Characterization of diamond-like carbon (DLC) thin films prepared by r.f. magnetron sputtering

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Diamond-Like Carbon (DLC) thin films were deposited on stainless steel and silicon substrates by a r.f. (13.56 MHz) magnetron sputtering technique. A carbon target (99.99%) and a gas mixture of Ar/CH₄ were used. During the deposition process the plasma discharge was monitored by Optical Emission Spectroscopy (OES) in order to analyze the state of the chemical species present in the plasma. The films were characterized by Raman Spectroscopy and by Reflection Absorption and Transmission Infrared Spectroscopy. The morphology of the deposited layers was analyzed by Scanning Electron Microscopy (SEM). The Raman intensity of the diamond and graphite peaks (I_D/I_G) depends on the percentage of CH₄ in the gas mixture. The relationship between the relative change of the plasma electronic temperature that, for the experiment conditions, does not depend significantly on the concentration of CH₄ in the mixture and its value was of the order of 1 eV. Optical Emission Spectroscopy shows that, besides of the atomic hydrogen peak (Hα, Hβ, Hγ), emission spectra are dominated by neutral CH species and the most intense peak in the spectra correspond to CH (A^2Σ → X^2Π at 431.5 nm) which is supposed to be the precursor species in the diamond-like films, beside in the Transmission Infrared Spectroscopy analysis were observed the sp³ CH₂ symmetric and asymmetric at 2870 and 2960 cm⁻¹ peaks. These peaks have been observed in diamond deposited at very high CH₂ concentrations and also in diamond-like carbon (DLC) films.

1. Introduction

The amorphous carbon thin films have had a growing interest during the last years due to the important properties that they exhibit such as their extreme hardness, high electric resistivity, optic transparency in the infrared and the visible and for the fact of being chemically inert. Different techniques are used for the preparation of these DLC films: ionic implantation, sputtering or plasma assisted chemical vapor deposition techniques (CVD). All these techniques have in common the use of different mixtures of hydrocarbons for the growth of carbon amorphous hydrogenate (a-C:H), films due to the role that hydrogen plays in the stabilization of the sp³ bonds of the diamond, on the surface of the film that are producing[1]. In the type sputtering discharges, the plasma of the discharge is used to generate the activation of such chemical precursors as the neutral radicals and the ions taken place by the decomposition of the hydrocarbons by electronic impact. Those precursors are absorbed by the surface of the substrate and therefore the films have an appreciable content of hydrogen incorporated in the structure like radical neutral CH which are associated with the deposition of the films type diamond [2]. The emission spectroscopy of the plasma has been recognized to be an efficient diagnostic tool of the plasma parameters and for the monitoring of the chemical species present in the plasma processes used for the deposition of thin films. Particularly the Optical Emission Spectroscopy (OES) is a powerful method for the investigation and the in situ diagnostic of the complex processes occurring during the glow discharge. Among the advantages that this sensitive detection technique offers is their high space resolution and the fact that it allows us to have in situ a real time information of the processes that are produced in the plasma, without producing any interference with them. The relationship between the relative intensities of the emission lines and the electronic temperature (Tₑ); it is a complicated function that depends on the sputtering conditions (pressure, temperature, ratio, etc. in the gas mixture), as well as the geometry and the reactivity of the target.

In this work, the plasma produced by a discharge magnetron sputtering r.f. (13.56 MHz) is monitored in situ by means of optical emission spectroscopy (OES) technique, used to grow diamond-like type thin films, using different Ar/CH₄ ratios in the mixture. The relationship between the intensities of the lines Hα/Hβ of the hydrogen represents a measure of the relative change in the electronic temperature of the plasma[3]. They are
correlated with the quotient \( \frac{I_\beta}{I_\alpha} \) between the intensities of the diamond and graphite peaks obtained from Raman spectroscopy analyses and with bonding structure of the a:C-H bonds in the films, determined by Infrared spectroscopy (IRS). In this way the optimum conditions that favor the growth of the diamond phase in the a-C:H films are reached.

2. Experimental procedure

A glow discharge plasma was obtained using a magnetron sputtering of r.f. (13.56 MHz) system, equipped with carbon target 99.999% in a Ar/CH4 mixture. Before introducing Ar and CH4 to the camera, this is evacuated until a pressure of \( 10^{-5} \) mbar. A pre-sputtering in pure argon is made in order to clean the target. Finally and with the purpose of improving the adherence of the DLC films, an intermediate layer of carbon is deposited using only Ar gas in the discharge, then the mixture Ar/CH4 is introduce to deposit the layer of DLC on steel and silicon substrates.

The optical emission spectrum of the plasma was obtained using a fiber optic that is coupled near the carbon target through the quartz window of the chamber where the discharge takes place. The fiber optic is connected to a monochromator SC of 0.3 m of focal distance and with a grid of 150 grooves/mm that allow to analyze the emission spectrum coming from the plasma. The wavelengths were in the range 250 and 750 nm, with a resolution of 4 nm. The spectrum is accumulated and processed by the Process Sentry System 400. It combines an optic spectrometer that has an arrangement of detecting photodiodes with the Process Sentry software that allows to visualize and to analyze in real time intensity vs wavelength measurements.

The r.f. power density (2 – 14 W/cm²), the concentration of CH4 in the mixture Ar/CH4(1.5, 2, 3, 5, 9, 24, and 40%), the total pressure in the chamber \( (4 \times 10^{-2} - 1.4x \times 10^{-1} \text{ mbar}) \) and the substrates temperature \( (100 – 300 \text{ C}) \) are systematically varied in the deposition process to study the influence of these parameters on the intensity of the lines in the emission spectrum of the chemical species present in the plasma. These results were correlated with the content of diamond of the films determine by Raman spectroscopy. The content and type of bonding of the hydrogen radicals incorporated in the a:C-H films has been determined by the IRS technique.

3. Results and discussion

A. Optic Emission Spectroscopy

A characteristic optical emission spectrum is observed in Figure 1(a), corresponding to a mixture of Ar/CH4(40% methane); this was obtained from a discharge (13.56 MHz) r.f magnetron sputtering. Some of the most intense argon (419, 519, 557, 591, 604, 638, 687, 697, 707 and 738 nm), lines are observed. It also exhibits the \( H_\alpha \) (transition \( n' = 3, n = 2 \) at 656.4 nm), and \( H_\beta \) (transition \( n' = 4, n = 2 \) at 486.2 nm) lines of the atomic hydrogen corresponding to the Balmer series. An intense peak corresponding to the band head from the transition \( \Delta^2 \Delta \rightarrow \chi^2 \Pi \) of the radical CH (431.5 nm) accompanied by one weak to 390 nm associated to the head of band of the transition \( \Delta^2 \Sigma \rightarrow \chi^2 \Pi \) the CH[4,5] is also observed next to these lines.

The table 1 shows the evolution of the intensities of the peaks of \( H_\alpha, H_\beta, \text{CH} \) and the relationship \( H_\alpha / H_\beta \), for different methane concentrations in the mixture Ar/CH4. The intensities of these peaks are normalized to the intensity of the 738 nm peak of the argon since their effective section presents an activation energy of \( \approx 13.3 \text{ eV} \) similar to that of the CH (431.5 nm) and to that of the line \( H_\alpha[6] \). The electron temperature was calculated using the relative intensity between two spectral lines corresponding to the transition to the same lower level according the following expression [7]:

\[
T = \frac{\frac{E_p}{k}}{\frac{I_{mn}}{I_{pn}} \frac{\lambda_{mn}}{\lambda_{pn}} \frac{\ln \left( \frac{g_p}{g_m} \right) A_{pn}}{A_{pn}}} \tag{1}
\]

Where \( T \) is the electronic temperature, \( I \) is the relative line intensity, \( g \) is the statistical weight, \( E \) is the energy of the upper level, \( A \) is the Einstein’s coefficient, \( K \) the Planck’s constant and \( \lambda \) is the wavelength of the emitted photon. For the \( H_\alpha \) (656.4 nm) and \( H_\beta \) (486.2 nm) lines these values are \( g_3 = 18; g_4 = 32; A_{32} = 4.41 \times 10^7; A_{42} = 8.41 \times 10^6; E_3 = 12.1 \text{ eV}; E_4 = 12.7 \text{ eV} \) and the calculated electron temperature was around1.0eV.

In table 1 it can see that the relationship \( I_{H\alpha}/I_{H\beta} \) practically does not depend on the variation of the content of CH4 in the mixture, indicating that under our conditions a significant change does not take place in the electronic temperature of the plasma. In a similar way one can see that the intensity of the band head of the transition \( \Delta^2 \Delta \rightarrow \chi^2 \Pi \) of the CH radical (431,5 nm) whose presence is an indicative of the formation of a-C:H, shows its largest

<table>
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<th>% CH4</th>
<th>( I_{H\alpha} )</th>
<th>( I_{H\beta} )</th>
<th>( I_{H\alpha}/I_{H\beta} )</th>
<th>( I_{CH} )</th>
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<td>0.87</td>
<td>0.79</td>
<td>1.11</td>
<td>NP</td>
</tr>
<tr>
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<td>0.88</td>
<td>1.08</td>
<td>NP</td>
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<td>1.16</td>
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<tr>
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<td>1.10</td>
<td>0.89</td>
</tr>
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<td>0.90</td>
<td>1.12</td>
<td>0.94</td>
</tr>
</tbody>
</table>

*NP: No Present.
intensity for high concentrations of CH₄ (40%) and it diminishes for small concentrations[2].

B. Raman Spectroscopy

Figure 1b shows the Raman spectrum of a DLC film that was deposited at a 40% methane concentration in the gas mixture. A wide peak centered in 1560 cm⁻¹ which is characteristic of the carbon type diamond can be observed[9].

In the order to obtain a quantitative information about the diamond content in the films, the experimental Raman Spectra were considered as a combination of diamond and graphite components. For this purpose, the bands corresponding to graphite centered at 1.550 cm⁻¹ and to the diamond centered at 1.333 cm⁻¹ were fitted by Gaussian curves. The diamond content was then calculated as the ratio between the peak area at 1.333cm⁻¹ and the area corresponding to graphite. The areas corresponding to the peaks are in a ratio between 2.0 and 2.4, which are in the same relationship I_D/I_G for 20% and 40% methane in the gas mixture. This indicates that a larger the CH₄ content in the gas mixture favored more sp³ bonds of the diamond type to be formed.

C. FTIR RESULTS

Figure 2 shows the Transmittance characteristic Spectrum of Infrared Fourier Transformed for the DLC film deposited at different methane concentration in the gas mixture. All the samples show the sp³ symmetric and antisymetric small peaks for CH₃ at about 2.870 and 2.960 cm⁻¹.

These peaks are reported for diamond samples deposited with high CH₄ concentrations and in DLC films[10]. Finally the bond concentration of hydrogen in the samples could be calculated using the transmittance method[11]. For 0.6 µm thin films the hydrogen bond concentration was approximately 2.9x10²¹ cm⁻³.

4. Conclusions

The species present in the plasma, determined by an OES study show that the relationship I_Hα/I_Hβ remains practically constant. This indicates that the electronic temperature (~1eV) doesn't have significant variations for the conditions of our experiment. In the order hand, the relative intensity of the band head at 431.5 nm corresponding to the A₂Δ → X₂Π transition of the CH radical, which is associated with the deposition of the DLC films, is larger at 40% methane concentration and decreases when the methane concentration decreases.

The Raman analysis show that at the same methane concentration (40%) the relationship between I_D/I_G is maximum and the IR results confirm that the sp³ symmetric (2.850 cm⁻¹) and asymmetric (2.920 cm⁻¹) peaks corresponding to CH₂ are larger at 40% and can’t observed at smaller methane concentration. So monitoring the plasma emission spectrum, the deposition parameters can be controlled during the process, to favor the diamond phase formation in the film.

Acknowledgements

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References

[8] NIST Atomic Spectroscopy Database.