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Deposition of hydrogenated amorphous carbon films from CH_4/Ar plasmas: Ar dilution effects

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Hydrogenated amorphous carbon (a-C : H) films were deposited, at room temperature, from a CH_4/Ar plasma produced by a radio frequency (r.f.) glow discharge system at 13.56 MHz, and different power values. Two different characterisation techniques, Raman and FTIR spectroscopies, have been used to investigate correlations between deposition conditions and properties of hydrogenated amorphous carbon films. The composition of the initial gaseous mixture and the r.f. power input are shown to affect significantly both mechanical and microstructural properties of deposited films. As the fraction of argon in the feed gas is increased, the deposition rate increases and the deposited film shows a higher friction coefficient, thus suggesting the production of a softer material. On the other hand, Raman measurements suggest the occurrence of a lower degree of structural order in the sp^2 lattice. Experimental findings are discussed in terms of the different chemical composition of the plasma. © *2001 Kluwer Academic Publishers*

1. Introduction

Besides diamond a new class of solid materials, the amorphous hydrogenated carbon (a-C : H), can be synthesized by chemical vapour deposition (CVD). Hydrogenated amorphous carbon films may be produced in a number of different ways and exhibit a wide range of characteristics [1]. These films, structured with both sp^3 and sp^2 hybridised bonds in an amorphous or microcrystalline form, are well known for possessing unique properties. Applications of such films include scratch resistant coatings, optical window coatings, overcoats for magnetic recording media, low friction coatings for tribological systems, antireflective coatings for optoelectronic devices and coatings for medical implants [1]. It has been reported that the properties of these films, like microhardness, optical refractive index, internal stress, low friction coefficients depend strongly on the preparation and may vary markedly from one deposition process to another. Among the various methods used to prepare a-C : H films, the deposition from r.f. glow discharge of hydrocarbons—usually a CH_4 plasma—is the most common. By manipulating the deposition parameters, a-C : H films can be produced with a broad range of mechanical properties ranging from soft (polymer-like) to very hard (diamond-like) films. Unfortunately mechanisms governing the deposition process are not fully understood yet, and no general consensus exists about the identification of the growth species. Different species have been proposed for this role such as methyl, acetylene, atomic carbon, and carbon C_2 dimers [2]. One way to pursue this issue consists in the investigation of effects related to the dilution of methane by rare gases. Since dilution implicates a different plasma chemistry, one can try to investigate correlations between the chemical composition of the plasma and the properties of the deposited material. So far, effects of CH_4 dilution by Ar have been the most reported in literature [3–5]. However, while there is a general agreement on the occurrence of effects related to the plasma composition, some discrepancies exist between experimental data. As an example, while some authors [2, 6] describe the increase of the deposition rate with the fraction of argon, others claim just the opposite [7]. Discrepancies about the temperature dependence of the growth rate are also reported. By using pure CH_4 the deposition rate declines by increasing the substrate temperature [8], whereas by using 1% methane in argon the growth rate increases with the substrate temperature [9]. One problem is that experimental conditions are often different and therefore a direct comparison of different works is difficult. On the other hand, differences reported above might indicate that a very different chemistry occurs in a CH_4 plasma with respect to a CH_4/Ar plasma. Thus it appears very important to investigate the relationship between the plasma chemistry and the properties of the deposited films.

In the present work we have investigated the structural properties of a-C : H films deposited from CH_4/Ar plasmas as a function of the initial gas mixture composition. In addition we have studied the effect of the substrate bias. We found that the deposition rate is strongly affected by both the Ar fraction and the bias voltage. Film properties are evaluated by Fourier-infrared and

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Raman spectroscopy for material deposited at high and low Ar percentage, respectively. The observed differences are related to the unlike chemical composition of the plasmas.

2. Experimental details

Hydrogenated amorphous carbon films were deposited on ⟨100⟩ silicon by radio frequency plasma enhanced chemical vapour deposition (r.f. PECVD), using a generator operating at a frequency of 13.56 MHz coupled to a 60 mm diameter powered electrode which also served as substrate holder. Before loading into the chamber, samples (10 mm × 10 mm × 0.5 mm) were cleaned in an ultrasonic bath of acetone and dried with nitrogen. Prior to deposition, the chamber was evacuated (0.01 Pa), and then Ar (condition: −200 V bias, 10 Pa, 5 min) was introduced for sputter cleaning in order to eliminate any impurity on the substrate. These pretreatments are typically applied to improve the adhesion of a-C : H layers onto the substrates [10]. Subsequently, the chamber was again evacuated to 0.01 Pa. This pressure was achieved by using a turbomolecular pump, backed by a rotary mechanical pump. All films were prepared with the substrate at room temperature. The deposition parameters were the gas pressure, the methane dilution by argon, and the r.f. power. The gas pressure ranged between 13.33 Pa and 53.32 Pa, the Ar fraction varied from 0% to 97%, and the r.f. power ranged from 10 W to 25 W. The self-bias voltage was measured.

The surface of the growing film is bombarded by positive ions due to the negative self-bias voltage developed at the substrate holder. This is proportional to the r.f. power (W) and to the discharge pressure [11]. In some studies [12, 13], the growth rates and the properties of a-C : H films have been related to the bias voltage (V_b), as have been also the relative amounts of sp^2, sp^3 hybridisation and the content of hydrogen.

The film thickness was measured by a Tencor surface profile measuring system. To this aim the silicon substrate was partially covered with an Al foil in order to produce a step between the portion of covered and uncovered silicon surface. Coating thickness varies from 0.1 μm to 1.5 μm, depending on deposition conditions, the most part of coatings being about 0.4 μm.

After deposition, film samples were characterised by Raman and Fourier transform IR spectroscopy. IR spectra were recorded using a Jasco 615 Fourier transform IR spectrometer. Raman spectroscopy measurements ware carried out at room temperature in 90° geometry with samples hold in air. Unpolarized Raman spectra were excited with 120 mW of the 488.0 nm Ar laser line, analysed with Jobin-Yvon (Ramanor model HG2-S) double monochromator, equipped with holographic gratinges (2000 lines/mm), and detected by a standard photon counting system. The experimental resolution was better than 4 cm^{-1}.

3. Results

3.1. Growth rate

The deposition rate of the film is found to be influenced by the process parameters (r.f. power, total gas pressure, gas composition and bias voltage).

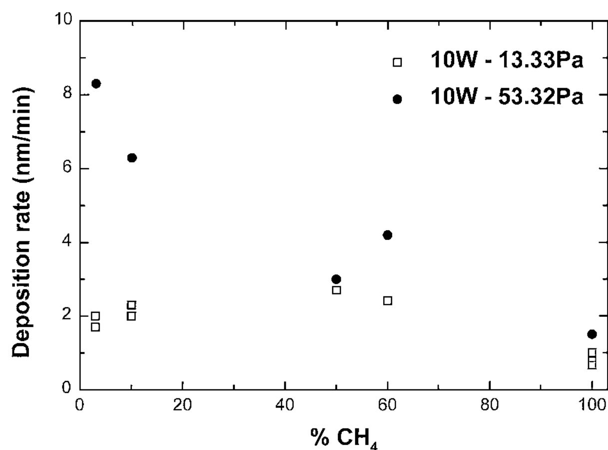

Figure 1 Deposition rate as function of methane content (deposition parameters: r.f. input power 10 W; pressures 13.33 Pa and 53.32 Pa, self bias voltage −100 V and −80 V respectively).

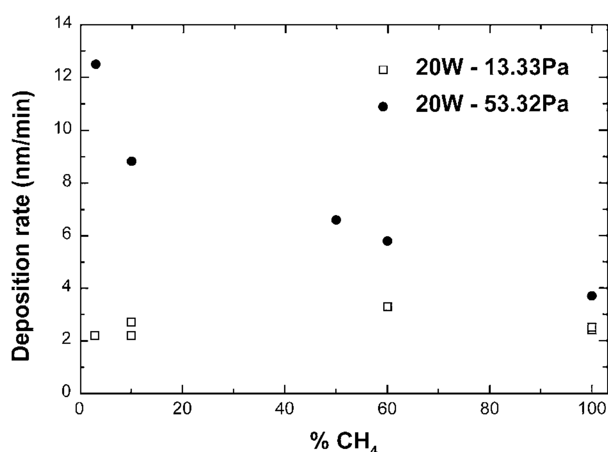

Figure 2 Deposition rate as function of methane content (deposition parameters: r.f. input power 20 W; pressures 13.33 Pa and 53.32 Pa, self bias voltage −200 V and −160 V respectively).

In Fig. 1, the film deposition rate is shown as a function of the methane fraction at a r.f. power of 10 W and at working gas pressures of 13.33 Pa and 53.32 Pa, respectively. At the lower pressure the measured growth rate is roughly constant. However, since the absolute carbon density depends on the fraction of CH_4, the deposition rate normalised on the actual amount of carbon increases with the argon fraction. The measured growth rate at a pressure of 53.32 Pa increases with the argon content, and also the rate normalised on the carbon density obviously behaves in the same way. The effect is particularly evident at the lowest CH_4 concentration: in spite of the fact that the carbon density is lower by about 30 times, the observed deposition rate increases by about a factor 3. Clearly a change in the branching ratio of the active species is occurring. A similar behaviour is observed at a r.f. input power of 20 W (Fig. 2) with the same total pressures.

3.2. Raman spectroscopy

Raman spectroscopy was used to get information on the structure of a-C : H films deposited under different deposition conditions. Raman spectra recorded between

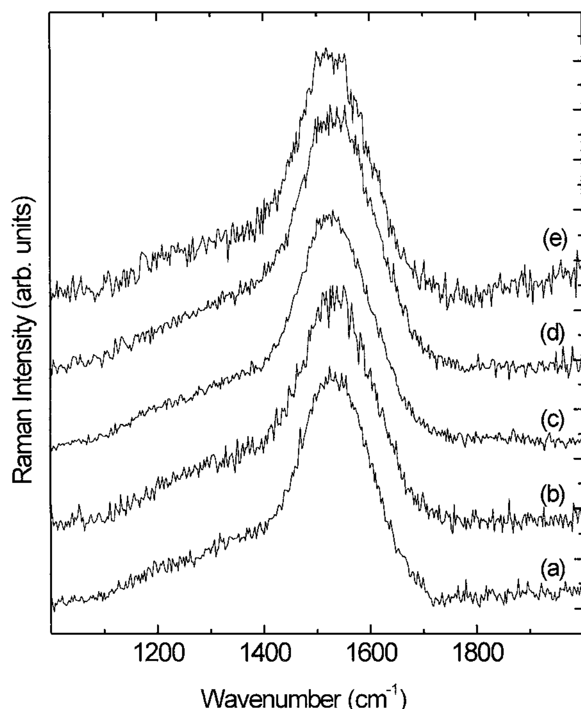

Figure 3 Experimental Raman spectra for samples prepared with different methane content: (a) 3%; (b) 10%; (c) 50%; (d) 60%; (e) 100% (total pressure 13.33 Pa, r.f. input power 20 W, self bias voltage −200 V).

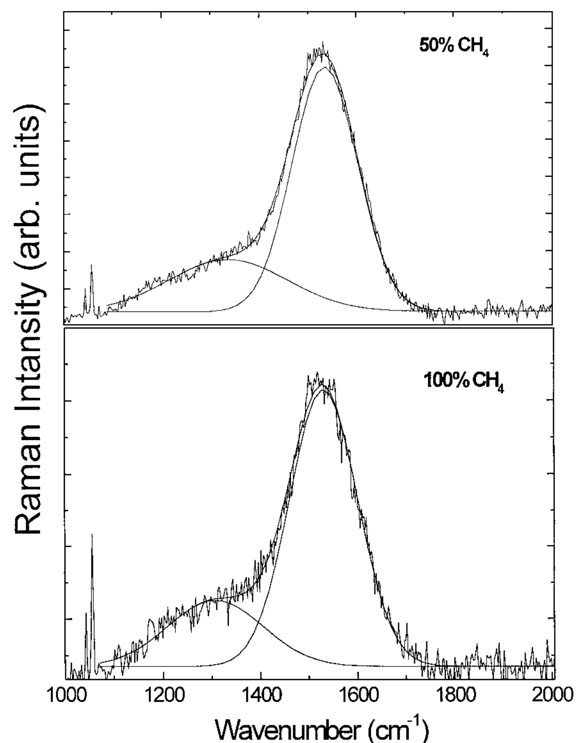

Figure 4 Raman spectra of a-C : H films (deposition parameters: total pressure 13.33 Pa, r.f. input power 20 W, self bias voltage −200 V, methane content 50% and 100%). The solid lines are the fitted spectra after the background subtraction, as discussed in the text.

500 and 2000 cm^{-1} in nearly back-scattering configuration for some a-C : H films synthesised at 13.33 Pa with a power of 20 W are reported in Fig. 3a–e. Similar spectra were observed from the samples deposited under different gas pressure and bias voltage values. All Raman spectra consist of two, very broad overlapping bands extending between 1200 cm^{-1} and 1700 cm^{-1}. These bands are usually referred as to D (disorder) and G (graphitic) bands because of their spectral features which recall the first order Raman spectrum of polycrystalline graphite [14]. However, their spectral widths and shapes clearly reflect the amorphous character of our films [15]. Finer insights on the microstructures of the films can be obtained by fitting the G and D bands with a non-linear least-square routine, using two Gaussian line shapes superimposed to a linear background [16]. The frequencies of the D and G bands, as well as their intensities and widths are used as fitting parameters. Fig. 4 provides an example of such fitting procedure, carried out from two typical spectra, after the background subtraction.

3.3. Fourier infrared spectroscopy

Further characterisation of the film structure was performed by IR spectroscopy. This technique provides information on the presence of hydrogen bonded to the carbon. Typical FTIR absorption spectra in the 700–4000 cm^{-1} range of a-C : H films under two different deposition conditions are reported in Fig. 5. The spectra show similar shape, consisting of a broad band peaked at about 2900 cm^{-1} resulting from the convolution of three different components: at 2866 cm^{-1} for sp^3 CH_3, at 2920 cm^{-1} for a superposition of sp^3 CH_2 + sp^3 CH, and at 3040 cm^{-1} for sp^2 CH stretching modes, as shown qualitatively in Fig. 6. The content of chemically bonded hydrogen can been estimated from the area under the broad band. As the substrate bias is increased above −50V, the peaks at 2866 cm^{-1} and 3040 cm^{-1} decrease and an overall reduction in the absorption intensity can be seen in the films deposited at higher bias voltages (Fig. 5). This suggests that the bonded hydrogen content decreases as the r.f. input power is increased from 10 W to 25 W. It is worth noting that these C-H absorption bands are related only to carbon atoms bonded to one or more hydrogen atoms and do not reveal anything about the unbounded hydrogen in a-C : H network.

4. Discussion

The thickness measurements of the films deposited under different plasma compositions indicate that the growth rate increases with the argon fraction. This behaviour suggests that the nature of the growth species depends critically on the initial gas mixture. Preliminary tribological measurements [17] indicate (Fig. 7) the deposition of a softer material from an argon rich plasma. Results of the fitting of the Raman spectra in terms of two gaussian lines used to reproduce the D and G bands respectively, are reported in Figs 8–10, in which the I_D/I_G ratio, the position and the width of the G-band are plotted vs. the initial plasma composition. If the CH_4 content in the plasma increases, the I_D/I_G ratio also raises, while the G band position shows a rather pronounced blue-shift, passing from about 1539 cm^{-1} to 1550 cm^{-1}. However, no appreciable change in its bandwidth occurs. According to the results of previous works [16, 18], the evolution of the fitting parameters

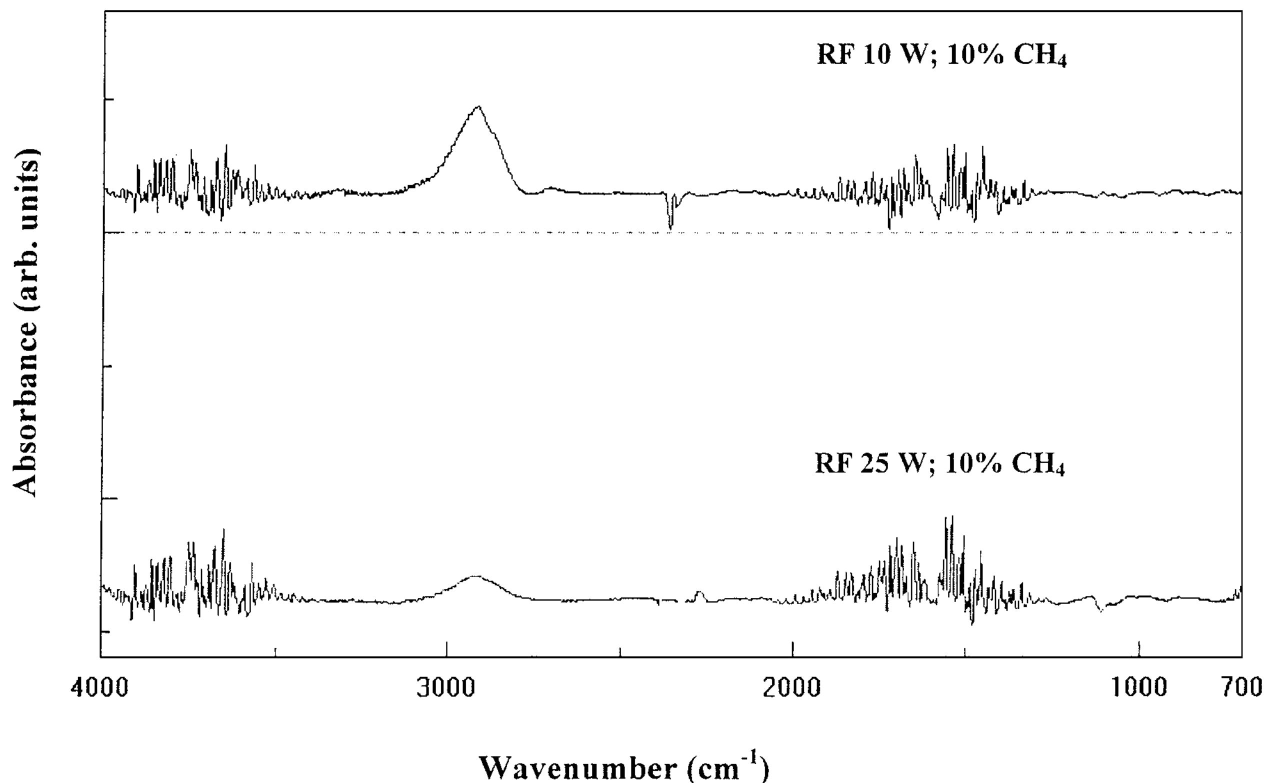

Figure 5 FTIR spectra of a-C : H films prepared at rf input power of (a) 10 W (self bias voltage −100 V), (b) 25 W (self bias voltage −250 V) and methane content of 10%.

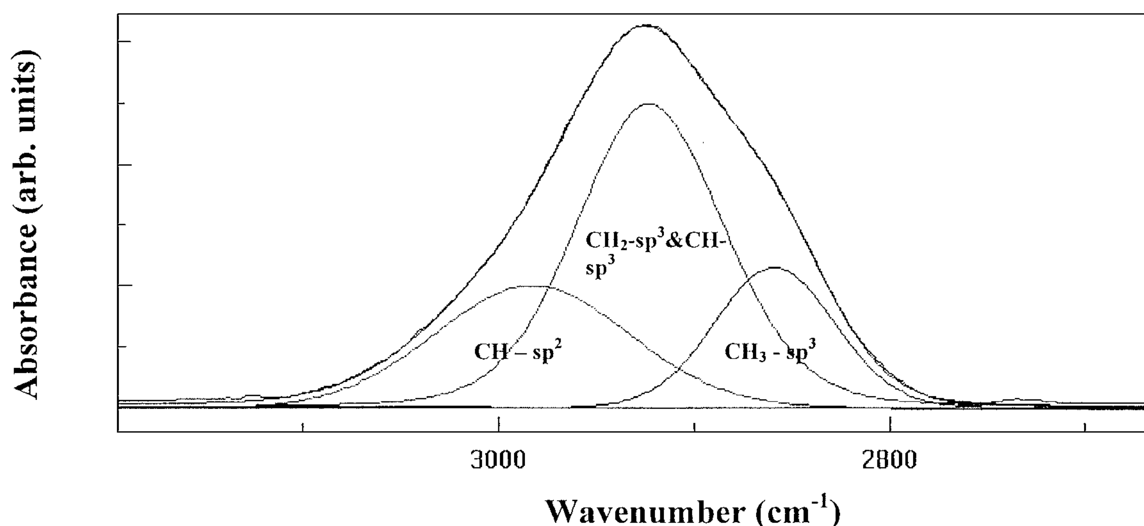

Figure 6 Deconvolution of the 2900 cm^{-1} FTIR, peak of a-C : H films.

(I_D/I_G ratio, position and width of the G band) versus the plasma composition suggests a stronger graphitic character of the films deposited from a CH_4-rich plasma with respect to films obtained from Ar-rich plasmas. Therefore our Raman results are consistent with a picture of a harder film (Fig. 7) deposited from methane-rich discharge.

Fig. 5 shows the self-bias voltage dependence of the FTIR spectra. At 10 W the film exhibits various peaks pertaining to C-H vibration modes which are characteristic FTIR spectra for a polymer-like films [19]. The hydrogen content in a-C : H films as a function of the methane concentration is shown in Figs 11 and 12; the vertical scale (in arbitrary units) was properly normalised by taking into account the film thickness. These results indicate that the hydrogen content in a-C : H films is constant with the CH_4 fraction, except for depositions at the lower bias, in which case it increases with the methane content. From Figs 11 and 12 it is also clear that the content of C-H bonds decreases by increasing the bias. It has been shown that by increasing the self bias voltage the ion energy increases almost linearly [11]. The bombardment of energetic ions can modify the structure and the properties of the film by breaking off weak bonds and trapped gas molecules. Here the ion bombardment effects are suggested by the reduction of the intensities of C-H stretching modes with the increase of the self bias voltage.

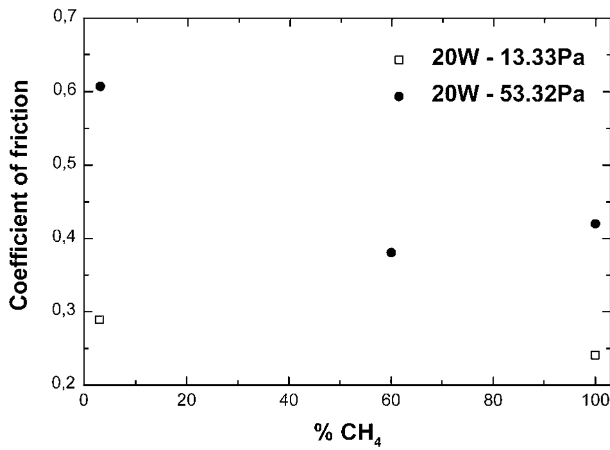

Figure 7 Friction coefficient as function of methane content (deposition parameters: r.f. input power 20 W; pressures 13.33 Pa and 53.32 Pa, self bias voltage −200 V and −160 V respectively).

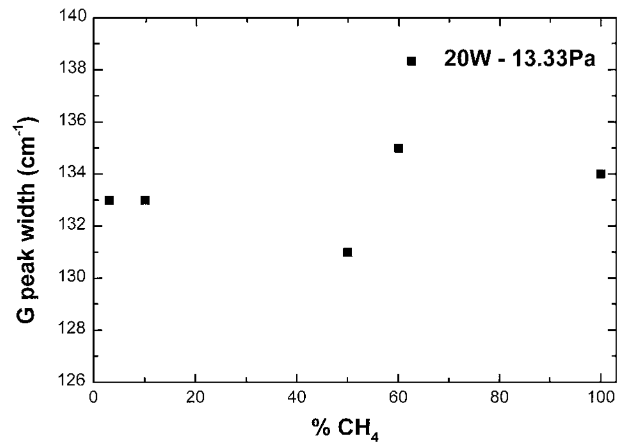

Figure 10 G peak width as function of methane content (deposition parameters: r.f. input power 20 W; pressure 13.33 Pa, self bias voltage −200 V).

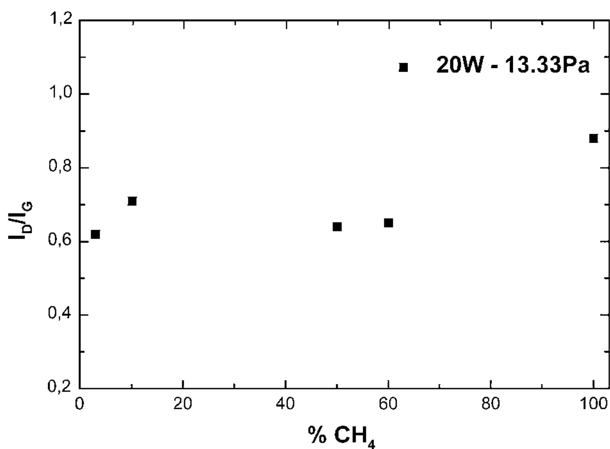

Figure 8 I_d/I_g ratio as function of methane content (deposition parameter: r.f. input power 20 W; pressure 13.33 Pa, self bias voltage −200 V).

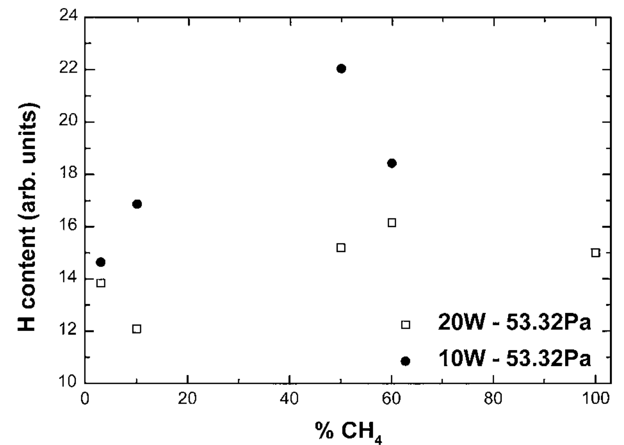

Figure 11 Hydrogen content as function of methane content (deposition parameters: r.f. input power (a) 10 W (self bias voltage −80 V) and (b) 20 W (self bias voltage −160 V); pressure 53.32 Pa).

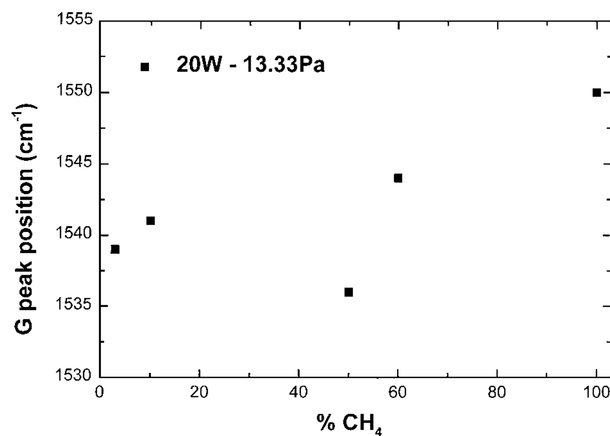

Figure 9 G peak position as function of methane content (deposition parameters: r.f. input power 20 W; pressure 13.33 Pa, self bias voltage −200 V).

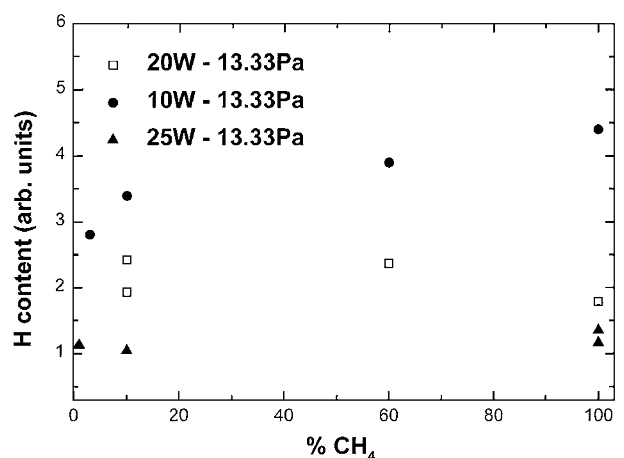

Figure 12 Hydrogen content as function of methane content (deposition parameters: r.f. input power (a) 10 W (self bias voltage −100 V), (b) 20 W (self bias voltage −200 V) and (c) 25 W (self bias voltage −250 V); pressure 13.33 Pa).

Results of the analysis of the films deposited from methane/argon plasmas can be summarized as follows: at room temperature, the effective growth rate (normalized on the effective carbon density) rises by increasing the fraction of Ar, and the films show increasing polymer-like properties, i.e. they are softer and more disordered. These findings are in substantial agreement with previous studies [7]. Concerning the effect of the substrate voltage, we found that films grow faster by increasing the bias, they are harder and show a higher degree of graphitisation.

While effects related to the substrate bias can be explained by ion bombardment, dilution effects are probably related to the different chemistry occurring at low

and high argon concentration, respectively. Concerning this subject, two recent papers are particularly interesting. Reference [8] deals with pure CH_4 plasma. In that paper the growth rate is reported to decline by increasing the substrate temperature, and a deposition model based on the primary role of chemical reactions between physisorbed CH_3 molecules and ions bombarding the growing surface of the film is suggested. On the contrary, reference [9] reports the temperature dependence of the growth rate for diamond films deposited from 1% methane in argon. The growth rate is found to increase with the temperature and a deposition mechanism based on the carbon dimer C_2 is proposed [2]. These two apparently contradictory experimental results can be reconciled by considering that two different mechanisms are operative, depending on the percentage of Ar in the initial gas mixture. Thus we assume that at low argon concentrations the main growth specie is CH_3, while at high argon levels it is C_2. This proposal has been recently suggested by the numerical simulation of the chemical kinetics in CH_4/Ar plasmas [20], which has shown that in pure CH_4 plasma the most abundant hydrocarbon radical is CH_3, whereas in plasma of CH_4 highly diluted by Ar, the most copious carbon containing radical is precisely C_2. One apparent inconsistence is that in contrast with references [2, 9], starting from a CH_4/Ar mixture we didn't obtain diamond but instead a polymer-like film. This discrepancy can be overcome by taking into account the activation energy for the growth of diamond from C_2. McCauley *et al.* [9] have measured a value of 24.45 ± 1.830 kJ/mol, thus it is not surprising that at room temperature the deposition of diamond from C_2 is negligible.

5. Conclusions

Different types of a-C : H films, from polymer-like to graphite-like, are obtained at room temperature from CH_4/Ar plasmas by varying the argon fraction and the substrate bias voltage. The deposition rate and mechanical and structural properties of the film depend on the degree of dilution, due to a different chemistry occurring in the plasma. When the amount of methane increases, Raman results show structural changes from a more disordered polymer-like structure to a less disordered graphitic arrangement. FTIR spectra show that our samples exhibit characteristic peaks of a-C : H films, in particular C-H stretching bands. The reduction of the bonded hydrogen content with the substrate bias is attributed to the breaking of C-H bonds caused by increasing ion bombardment. Experimental results are found to be consistent with theoretical calculations [20] that predicts the existence of carbon C_2 dimers in an Ar-rich CH_4 plasma. No evidence of diamond phase was found in our samples, due to the activation energy required for insertion of C_2 dimers in the growing surface.

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