



# a-C(:H) and a-CN<sub>x</sub>(:H) films deposited by magnetron sputtering and PACVD

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## Abstract

Hydrogenated amorphous carbon films (a-C:H) and hydrogenated carbon films containing as much as 15 at.% nitrogen (a-CN<sub>x</sub>:H) were synthesised by a plasma-assisted chemical vapour deposition (PACVD) apparatus. By changing the gaseous precursor (CH<sub>4</sub>, C<sub>6</sub>H<sub>12</sub>, C<sub>6</sub>H<sub>6</sub>, C<sub>2</sub>H<sub>2</sub>) the hydrogen content of the films can be varied between 26 and 58 at.%; serious adhesion problems were found when the hydrogen percentage attains the highest value. Hydrogen-free layers were deposited by magnetron sputtering in Ar (a-C) and N<sub>2</sub> (a-CN<sub>x</sub>): nitrogen fractions range from 8 to 28 at.% and increase when the substrate is closer to the graphite target during deposition. Film hardness was evaluated by nanoindentation in order to avoid inflation of the assessed value consequent to the elastic recovery, which results to be quite large in the examined layers. The hardness measurements show values up to ~30 GPa and point out that both nitrogeneration of a-C:H films and deposition by magnetron of hydrogen-free a-C layers lead to softer materials (~18 GPa). Main features of Raman spectra are broad 'G' and 'D' peaks, characteristic of DLC layers: correlation between parameters of these peaks is discussed. © 1998 Elsevier Science S.A.

*Keywords:* Magnetron sputtering; PACVD; a-C:H

## 1. Introduction

Amorphous carbon films (a-C) and hydrogenated ones (a-C:H) with diamond-like characteristics (DLC) are extensively investigated on account of their unusual and excellent properties such as hardness, low coefficient of friction, chemical inertness and infra-red transparency.

DLC films can be prepared by various techniques: a common feature is that the growing film is subject to collision by medium-energy ions [1,2].

The objective of this work is deposition and characterization of DLC films grown on low-temperature substrates by plasma-assisted chemical vapour deposition (PACVD) or magnetron sputtering. The effect of precursor modification on composition, hardness and Raman spectrum of DLC layers is investigated.

## 2. Experimental details

Hydrogenated films were grown in a PACVD reactor, where the substrate is located outside of the plasma glow region, created by a dc power supply. The entering gas

flows through the discharge volume and the reactive species produced therein collide with the substrate placed downstream, as in the general scheme of remote-plasma reactors.

Background pressure lower than  $2 \cdot 10^{-3}$  Pa is maintained by a diffusion pump and the operating pressure, controlled by admitting valves, ranges from 0.1 to 1 Pa. Deposition precursors for nitrogen-free layers were pure hydrocarbons, cyclohexane (C<sub>6</sub>H<sub>12</sub>), benzene (C<sub>6</sub>H<sub>6</sub>), methane (CH<sub>4</sub>) and acetylene (C<sub>2</sub>H<sub>2</sub>), which differ for hydrogen fraction and carbon hybridization in the molecule. a-CN<sub>x</sub>:H films were prepared from a C<sub>6</sub>H<sub>12</sub>-N<sub>2</sub> mixture: N<sub>2</sub> partial pressure (0.08 Pa) was selected to provide significant nitrogeneration of the film and to avoid film growth inhibition consequent to inert-gas enrichment.

The substrates (austenitic stainless steel and silicon single-crystal) were ultrasonically cleaned in acetone and then sputter-etched by argon plasma inside the reactor, prior to deposition. Temperature at the end of the film growth was typically under 360 K.

a-C and a-CN<sub>x</sub> layers were prepared by dc magnetron sputtering in argon or nitrogen atmosphere. The cathode is a graphite disk 16 cm in diameter and the target to substrate distance was 5 or 9 cm. Preliminary cleaning in argon plasma was performed also in this case.

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The elemental composition of the films was determined by a Fisons EA1108 elemental analyzer, where a known amount of the sample is burnt and the fractions of water vapour, carbon dioxide and nitrogen in the combustion gas are measured by chromatographic analysis.

The elastic modulus  $E$  and the hardness  $H$  were measured by an ultra-low depth sensing nanoindenter (Nano Instruments—Type II) from the loading–unloading curves. The impressions on each sample were taken by using a Berkovich indenter. The displacement rate was maintained constant (3 nm/s) during the loading segment until the final depth of  $\sim 50$  nm was reached. A peak-load hold segment was included for allowing the relaxation of the time-dependent plastic effects. The unloading segment was obtained by decreasing the loading force at a constant rate. The penetration depth was chosen not exceeding 10% of the thickness of the thinnest coating, in order to avoid the effect of the substrate on the measurements. The geometry and the stiffness of the tip were taken into account to provide accurate determination of  $E$  and  $H$ . The necessity of introducing these corrections is more relevant in the case of stiff specimens and small contact area, such as the systems under investigation.

Raman spectra were recorded at room temperature in a backscattering geometry, using a I.S.A. Jobin-Yvon triple grating spectrometer with a liquid-nitrogen-cooled camera detection system; the spectral resolution was about  $3\text{ cm}^{-1}$ . The 514.5 nm line of an argon ion laser was used as excitation source; the beam was focused on a spot of about  $15\ \mu\text{m}$  diameter.

### 3. Results and discussion

Elemental compositions of prepared films are reported in Table 1, together with deposition parameters, i.e., voltage ( $V$ ), discharge current ( $I$ ) and gas pressure ( $P$ ). With the exception of film synthesised from methane, the hydrogen fraction in a-C:H layers fluctuates in a relatively narrow range, 26 to 32 at.%, in spite of changing reactant gas and deposition parameters. Deposits from methane are significantly richer in hydrogen and suffered spontaneous detachment from stainless steel after deposition, when thickness exceeded about  $0.2\ \mu\text{m}$ .

a-CN<sub>x</sub>:H films grown by PACVD in a C<sub>6</sub>H<sub>12</sub>/N<sub>2</sub> mixture show N-fractions around 12% and hydrogen content again close to 30%. In a-CN<sub>x</sub> films prepared by magnetron sputtering, N-fractions are comparable to those of hydrogenated deposits and are observed to rise with N<sub>2</sub> pressure; an appreciable increase in N-content is found when the distance between target and substrate is decreased from 9 to 5 cm.

The loading–unloading curves, measured in nanoindentation experiments, are shown in Fig. 1 for films deposited using PACVD and magnetron sputtering. Young's modulus and hardness were determined from the unloading data

Table 1

Elemental composition and deposition parameters (voltage  $V$ , discharge current  $I$ , gas pressure  $P$ ) of prepared films

PACVD						
Gas	$V$ (kV)	$I$ (A)	$P$ (Pa)	C (at.%)	H (at.%)	N (at.%)
C <sub>6</sub> H <sub>12</sub>	1.2	0.10	0.2	72	28	
C <sub>6</sub> H <sub>12</sub>	1.2	0.14	0.3	72	28	
C <sub>6</sub> H <sub>12</sub>	1.4	0.22	0.2	66	34	
C <sub>6</sub> H <sub>6</sub>	1.2	0.12	0.3	68	32	
C <sub>6</sub> H <sub>6</sub>	1.2	0.22	0.5	70	30	
C <sub>6</sub> H <sub>6</sub>	1.2	0.32	0.7	74	26	
C <sub>2</sub> H <sub>2</sub>	1.2	0.22	0.5	71	29	
C <sub>2</sub> H <sub>2</sub>	1.9	0.22	0.2	73	27	
CH <sub>4</sub>	1.6	0.20	0.3	42	58	
C <sub>6</sub> H <sub>12</sub> + N <sub>2</sub>	1.0	0.14	0.2	55	32	13
C <sub>6</sub> H <sub>12</sub> + N <sub>2</sub>	1.6	0.24	0.2	55	33	12
Magnetron sputtering						
N <sub>2</sub> <sup>a</sup>	0.67	4.6	0.15	92		8
N <sub>2</sub> <sup>a</sup>	0.64	4.8	0.2	86		14
N <sub>2</sub> <sup>b</sup>	0.67	4.6	0.15	73		27

<sup>a</sup>Target to substrate distance: 9 cm.

<sup>b</sup>Target to substrate distance: 5 cm.

following the procedure extensively described by Oliver and Pharr [3]. In Table 2, the average values for  $E$  and  $H$  are reported together with the percentage of elastic recov-

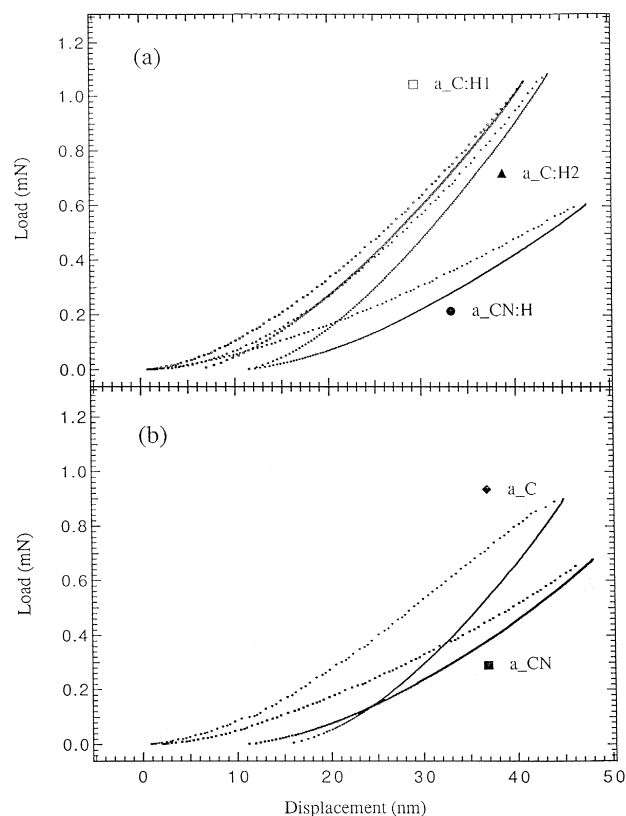


Fig. 1. Loading–unloading curves for films deposited using: (a) PACVD with cyclohexane (a-C:H<sub>1</sub>), acetylene (a-C:H<sub>2</sub>), cyclohexane/nitrogen mixture (a-CN:H); (b) magnetron sputtering with argon (a-C), nitrogen (a-CN). See Table 2 for deposition parameters.

Table 2

Average values of elastic modulus ( $E$ ) and hardness ( $H$ ) and elastic recovery (% $R$ ) for films prepared by PACVD and magnetron sputtering; Deposition parameters are also listed: voltage  $V$ , discharge current  $I$ , gas pressure  $P$

Code	Deposition technique	Gas	$E$ (GPa)	$H$ (GPa)	% $R$	$V$ (kV)	$I$ (A)	$P$ (Pa)
a-C:H <sub>1</sub>	PACVD	C <sub>6</sub> H <sub>12</sub>	283	37	83	1.4	0.22	0.2
a-C:H <sub>2</sub>	PACVD	C <sub>2</sub> H <sub>2</sub>	267	30	73	1.9	0.22	0.2
a-CN:H	PACVD	C <sub>6</sub> H <sub>12</sub> + N <sub>2</sub>	135	17	75	1.6	0.24	0.2
a-C	sputtering	Ar	186	20	65	0.81	3.2	0.2
a-CN	sputtering	N <sub>2</sub>	124	16	76	0.67	4.6	0.15

ery (% $R$ ). The values of  $E$  and  $H$  measured in different points of each specimen do not present large oscillations, giving no indication of evident inhomogeneity.

The amount of elastic deformation ranges between 65% and 83%. a-C:H grown by PACVD with cyclohexane shows the highest values of  $E$  and  $H$  and also the largest % $R$ . The films produced using acetylene exhibit still high hardness but lose elasticity.

The presence of nitrogen always makes the films softer, as observed in other investigations [4–6], even if the elastic recovery remains relatively high.

Raman spectra of a-C:H deposits were analyzed by subtracting the background signal and fitting with Gaussian curves, whose parameters—position, line-width (FWHM) and intensity ratios—are listed in Table 3.

Main features are broad peaks centred near the positions of G and D lines in disordered-graphite spectra, where the G band is assigned to E<sub>2g</sub> C–C stretching mode and the D band is attributed to an A<sub>1g</sub> mode, which becomes Raman-active in small crystallites [7,8].

Calculated parameters have been substituted in plots proposed by Tamor and Vassell [9]: general agreement is

observed, except in two main features. First, hardness values reported in [9] as a function of G-line width for a-C:H films lie below 20 GPa, i.e., are lower than those measured in the present work (around 30 GPa), although the values of G-line width are in the same range. Second, D-line position plotted against G-line position follows the increasing trend shown in [9], except that D lines centred above 1400 cm<sup>-1</sup> are found in our spectra, while values reported in [9] flatten around 1400 cm<sup>-1</sup>.

From data in Table 3 emerges that the width of D-line increases approximately linearly with D-line position (Fig. 2) and the ratio of the integrated areas  $I_D/I_G$  grows faster than linearly (a parabolic fitting can be applied), as D-line position moves to higher wave numbers. The latter trend can be related to the observation that the peak-height ratio ( $H_D/H_G$ ) exhibits a nearly linear increase (correlation coefficient = 0.94) with D-line position, as D-line width does.

Raman spectra characterized by low values of  $I_D/I_G$  appear as a broad asymmetrical peak and resemble those observed in hydrogen-free films, deposited from C ion beams, where the sp<sup>2</sup> fraction (larger than ~0.4) is

Table 3

PACVD parameters and fitting values calculated from Raman spectra: position (cm<sup>-1</sup>), width (FWHM, cm<sup>-1</sup>), integrated areas ratio ( $I_D/I_G$ ) and heights ratio ( $H_D/H_G$ ) of Gaussian peaks

Gas	C <sub>6</sub> H <sub>12</sub>	C <sub>6</sub> H <sub>12</sub>	C <sub>6</sub> H <sub>12</sub>	C <sub>6</sub> H <sub>12</sub>	C <sub>6</sub> H <sub>12</sub>	C <sub>6</sub> H <sub>6</sub>	C <sub>6</sub> H <sub>6</sub>	CH <sub>4</sub>
$V$ (kV)	1.2	1.2	1.2	1.2	1.9	1.2	1.2	1.2
$I$ (mA)	120	180	300	320	300	120	220	280
$P$ (Pa)	0.2	0.4	0.6	0.8	0.2	0.3	0.5	0.7
G centre	1538	1534	1554	1548	1556	1566	1546	1564
G width	151	174	155	146	132	183	153	132
D centre	1343	1303	1410	1364	1440	1383	1343	1410
D width	289	207	366	280	385	319	268	309
$I_D/I_G$	0.62	0.30	1.87	0.89	3.10	0.77	0.59	1.78
$H_D/H_G$	0.33	0.26	0.79	0.47	1.07	0.44	0.34	0.76

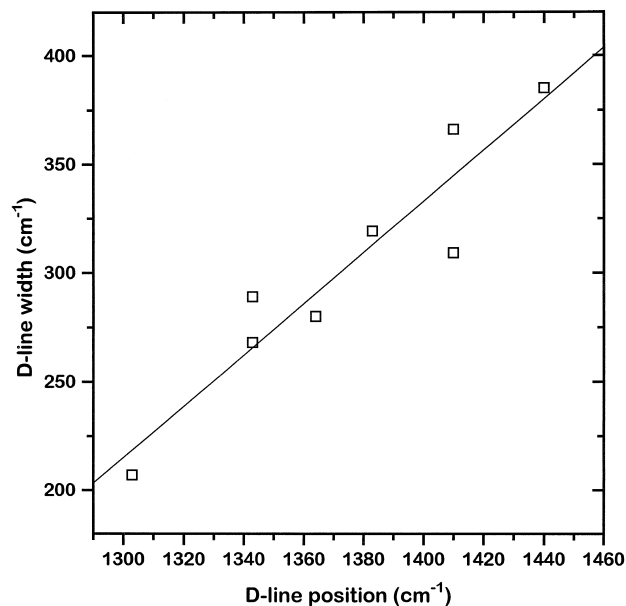


Fig. 2. Width of D-line in Raman spectra as a function of its position. Correlation coefficient is 0.94.

supposed to be present as a densely packed, amorphous structure, rather than in graphitically bonded clusters [10]. Qualitatively similar spectra are also found when  $I_D/I_G$  rises: as discussed above, higher and broader D-peaks are centred closer to G-line (up to  $1440\text{ cm}^{-1}$ ) and a single asymmetrical peak can form again.

#### 4. Conclusions

a-C:H layers with high hardness and large elastic recovery have been prepared by PACVD; these films can be harder than hydrogen-free a-C layers grown by magnetron sputtering. Nitrogen incorporation ( $\sim 10\text{ at.}\%$ ) results in softer films in both deposition techniques. Hydrogen fraction varies slightly when different hydrocarbon precursors and plasma discharge parameters are selected; higher hydrogen content is found in deposits from methane.

Analysis of Raman spectra of a-C:H films suggests that D-line parameters are mutually correlated: the peak becomes more intense, with respect to the G-line, and broader as it approaches the G-line.

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