



## Deuterated amorphous carbon films: Film growth and properties

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### ABSTRACT

Deuterated amorphous carbon films (a-C:D) have been studied in the last few years in order to investigate possible isotopic effects in the film properties. When compared with films deposited in methane atmosphere, an important reduction of the deuterium content of the films was observed and the reasons for that are not well understood. In this work, we deposited amorphous carbon films by PECVD using methane and deuterated methane gas mixtures as precursor atmospheres. We also investigated the effects of the self-bias voltage. The hydrogen and deuterium content was measured by elastic recoil detection analysis and we observed the preferential incorporation of hydrogen over deuterium. The precursor atmosphere was monitored by mass spectrometry and only small differences can be observed in the obtained mass spectra. The possible reasons for the total hydrogen content are discussed. The film deposition rate, the film microstructure as revealed by Raman spectroscopy, the film hardness determined by nanoindentation and the internal stress are dependent on the precursor atmosphere, however a much stronger dependence on the self-bias voltage was observed for deuterated carbon films.

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### 1. Introduction

Diamond-like carbon (DLC) films have attracted much attention due to their outstanding physical and chemical properties [1]. DLC can be defined as an amorphous carbon material, that can be hydrogenated (a-C:H) or not (a-C), with a significant fraction of  $sp^3$  carbon-bonds and with high mechanical hardness and wear resistance, chemical inertness and low friction [1–3]. The properties of films, which are closely related to their microstructure, can be tuned by the deposition technique employed and by the growth conditions, with the energy of the impinging species playing the main role in the control of the film properties [4,5]. Optimization of the deposition process is usually achieved by empirical methods, among them, the incorporation of different elements during the film growth. For example, nitrogen incorporation improves the mechanical properties of the films while fluorine incorporation results in a strong friction reduction [6]. Deuterated amorphous carbon films (a-C:D) deposited by plasma assisted chemical vapor deposition (PECVD) using deuterated hydrocarbons as precursor gases were also investigated for some specific applications, like storing ultra cold neutron devices [7] or as neutron mirror [8]. In order to tailor the film properties in a controlled way, a fundamental understanding of the microscopic deposition process is necessary. Among the several aspects that need to be clarified, the preferential incorporation of hydrogen over deuterium in amorphous carbon films deserves investigation. When it was observed for the first time, the purity of the  $C_2D_2$  gas used in the

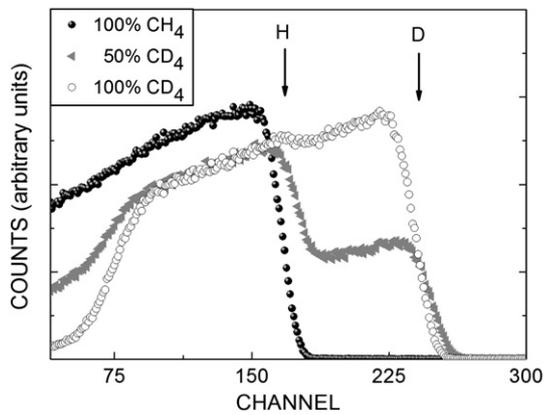
experiment was mentioned as one of the possible reasons for the differences revealed by IR spectroscopy [9]. In the last few years many experiments reporting differences in the incorporation of hydrogen and deuterium were published [10,11]. Differences in the deposition rate, smaller for films deposited from  $CD_4$  than  $CH_4$ , keeping fixed all other deposition parameters were also observed [12], indicating that further investigations are still needed.

In the present work, we measured the hydrogen and deuterium content in the film by using elastic recoil detection analysis (ERDA), while the precursor atmosphere was monitored during deposition by mass spectrometry. The effects of deuterium incorporation in a-C:H film microstructure and mechanical properties were also investigated.

### 2. Experimental procedures

Amorphous hydrogenated carbon films (a-C:H) were deposited by plasma enhanced chemical vapor deposition (PECVD) with  $CH_4$ – $CD_4$  mixtures as precursor gas employing an asymmetrical capacitively coupled deposition system. The base pressure around  $10^{-4}$  Pa was achieved using a diffusion pump system. Silicon substrates were mounted on a water-cooled 7.5 cm-diameter copper cathode fed by a rf (13.56 MHz) power supply. The films were deposited with a total pressure of 8 Pa and total incoming gas flux of 10 sccm up to a thickness of about 400 nm. Details of the deposition procedure can be found elsewhere [13]. In a first series of depositions, the self-bias voltage ( $V_B$ ) was fixed at  $-350$  V and the  $CH_4$  partial pressure varied from 100% (a-C:H films) to 0% (deuterated carbon films, a-C:D). For the second series, a-C:D films were deposited at different self-bias voltage in the range between  $-150$  and  $-650$  V by adjusting the rf power input. A

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**Fig. 1.** Elastic recoil detection spectra obtained from an a-C:H film (black dots); a-C:D film (open circles) and an a-C:H:D film (gray symbol) deposited by PECVD (8 Pa,  $-350$  V) in a 50:50  $\text{CD}_4$ - $\text{CH}_4$  gas mixture as precursor atmosphere. The positions of H and D when they are at the sample surface are indicated by arrows.

quadrupole mass analyzer was installed in the deposition chamber connected through a 1 mm diameter collimator. The region between the collimator and the quadrupole mass analyzer was pumped by a turbomolecular pump with pumping speed of 55 l/s for  $\text{H}_2$ .

The chemical composition was determined by Rutherford backscattering spectrometry (RBS) and ERDA employing a 4 MV Van de Graaff accelerator to produce a 2 MeV  $^4\text{He}^+$  beam. For RBS the particle detector was positioned at  $165^\circ$  with respect to the incident beam, while for ERDA measurements the detector was positioned at  $30^\circ$ . The sample was tilted by  $75^\circ$  with respect to the incident beam. The atomic density was inferred by combining the areal atomic density ( $\text{at}/\text{cm}^2$ ) provided by RBS and ERDA and the thickness obtained by stylus profilometry.

The atomic arrangement of the films was probed by Raman spectroscopy performed in air at room temperature with a ND-MDT Ntegra-Spectra System equipped with a solid state laser ( $\lambda = 473$  nm).

The stress determination was made by measuring the curvature of the films by means of a stylus profilometer and by applying Stoney's equation, as described in detail elsewhere [14]. The hardness of the films was measured by employing a Hysitron TI 9000 TriboIndenter with loads in the range of 100 to 800  $\mu\text{N}$ . The film hardness was obtained according to the Oliver and Pharr method [15].

### 3. Results and discussions

Elastic recoil detection spectra obtained from different films are presented in Fig. 1. The spectra show that both H and D concentrations are constant throughout the film. The atomic density, the deposition rate, the hydrogen and deuterium concentrations are presented in Table 1. Absolute hydrogen and deuterium concentrations were obtained using the accurate measurements of the absolute cross sections for elastic recoil of H and D using low-energy  $^4\text{He}^+$  beams

[16]. The results for the absolute H or D concentrations quoted in the literature show a large deviation that is usually higher than the errors stated by the experimentalists [17]. In this work, more relevant than the absolute value are the relative errors for the ratio between the hydrogen and deuterium cross sections that are  $\pm 2\%$  [16].

Our data confirm previous results and show an important preferential incorporation of H over D [11]. In fact, in our experimental conditions, hydrogen concentration in an a-C:H film is 18% higher than deuterium concentration in a-C:D films. The same is observed in a film deposited using a 50:50 mixture of  $\text{CD}_4$  and  $\text{CH}_4$ . Since the purity of our gases is higher than 99%, we can discard the H contamination in  $\text{CD}_4$  as the reason for the H higher content in the films. For a-C:D films deposited at different  $V_B$ , the D concentration decreases upon the increase of  $V_B$ . The D concentration is reduced by a factor of two in the  $V_B$  range from  $-250$  V to  $-550$  V. On the other side, for a-C:H films deposited in the same  $V_B$  range in pure methane atmosphere the H content decreases from 25 to 18 at.% [18]. One of the possible explanations for these results was presented by Johnson et al. [10]. They attributed the preferential incorporation of H to the different pumping speeds for the different molecules when turbomolecular pumps are used since they are more efficient for heavier molecules. In order to compensate this effect higher flow ratios for  $\text{CD}_4$  can be used. However, our chamber is pumped by a diffusion pump and the differences in the pumping speeds are minimal for this range of molecular weight.

Differences in deuterium plasma chemistry can also be responsible for the differences in the incorporation of H and D, but there are few available experimental data [10]. In order to bring new information to this subject, we monitored the precursor atmosphere by mass spectrometry during the film deposition. The mass spectra are presented in Fig. 2 for several  $\text{CD}_4$ - $\text{CH}_4$  mixtures. The spectra show a small peak at mass 2 (4) due to  $\text{H}_2$  ( $\text{D}_2$ ), a group due to  $\text{CH}_4$  ( $\text{CD}_4$ ) and its fragments around mass 16 (20) and a third group at around 28 (32) attributed to  $\text{C}_2\text{H}_n$  ( $\text{C}_2\text{D}_n$ ) at around mass 28 (32). The same relative intensity between the second and the third group is observed for all  $\text{CD}_4$ - $\text{CH}_4$  mixtures. The mass spectra were also measured without power applied to the cathode. The spectra are similar to those shown in Fig. 2 with some differences: the peak due to  $\text{H}_2$  ( $\text{D}_2$ ) is below the detection limit of our quadrupole analyzer and the intensity of the peaks attributed to  $\text{C}_2\text{H}_n$  ( $\text{C}_2\text{D}_n$ ), when we normalized the spectra by the mass 16 peak, is much smaller than one can observe in Fig. 2. The mass spectra did not indicate any isotopic effect during deposition. In fact, the intensities of  $\text{C}_n\text{H}_m$  or  $\text{C}_n\text{D}_m$  radical peaks observed in the mass spectra can be directly correlated with the partial pressure in the precursor atmosphere of methane or deuterated methane, respectively. The same was observed for the peaks corresponding to masses 2 and 4. These results also support the statement made above that there is no preferential pumping of deuterated species over hydrogenated ones in our deposition system.

The preferential incorporation of H over D and the more important reduction of D, when compared to H, in films deposited with higher  $V_B$ , can be attributed to an enhancement of the dehydrogenation

**Table 1**

Atomic density and hydrogen and deuterium concentration measured by nuclear techniques as functions of the precursor gas mixture and the self-bias voltage.

Precursor gas mixture	Self-bias voltage (-V)	Atomic concentration (at.%)		Atomic density ( $10^{23}$ atoms/ $\text{cm}^3$ )	Deposition rate (nm/min)
		D	H		
100% $\text{CH}_4$	350	-	20	1.3	$12.1 \pm 0.9$
75% $\text{CH}_4 + 25\%$ $\text{CD}_4$	350	5	14	1.3	$12.7 \pm 0.9$
50% $\text{CH}_4 + 50\%$ $\text{CD}_4$	350	8	10	1.3	$10.7 \pm 0.9$
25% $\text{CH}_4 + 75\%$ $\text{CD}_4$	350	11	7	1.3	$11.5 \pm 0.9$
100% $\text{CD}_4$	350	17	-	1.3	$10.9 \pm 0.6$
100% $\text{CD}_4$	250	26	-	1.1	$7.3 \pm 0.4$
100% $\text{CD}_4$	450	17	-	1.3	$16.1 \pm 0.6$
100% $\text{CD}_4$	550	14	-	1.4	$22.0 \pm 1.8$

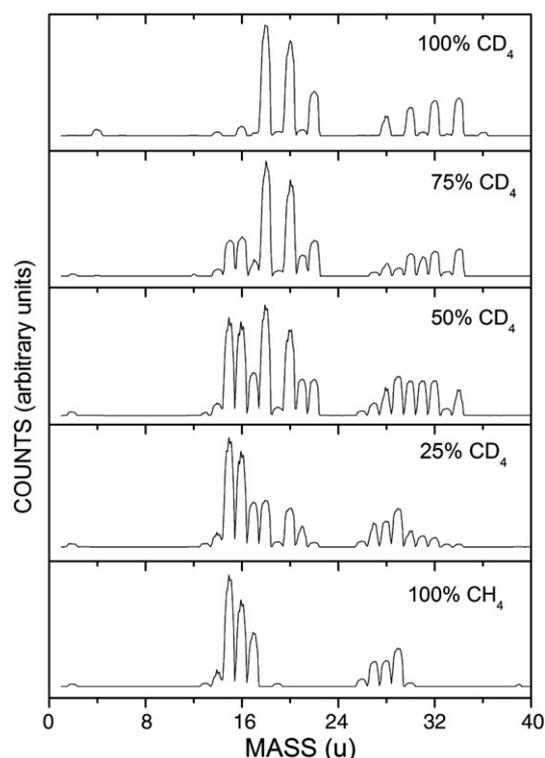


Fig. 2. Mass spectrum obtained during film deposition by PECVD (8 Pa,  $-350$  V) with different precursor atmosphere, as indicated in the figure.

process when deuterium is involved, favoring the loss of the heaviest isotope. The energy of the plasma is sufficient to allow sputterplation of hydrogen ions, which have enough kinetic energy to modify the subsurface by removing bonded hydrogen. For the same  $V_B$ , both D and H ions will have the same kinetic energy, but probably, a shallower modified layer will be found in a-C:D films resulting in a more efficient hydrogen species removal during deposition, explaining at least partially, the less efficient D incorporation.

The film atomic density is, within our experimental errors ( $\pm 10\%$ ), independent on the precursor gas used, in good agreement with neutron reflectivity experiments [19]. The atomic density increases upon the increase of  $V_B$ , as a result of the increase of the ion bombardment intensity. The same behavior was verified for a-C:H films deposited from methane by PECVD [18].

The deposition rates for films deposited at different gas mixtures are shown in Table 1 and the quoted errors are the standard deviation calculated from the film thickness measured in samples deposited in the same deposition conditions but in different experiments. A progressive reduction on the deposition rate can be observed for films deposited in  $CD_4$  richer plasma atmospheres. On the other hand, the deposition rate as a function of  $V_B$  shows an increase since higher  $V_B$  was achieved by increasing the rf power applied to the plasma, resulting in a higher degree of plasma dissociation.

The differences in deposition rate suggest that films with different microstructure were formed. It was probed by Raman spectroscopy. The spectra obtained from both a-C:D and a-C:H films are typical of amorphous carbon films presenting two overlapping bands known as the D and G bands. The spectra can be fitted using two Gaussian lines. The  $I_D/I_G$  intensity ratios, together with the G-band peak position and width are listed in Table 2. The D-band peak position is nearly constant ( $1380\text{ cm}^{-1}$ ), while the D-band width is typically of  $290\text{ cm}^{-1}$ . The main result shown in Table 2 is the drastic reduction of  $I_D/I_G$  ratio for a-C:D films while the G band shifted to lower values. No dependence with  $V_B$  was observed for a-C:D films. These results can be attributed to a reduction of graphitic domains, either in number or in size [11,18], in

Table 2

$I_D/I_G$  ratio, position and width of the G-Raman band as functions of the precursor gas mixture and the self-bias voltage.

Precursor gas mixture	Self-bias voltage ( $-V$ )	G-band		$I_D/I_G$
		Position ( $\text{cm}^{-1}$ )	Width ( $\text{cm}^{-1}$ )	
100% $CH_4$	350	1551	130	0.86
75% $CH_4$ + 25% $CD_4$	350	1546	132	0.76
50% $CH_4$ + 50% $CD_4$	350	1543	131	0.86
25% $CH_4$ + 75% $CD_4$	350	1542	130	0.85
100% $CD_4$	350	1535	132	0.53
100% $CD_4$	250	1532	133	0.40
100% $CD_4$	450	1537	133	0.52
100% $CD_4$	550	1535	136	0.55

a-C:D films compared to a-C:H films deposited in the same experimental conditions.

Figs. 3 and 4 present the results of the mechanical properties as a function of the precursor gas mixture and  $V_B$ . The internal compressive stress, presented in Fig. 3, and the hardness presented in Fig. 4 have the same behavior. The errors are the standard deviation. In particular, the hardness values correspond to the average of 10 indentations carried out in different spots for penetration depths in the range of 20 to 30 nm that are shallower than 10% of the samples thickness. Several samples deposited in the same depositions conditions were measured. Films deposited in deuterated methane rich atmospheres show lower stress and hardness, while the existence of a maximum observed for a-C:D films when these quantities are plotted as a function of  $V_B$  can be explained by the sputterplation model that was already used to explain similar results for a-C:H films [4]. However, the low values of hardness and stress measured for films deposited in pure  $CD_4$  atmosphere cannot be explained in terms of the

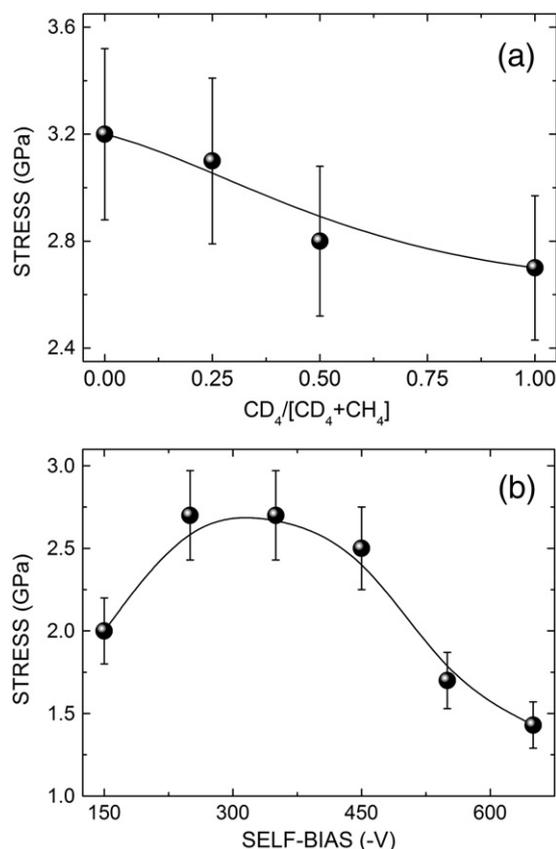


Fig. 3. Internal compressive stress as a function of: (a) precursor gas mixture, and (b) the self-bias voltage.

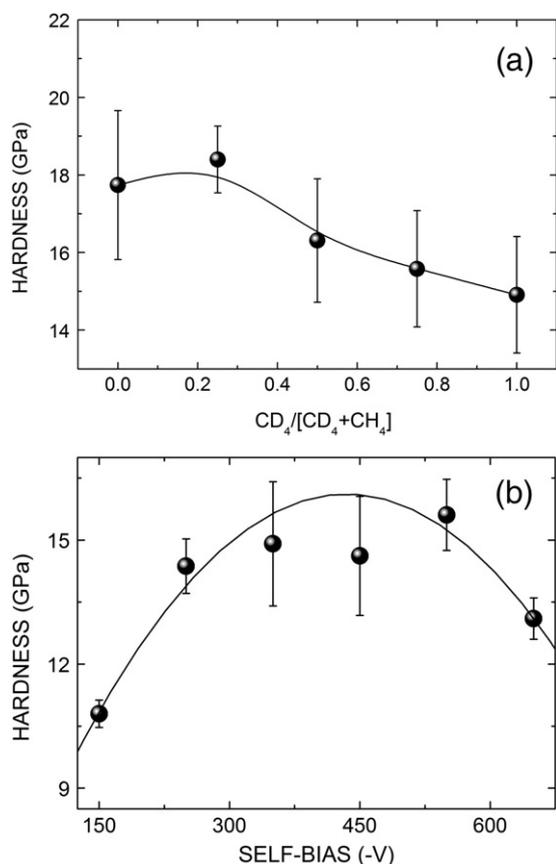


Fig. 4. Hardness as a function of: (a) precursor gas mixture, and (b) the self-bias voltage.

average coordination number. In fact, hydrogen can only make terminal bonds and its incorporation reduces the average coordination number in a-C materials. Since a-C:D films have lower D content when compared to H in a-C:H films, we can expect a higher degree of overconstraining in these films due to an enhanced cross-linking. The enhanced cross-link usually leads to higher values of hardness and density, as well as high values of internal stress, due to bond angle and bond length distortions. The possible enhancement of the film disorder can explain the Raman results, but it is difficult to conciliate the observed mechanical properties with the trend measured by Raman spectroscopy.

#### 4. Summary and conclusions

We deposited a-C:D, a-C:D:H and a-C:H films by PECVD using methane and deuterated methane mixtures as precursor atmo-

spheres. We measured the hydrogen and deuterium content in the films and verified the preferential incorporation of hydrogen over deuterium. In our experimental conditions, both the purity of the precursor gas and effects of the pumping system can be discarded as possible reasons for this result. We suggested that it can be attributed to a more efficient dehydrogenation process when deuterium is present in the plasma atmosphere and favoring the desorption of the heaviest isotope.

The lower D content in the films is expected to increase the degree of overconstraining of the amorphous skeleton resulting in an enhancement of the bond angle and bond length distortions, and so, higher values of hardness and stress. This possible increase of the film disorder can explain the Raman results, but it is difficult to conciliate it with the mechanical properties. In fact, hardness and internal stress decrease upon deuterium incorporation. Our results indicate the need for further investigations to clarify the effects of deuterium investigation in DLC films.

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