electrons; cross: ions), and (c) plasma and floating potentials (full symbols: \(V_p\); open symbols: \(V_f\)). Squares: -700 V; circles: -900 V; rhombus: -1100 V.](image)
The density of the cold electrons increases exponentially during the ON phase, reaching a peak at $7 \times 10^{10}$ cm$^{-3}$ at the end of the pulse. At the same time, the hot electron population is gradually extinguished, possibly enhancing the ionization rate and providing a higher density of cold electrons.

Values of 1-2 $\times 10^{10}$ cm$^{-3}$ along the pulse were obtained for $n_e$, which agree in order of magnitude with $n_{e,\text{cold}} + n_{e,\text{hot}}$. To fit the ion saturation region, we have assumed that the most abundant ion is CH$^+$. As mentioned above, we used the OML theory. This is the simplest model to evaluate the ion density, since it does not consider collisions of the ions inside the probe sheath. However, the fast transients of the voltage in a pulsed discharge promote strong oscillations of the probe sheath thickness. This avoids an accurate measure of the ion density [8].

Plasma potential was smoothly increased within a pulse, indicating that the discharge was progressively enhanced during each cycle and that it was never extinguished. The floating potential follows an evolution opposite to that of the electron temperature.

The plasma parameters averaged over one pulse cycle are listed in Table 2. Only the electron density shows a significant variation coherent with the peak voltage increase. Indeed, a higher ionization degree is expected for more energetic plasmas. Concerning $T_e$, $V_p$, and $V_f$, no defined trend is observed. Despite this stability in the averaged values, the parameter evolution within a pulse cycle did change with peak voltage variation. Indeed, as shown in Fig. 3(a), $T_e$ at -700 V underwent a relatively acute and strong increment up to 12 eV when the ON phase started. At the following microseconds, this parameter was stabilized at lower values. At -900 V of peak voltage, $T_e$ remained most of the time around 10 eV, whereas at -1100 V there was a smooth increase along with the pulse time.

Table 2. Plasma parameters averaged over one pulse at different peak voltages.

<table>
<thead>
<tr>
<th>Peak V (V)</th>
<th>$T_{e,\text{sat}}$ (eV)</th>
<th>$T_{e,\text{hot}}$ (eV)</th>
<th>$n_{e,\text{cold}}$ ($\times 10^5$ m$^{-3}$)</th>
<th>$n_{e,\text{hot}}$ ($\times 10^5$ m$^{-3}$)</th>
<th>$n_e$ ($\times 10^5$ m$^{-3}$)</th>
<th>$V_p$ (V)</th>
<th>$V_f$ (V)</th>
</tr>
</thead>
<tbody>
<tr>
<td>-700</td>
<td>0.60</td>
<td>5.7</td>
<td>19</td>
<td>1.0</td>
<td>9.8</td>
<td>30</td>
<td>20</td>
</tr>
<tr>
<td>-900</td>
<td>0.64</td>
<td>5.6</td>
<td>20</td>
<td>1.4</td>
<td>16</td>
<td>30</td>
<td>21</td>
</tr>
<tr>
<td>-1100</td>
<td>0.55</td>
<td>5.8</td>
<td>21</td>
<td>1.9</td>
<td>14</td>
<td>31</td>
<td>19</td>
</tr>
</tbody>
</table>

The electron density was also connected to the peak voltage variation. Generally, the maxima in $n_{e,\text{cold}}$ were increased together with the supplied power. The floating potential did not exhibit a clear tendency, whereas the variation of plasma potential had a higher slope for higher peak voltages. Further experiments performed at different pulse frequencies could clarify the dependence of plasma parameters with the input power or peak voltage variation.

3.2. Sheath dynamics

The splitting into two electron populations is associated to the rapid advancing of the sheath-edge at the OFF-ON phase transition [9]. The thickness corresponding to a collisional sheath, $s$, is expressed as following:

$$s = \frac{4.12 \left( \frac{eV_p}{kT_e} \right)^{3/2}}{\lambda_{\text{De}}^{1/2}} \lambda_i^{3/2}$$

(5)

where $\lambda_i$ is the mean free path of the ions (1.2 mm according to [10]) and $\lambda_{De}$ is the Debye length at the sheath-edge. The plasma density at the sheath-edge is assumed to be $n_{e,0}=0.63n_e$. Here, $V_p$ is identified as the plasma potential minus the cathode voltage. On the other hand, the speed of ionic sound (Bohm velocity), $u_i$, is:

$$u_i = \left( \frac{kT_e}{M_i} \right)^{1/2}$$

(6)

Fig. 4 shows the evolution of the sheath thickness and sheath-edge velocity, respectively at different times within the pulse waveform. The peak voltage is -900 V. At the beginning of the ON phase (2.3 μs), the plasma sheath expands at a velocity one order of magnitude higher than $u_i$. This supersonic expansion lasts until $t=3$ μs, where the sheath achieves 0.9 cm thickness. During this interval, instabilities due to energetic acoustic waves may cause the generation of the hot electron population. Previous works have reported an increase in electron temperature measured in pulsed plasmas due to a burst of energetic electrons coming from the sheath-edge [5]. After this rapid expansion, between $t=3.8$ and $8.0$ μs, the cathode sheath contracts while the cathode voltage reaches its maximum. The sheath-edge expands again approximately 2 μs after the peak voltage takes place, where the ON phase is finishing and the subsequent OFF time is about to commence.

![Fig.4 Variation of the sheath thickness and sheath and ionic velocities estimated from the plasma parameters calculated for -900 V of peak voltage.](image-url)

In this scenario, the stochastic heating seems related to the fast increase of voltage at the OFF-ON transition. Then, the temperature of hot electrons, as well as their density, smoothly decreases due to the stabilization of the cathode voltage. Although this heating mechanism is dominant at low pressures, this has been detected at high pressure (10 Pa) probably due to an effect of the pulse frequency. Indeed, hot and cold electron populations could thermalise at longer ON times, but pulse duration limits the ON phase,
thus causing possibly the plasma to be in a transient state. This could be proved by performing Langmuir probe diagnostics in discharges powered by lower frequency pulses.

### 3.3. Input power and deposition rate

In the context of plasma polymerization processes, the energy absorbed per precursor molecule is of paramount importance in the growth rate and surface properties of the resulting coating [11,12]. The following expression relates the generalized activation energy, $E_a$, with the input power per gas flow in the discharge, $W/F$:

$$ \frac{R_m}{F} = G \exp \left( -\frac{E_a}{W/F} \right) $$

where $R_m$ is the mass deposition rate and $G$ is a reactor-dependent factor, which is proportional to the conversion factor of the precursor. These parameters are calculated from the linear fit analysis of the experimental data. $W/F$ is a key parameter that controls the growth kinetics in PECVD processes, and it is interpreted as the input energy per molecule. When it equals $E_a$, the fragmentation of the precursor is considerable. Therefore, this $W/F$ constitutes a measure of the bond breakages of the precursor molecule. Moreover, it permits to establish a gradation of the fragmentation rate of the precursor, since $E_a$ is characteristic of the process gas. Fig. 5 depicts the variation of $R_m/F$ vs. $W/F$ in an Arrhenius-type plot. It is worth noting that there was not only defined one linear region, but the slope was changing gradually. For the calculation of $R_m$, an average density of 1.9 g/cm$^3$ for DLC was assumed, according to Table 1.

Fig.5 Arrhenius-type plot of $R_m/F$ against $(W/F)^{-1}$ for DLC films grown at different input energies (peak voltage).

The coatings prepared in the low energy region are usually soft, polymer-like. There, the growth process is characterized by a low $E_a$. Contrarily, in the case of coatings grown in the high energy region, one obtains hard materials more suitable for protective coating applications. Hence, the most ceramic-like coatings obtained in this work were deposited at the highest input powers, i.e. maximal peak voltage [13].

Approximate values of $E_a$ ranged between 1.0 and 3.8 W/sccm for low and high input energy levels, respectively. This indicated a major dissociation degree for pulsed-DC discharges carried out at higher peak voltages, probably due to the enhancing of alternative growth mechanisms. Such parameters modulated thus the growth kinetics of DLC. Indeed, the major energy absorption by the precursor molecules leads to a more active discharge, by increasing the deposition rate and improving the mechanical performance of the coatings due to a major cross-linking in the amorphous carbon structure.

### 4. Conclusions

Pulsed-DC discharges of CH$_4$ at 100 kHz to deposit DLC coatings have been successfully characterized in time-resolved mode with a modified Langmuir probe setup. The I-V curves were acquired synchronously with the pulse signal, providing an accurate tracking of the plasma parameters. Although their values did not undergo a significant change with the peak voltage variation, such parameter permitted to tailor the behaviour of plasma parameters within a pulse cycle. Moreover, peak voltage had a relevant influence on the growth kinetics. This effect was evidenced by the modulation of the activation energy of the gas precursor carried out by the input energy in the discharge.

### References