Diamond-like carbon deposited by plasma technique as a function of methane flow rate

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Abstract

In this work we investigate diamond-like carbon (a-C:H) prepared by plasma enhanced chemical vapor deposition (PECVD) as a function of methane gas flow rate, including films deposited at zero flow rate, i.e., without the use of vacuum pumps during the deposition. The deposition rate and film structure (investigated by Raman spectroscopy) depend on the methane gas flow rate. A maximum for deposition rate was found at methane flow much smaller than the flow usually adopted in conventional procedures.

Introduction

Diamond-like carbon (DLC) have been used in a number of application such as hard coating for tools, cold cathode electron emitters, micro-electro-mechanical systems **(**MEMS**)**, car parts and protective coating in hard disk drives. These applications are mainly associated with the high hardness and low friction coefficient of DLC [1-6]. One of the most used techniques is the plasma enhanced chemical vapor deposition (PECVD). In this technique, a continuous supply of methane gas is required to guarantee that the atmosphere be constant along the deposition. This procedure results in the waste of a considerable amount of methane gas to the atmosphere. In this work we investigated diamond-like carbon (a-C:H) prepared by PECVD in a wide range of methane gas flow rate, including films prepared at zero flow rate.

Experimental

The films were deposited in an ultra-high-vacuum system to reduce desorption of contaminating gases from the walls of the reactor chamber. In addition, the reactor chamber was baked for more than 10 hours at a temperature of about 120 °C and pumped down to about 10^{-8} torr. Films were then deposited by PECVD on the cathode electrode as a function of methane gas flow rate. For the deposition at zero flow, the chamber was closed and methane gas was introduced until the desired pressure was reached. Using this procedure, hydrogenated amorphous carbon (a-C:H) films with diamond-like structure were obtained. Micro-Raman scattering spectroscopy was carried out in air at room temperature in an Acton Research SpectraPro 500i analyzer, using the 488 nm Ar^+ laser line with 10 nW emission power.

Results and Discussion

The deposition rate of the DLC films (Fig. 1) changes significantly in the methane flow rate range investigated. A maximum is found at a relatively low flow, 4 sccm, with deposition rate of about 50 % higher than in normal condition (10-40 sccm range). The increase in the deposition rate as the methane flow rate decreases from 80 sccm to about 4 sccm (Fig. 1), is related to an increase in the methane dissociation, which is supported by the work of Zhang and Catherine [7].

The reduction of the deposition rate for methane flow rate below 4 sccm is related to the enrichment of the atmosphere with H_2 molecules coming from the dissociation of methane. The use of low flow rate gives an expressive decrease in the amount of CH_4 consumed in the deposition. As can be observe in the inset of figure 1, the consumption of methane as a function of the flow rate can be reduced by about two orders of magnitude at 4 sccm, and by three orders of magnitude without pumping the reactor chamber during deposition. This represents a huge reduction of consumed gas, beside the beneficial effect to the environment.

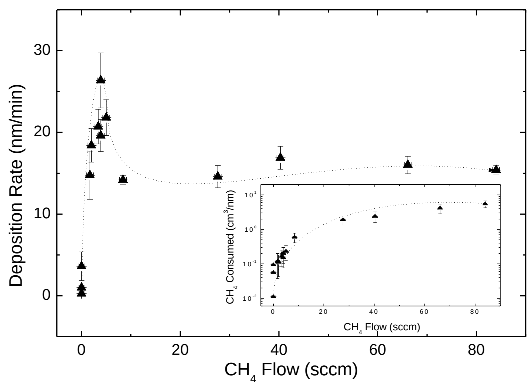

Figure 1 – Deposition rate of diamond-like carbon films deposited by PECVD as a function of methane flow. The inset shows the consumption of methane in the same flow range.

Figure 2 shows the concentration of hydrogen as a function of the methane flow obtained from the integrated area of the C-H stretching mode (in the 2800 -3100 cm^{-1} frequency range, determined by FTIR). It is observed that the concentration increases as the methane flow decreases. This effect must be related to the increase in the partial pressure of H_2 in the atmosphere, promoted by the reduction of the pumping speed.

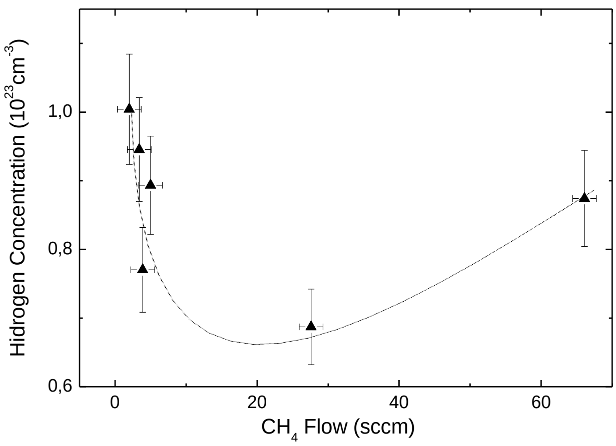

Figure 2- Hydrogen concentration of a-C:H films, using the integrated area of the C-H stretching mode (2800-3000 cm^{-1} wavelength range), as a function of methane flow rate.

Figure 3 shows the fitting results of Raman spectra for the films as a function of the methane gas flow rate. It shows the G peak position (3a), full width at half maximum, FWHM, of the G peak (3b) and the ratio between the intensities of the D peak by the G peak, I(D)/I(G), (3c). They show characteristic patterns of diamond like-carbon. The D peak is related to closed sp^2 structures (aromatics), and the G peak is related either to closed as well as open (olefenics) sp^2 structures. The full width at half maximum (FWHM) of the G peak (Fig. 3b) is associated with the structural order (angles and length of chemical bonds) of all sp^2 sites presented in the film. The I(D)/I(G) ratio (Fig. 3c) gives qualitative information about the number and the order of aromatic structures. It indicates a slight decrease in the graphitic characteristic as the methane flow decreases. On the other hand, the FWHM displayed in Fig. 3b indicates that all samples have similar structural order with exception to the sample deposited at zero flow, where the value of FWHM (G) was lower, revealing a more organized film. In view of this result, the I(D)/I(G) ratio is probably related to aromatic structures only.

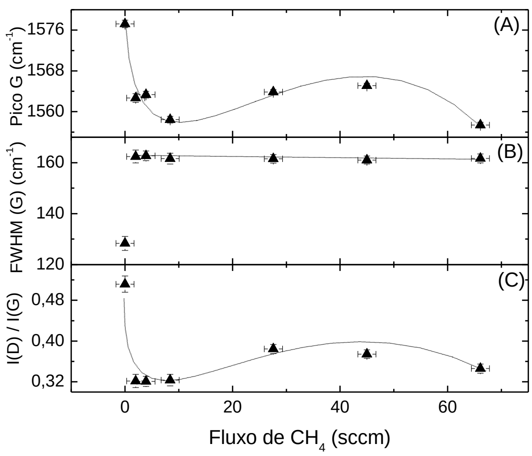

Figure 3 – (a) Wavenumber (Raman shift) position of the G peak; (b) full width at half maximum (FWHM) of the G peak and (c) ratio between the intensities of the D and G peaks, I(D)/I(G), as a function of methane flow rate.

The sample deposited at zero flow rate presents a behavior quite different from the others. We ascribed this behavior to the condition of the deposition of this film. When the system is not pumped, a rapid enrichment with H_2 in the atmosphere is established and the deposition process stops after the depletion of methane gas and the radicals containing carbon atoms (C_2H_2, C_2H_4, and others, generated by the methane plasma). That means the deposition is performed with a significant variation in the composition of the atmosphere, which varies from pure methane to pure hydrogen plasma. The enrichment of H_2 molecules in the atmosphere changes the film properties.

Conclusion

Diamond like carbon (a-C:H) were deposited by PECVD as a function of methane gas flow rate. It was observed that the deposition rate has a maximum at a relatively low methane flow rate (about 4 sccm for our system). Raman measurements indicate that at low methane flow rate the material becomes less graphitic. The film prepared at zero flow can be deposited with an extremely reduced amount of methane gas, been 2 to 3 orders of magnitude smaller than that adopted for the deposition of films following traditional procedures.

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