STRUCTURAL AND MECHANICAL PROPERTIES OF DIAMOND-LIKE CARBON FILMS PREPARED BY PULSED LASER DEPOSITION WITH VARYING LASER INTENSITY

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ABSTRACT

Diamond-like carbon (DLC) films have been prepared by pulsed laser deposition (PLD) (wavelength 248 nm), ablating highly oriented pyrolytic graphite (HOPG) at room temperature in a vacuum of 10^{-2} Pa, at fluences between 0.5 and 35 Jcm^{-2}. Films have been deposited on Si(100) with and without a SiC interlayer. Structural analysis, such as visible and UV Raman, Infrared and Electron Energy Loss (EEL) spectroscopies show that the films are hydrogen-free and undergo a transition, from mainly disordered graphitic to up to 80% tetrahedral amorphous carbon (ta-C), above a laser threshold fluence of 5 J cm^{-2}. The measured residual stresses of as deposited ta-C films do not exceed 2 GPa. Scratch tests show excellent adhesion properties. Low friction coefficients (0.05-0.1) have been measured in ambient humidity. Nanoindentation indicates that film hardness is as high as 70 GPa.

INTRODUCTION

Growing interest has been devoted to Pulsed Laser Deposition (PLD) of diamond-like carbon (DLC) films with a high content of tetrahedrally coordinated atoms [1]. With respect to mechanical applications, the main limitation of the films are limited thicknesses and often problematic film-substrate adhesion due to high compressive stresses. We prepared DLC films by PLD and characterized them both structurally and mechanically.

EXPERIMENTAL PROCEDURES

The films were deposited in a vacuum chamber with a base pressure of 10^{-3} Pa, and operating at a pressure of 10^{-2} Pa. Highly oriented pyrolitic graphite (HOPG, purity, 99.99%), was ablated with laser pulses from a Lambda Physik LPX220I Excimer Laser (wavelength $\lambda = 248$ nm, pulse duration τ = 20 ns, repetition frequency 10 Hz, incidence angle 45°), changing the fluence between 0.5 Jcm^{-2} and 35 Jcm^{-2}. Different types of ultrasonically cleaned substrates were used, as shown in Table I. We chose Si(100) for structural analyses and Si(100) coated with sputter deposited SiC to reduce substrate effects in nanoindentation. Film and substrate thicknesses, as determined with a DEKTAK IIA profilometer, are reported in Table I together with the laser fluences. Usually deposition rates were of the order of 0.6 nms^{-1} at our repetition frequency.

Unpolarised visible Raman spectra were recorded in backscattering geometry for 514.5nm excitation from an Ar ion laser using a Jobin-Yvon T64000 triple grating spectrometer. UV

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Raman spectra were collected on an UV-enhanced CCD camera on a Renishaw micro-Raman System 1000 spectrometer, modified for use at 244nm, with fused silica optics throughout. FTIR spectra were taken at room temperature, in dry air, using a Win Rad Fast Trasform spectroscope over the 400-4000 cm^{-1} range. EELS measurements were carried out on a dedicated VG501 scanning transmission electron microscope fitted with a spectrometer with a McMullan parallel EELS detection system [2]. The residual internal stresses of the films deposited on Si were determined by Stoney's equation, measuring film curvature by a UBM Messtechnik Laser Microfocus profilometer. Film hardness was determined by a Nano Instruments (type II) ultra low load depth-sensing nanoindenter (ind. Depth ~50 nm), analyzing data by the Oliver-Pharr procedure [3]. Film-substrate adhesion was tested by scratch tests, performed with a CSEM Revetest Automatic Scratch-Tester equipped with a Rockwell shaped diamond indenter (conical angle 120°, hemispherical tip of 100 μm radius), at a scratching speed of 10 mm min^{-1} and a loading rate of 10 N mm^{-1}.

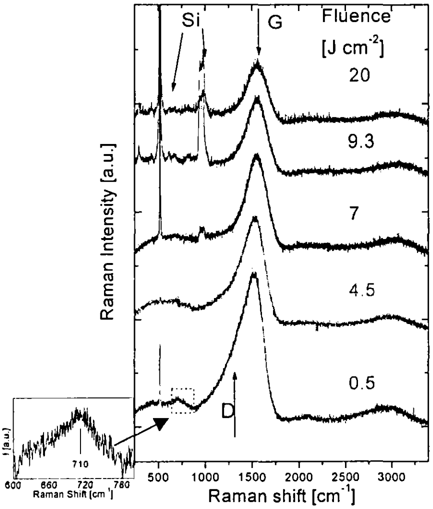

Fig. 1 Visible Raman spectra of DLC films grown by PLD at increasing laser fluences. The inset shows a magnification of the band centered around 710 cm^{-1} in a film deposited below f_t.

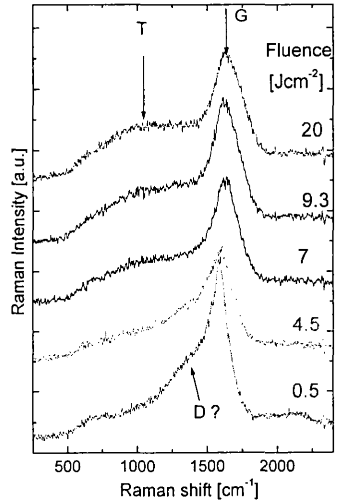

Fig 2. UV Raman spectra of DLC films grown by PLD at increasing laser fluences

RESULTS AND DISCUSSION

In Fig.1-2 the Visible and UV Raman spectra are reported for films grown at different fluences. Visible Raman spectra show two main features, the D peak (~1350 cm^{-1}), due to breathing modes of rings, and the G peak (~1560 cm^{-1}) due to the relative motion of sp^2 carbon atoms [4-6]. The UV Raman spectra consist of a G peak at ~1660 cm^{-1} and a T peak at ~1100 cm^{-1}, attributed to all sp^3 C-C bond vibrations[7]. However, for low laser fluences, another peak at ~1400-1430 cm^{-1} becomes evident. This peak has not been reported before and we could consider it as the correspondent of the D peak. Further work will be devoted to study its nature. Visible Raman spectra, were fitted with a combination of a Breit-Wigner Fano for the G peak, and a lorentzian for the D. UV Raman spectra were fitted with 2 lorentzians, for the G and T peak, and, at low fluences, with another lorentzian for the extra peak. Fig 3-4 show the evolution of Raman parameters with increasing laser fluence. Note that the maximum of the BWF is reported, rather than it's centre, to allow comparison with literature data using symmetric lineshape fitting [6].

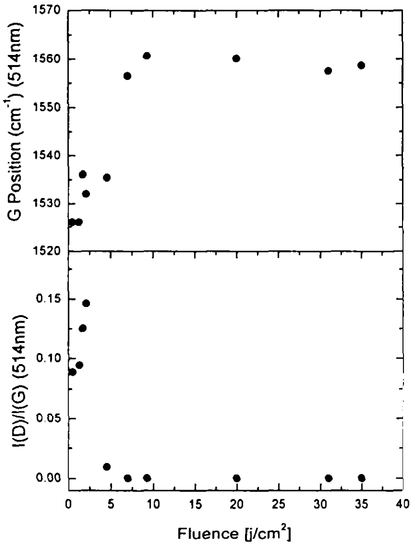

Fig 3. I(D)/I(G) and G Position in function of fluence for 514nm excitation

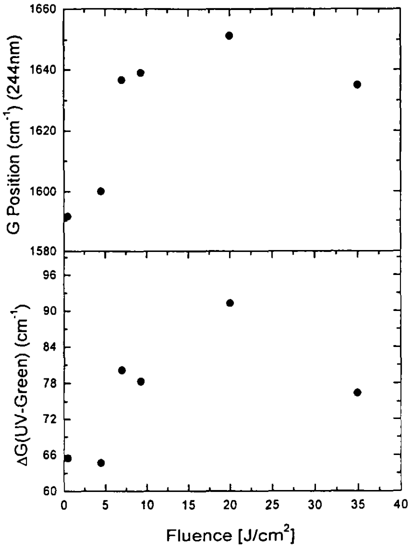

Fig 4. G position for UV excitation and difference in G position for UV and green excitation, ΔG

Data in Fig 3 indicate that above a threshold fluence (f_t) value of 5 Jcm^{-2} the films consist largely of amorphous tetrahedrally bonded carbon (ta-C) [4,6]. Indeed, I(D)/I(G)~0 in combination with an high G peak position is a sufficient condition to confirm the high sp^3 in the films [4,6]. Moreover, the intensity of the T peak relative to the G peak is maximum in UV Raman for $f>f_t$, indicating high sp^3 fraction [7]. G peak position in UV-Raman is blue shifted with respect to G peak in green Raman due to the resonant selection of wider band gap π states, from sp^2 groups with higher vibrational frequency [6, 7]. Fig 4 shows that ΔG(UV-green) is max for 20 J/cm^{-2}, consistent with shortest sp^2 chains and highest sp^3 fraction. ΔG(UV-green) is minimum for $f<f_t$, thus indicating clustering of the sp^2 phase and lower sp^3 content. A deeper discussion of the trends in visible and UV Raman will be presented elsewhere. The magnification of the low frequency Raman spectrum of a film deposited at 0.5 Jcm^{-2} (inset of Figure 1) shows a broad band centered on 710 cm^{-1}. Such a feature, which is absent in films deposited at high fluences, could be attributed to a collective in-plane deformation of graphitic islands, which results in a peak in the vibrational density of states [5]. Typical FTIR transmission spectra of representative films deposited on Si are reported in Figure 5. Two bands are evident in the spectra of films deposited at fluences

below f_t: the first, around 710 cm^{-1}, is attributable to the graphite vibrational mode observed also in Raman spectra [5], while the second, around 1250cm^{-1}, was attributed to the stretch of mixed sp^2-sp^3 C-C bond [8].

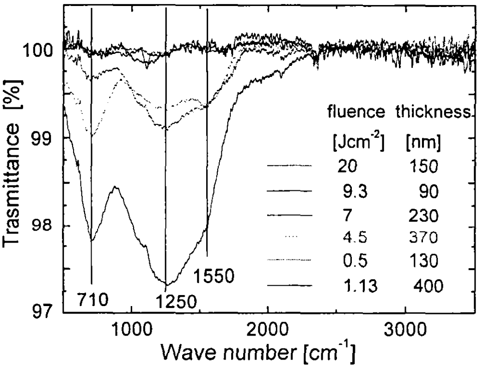

Fig 5. FTIR transmission spectra. From the top to the bottom Fluence is, 20, 9.3, 7, 4.5, 0.5, 1.13 J/cm^{-2}

The shoulder at about 1550cm^{-1} is due to the vibrations of the sp^2 C=C bonds [8]. No evidence of the above bands is present in the spectra of the films deposited above f_t, which are transparent, confirming that, for increasing fluence, a structural transition from graphitic carbon to ta-C occurred. In all spectra, the lack of absorption bands around 2800- 3100 cm^{-1}, attributed to the C-H_x stretching modes, indicates that our films are hydrogen free (H content is lower than the detectable limit of 0.5at.%) [8].

The sp^3 fraction in the film deposited at 0.5 J/cm^{-2} , as measured by EELS, is around 40% while in the films deposited at 20 Jcm^{-1} it is 80%. For the same samples X-ray reflectivity measurements gave bulk densities of 2-2.2 g/cm^{-2} and 2.9-3 g/cm^{-2}, with the presence of layers [9]. Referring to Table I, all films deposited at fluences below f_t show a *low* content (not lower than about 40%) of fourfold coordinated carbon, while in films deposited at fluences above f_t sp^3 content is progressively increasing up to 80%.

Film stresses are compressive and increase with fluence, still being not higher than 2 Gpa. This value is the lowest reported to date for an as-deposited ta-C film, with no B, Si introduction or post deposition annealing. In fact the usual range of internal stresses in as deposited ta-C films is of the order of 10 Gpa, or more [10,2].

In films deposited on Si, the upper critical load LC2 (at this load the film is completely removed from the scratch path) increases with both laser fluence and film thickness. As a rule, films deposited above f_t, with thickness not shallower than 100 nm, show LC2 between 16 and 20 N, corresponding to maximum Hertzian contact pressures p_{max} around 16 Gpa. These values for LC2 and p_{max} are considerably higher than those reported for single layer DLC films 500 nm thick, deposited on 440 steel (LC2 ~10 N, p_{max} ~1Gpa) [11, 12]. In films deposited on Si+SiC, LC2 values are around 15 N. This does not mean that DLC films deposited on SiC show adhesion and load supporting capacity worse than those of films deposited on Si, since harder substrates sink-in less under the indenter, so that stress and strain distributions in the film and at the interface are modified. Scanning Electron

Microscopy (SEM) images of scratches corresponding to LC2s indicate that scratch diameters are larger in films deposited on Si than on Si+SiC; notwithstanding the different LC2 values, p_{max} is comparable in the two films. Friction coefficients, as deduced from scratch tests in ambient humidity, are lower than 0.08, with minimum values of about 0.05 (see Table I). Scratch tests indicate that ta-C adhesion to Si+SiC is better than to Si. Due to the relevant thickness changes between films deposited on Si respectively at low and high fluences (see Table I), it was not possible to identify a fluence value marking a sharp transition in film mechanical properties, although they are improved in films deposited at higher fluences. In films deposited on Si, hardness increases with fluence up to values of 40 Gpa. As the harder films are not thicker than 130 nm and the indentation depth is 50 nm, film hardness is certainly underestimated due to the influence of the comparatively soft substrate. Indeed in ta-C films deposited on Si+SiC at the same fluences as those deposited on Si, hardness is as high as 70 Gpa, which is more reliable due to the reduction in substrate effects (see Table I).

Fluence [J/cm^2]	**Substrate**	**Thickness [nm]**	**sp^3 [%]**	**Internal stress [GPa]**	**LC2 [N]**	**Friction coefficient**	**Hardness [GPa]**
0.5	Si (100)	120	42	0	8	0.07	27
1.13	Si (100)	400	low	0.30	20	0.065	-
4.5	Si (100)	370	-	0.92	17	0.06	-
7	Si (100)	230	high	1.6	18.5	0.077	-
9.3	Si (100)	90	high		14	0.053	-
20	Si (100)	130	80	1.7	18.5	0.07	36
29	Si(100)+ 500nm SiC	210	high		14	0.11$^{(*)}$	70

(*) Surface roughness about 10 nm.

Table I Collection of relevant data on deposition parameters, structural and mechanical properties of DLC films.

CONCLUSION

We deposited PLD ta-C films 100-200 nm thick on Si both with and without a SiC interlayer, working in a vacuum of 10^{-2} Pa. Structural characterizations showed that above a threshold fluence of 5 Jcm^{-2} the films largely consist of ta-C, with low stress (<2Gpa), up to 80% sp^3 and hardness of 70 Gpa. The better adhesion properties are shown by ta-C on SiC.

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