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Chemical Papers 64 (1) 46–50 (2010)
DOI: 10.2478/s11696-009-0092-9

ORIGINAL PAPER

A Raman spectroscopy study on differently deposited DLC layers in pulse arc system[‡]

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Received 26 November 2008; Revised 12 August 2009; Accepted 13 August 2009

This study is focused on Raman spectroscopy investigations of differently deposited diamond-like carbon (DLC) layers due to varying: (i) Ar and/or N_2 flow rate, (ii) number of impulses, and (iii) bias voltage during the growth process. Samples were prepared by a physical vapor deposition method in a pulse arc system. It is shown that Ar and N_2 flow rates as well as the bias voltage influence the morphology and chemical composition of the deposited DLC layers. By changing the number of impulses, the number of carbon atoms sputtered from target in the vacuum chamber changes, which is reflected in the thickness and morphology of the DLC layers. Visible light Raman spectroscopy of 632 nm excitation wavelength was used for deep analysis of the deposited layers.

Keywords: diamond-like carbon thin films, carbon nitride, Raman spectroscopy, pulse arc deposition

Introduction

Diamond-like amorphous carbon (DLC) films are mainly used for tribological and protective layer applications due to their hardness and chemical inertness. They are neither diamond nor graphite and can be considered as metastable carbon produced in the form of thin coatings with a broad range of structures (primarily amorphous with variable sp^2/sp^3 bond ratio) and compositions (variable hydrogen concentration) (Pierson, 1993). DLC is a harder material with a smaller optical gap, lower content of hydrogen, and a significant fraction of sp^3 bonds in comparison with other amorphous carbons; e.g., hydrogenated amorphous carbon (a-C:H) has rather small C—C sp^3 content. DLC with higher sp^3 content is called tetrahedral amorphous carbon (ta-C).

Several analytical techniques are used to characterize the bonding in DLC films: X-ray diffraction (Kim et al., 2007), electron energy loss spectroscopy (EELS), and laser-Raman spectroscopy (Ferrari & Robertson, 2000). Raman spectroscopy is the most frequently used analytic method because of its high sensitivity for carbon phases; moreover, it is a non-destructive and very fast method. It is based on inelastic scattering of monochromatic light, usually from a laser in the visible range. The laser light interacts with phonons or other excitations in the system, resulting in a shift of the laser photons energy. The shift in energy gives information about the phonon modes in the system.

The Raman spectroscopy analysis of DLC layers usually favors the 1000–1700 cm^{-1} region largely dominated by the bands originating from the A_{1g} breathing (D-band) and E_{2g} stretching (G-band) modes of C sp^2 atoms (Santangelo et al., 2003) centered at about 1355 cm^{-1} and 1550 cm^{-1}, respectively. The G-band is the so-called graphitic-band and D- is the "disordered"-band, from which it is possible to obtain useful information about bonding in the DLC layers

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[‡] Presented at the XIX-th Slovak–Czech Spectroscopic Conference, Častá-Papiernička, Slovakia, 12–16 October 2008.

Table 1. First experiment – investigation of Ar/N_2 flow rate influence; summarized flow rate conditions during the DLC layer deposition process

Sample		1	2	3	4	5	6	7	8	9	10	11
1. Ion cleaning (IC)/min		10	10	10	10	10	10	10	10	10	10	10
2. Deposition	$\dot{V}_{\mathrm{Ar}}/(\mathrm{cm^3\ min^{-1}})$	0	30	50	70	0	0	0	0	30	50	70
	$\dot{V}_{\mathrm{N_2}}/(\mathrm{cm^3\ min^{-1}})$	0	0	0	0	30	50	70	100	30	50	70

Table 2. Second experiment – investigation of impulse number influence; summarized deposition conditions of samples

Sample		12	13	14
1. Ion cleaning (IC)/min		10	10	10
2. DLC	$\dot{V}_{\mathrm{Ar}}/(\mathrm{cm^3\ min^{-1}})$	70	70	70
	$\dot{V}_{\mathrm{N_2}}/(\mathrm{cm^3\ min^{-1}})$	60	60	60
	Number of impulses	1	3	5
	Pulse frequency/Hz	5	5	5

Table 3. Third experiment – investigation of bias voltage influence; summarized deposition conditions of samples

Sample		15	16	17	18
1. Ion cleaning (IC)/min		10	10	10	
2. DLC	$\dot{V}_{\mathrm{Ar}}/(\mathrm{cm^3\ min^{-1}})$	70	70	70	70
	$\dot{V}_{\mathrm{N_2}}/(\mathrm{cm^3\ min^{-1}})$	70	70	70	70
	Number of impulses	10	10	10	10
	Pulse frequency/Hz	5	5	5	5
Ion bombardment		–	Yes	Yes	Yes
Low voltage/V		–	–	50	50
High voltage/V		–	–	800	–

which characterizes the hardness and chemical composition. Their shape depends on: (i) clustering of the *sp*^{2} phase; (ii) bond length and bond angle disorder; (iii) presence of *sp*^{2} rings or chains; (iv) *sp*^{2} imperfections/*sp*^{2} ratio (Ferrari, 2006; Paik, 2005; Ha et al., 2007). Visible Raman spectra are primarily used to determine the *sp*^{2} bonds and the *sp*^{2}/*sp*^{3} ratio because they are 50–230 times more sensitive to *sp*^{2} in comparison to *sp*^{3} sites. However, it is also possible to derive the *sp*^{3} fraction of DLCs indirectly (Ferrrari & Robertson, 2000).

Experimental

Deposition of DLC layers was carried out using the physical vapor deposition method in a UVNIPA-1-001 vacuum system (Trakhtenberg et al., 2001). This system is equipped with three sources: gas ion source for cleaning, electric arc source for non-magnetic metal sputtering, and pulse arc carbon source for DLC deposition.

Our deposition process consisted of two steps: (i) cleaning of the substrate surface and vacuum chamber by an Ar ion beam, usually for 10 min, and (ii) deposition of DLC layers by pulse arc source under different gas conditions in the system (Table 1). The amount of carbon from the graphite target present in the vacuum chamber depends on the pulse source frequency and on pressure. The pulse count determines the film thickness. In the first case, the frequency was 5 Hz for each sample and the pulse count was 5000. Further, also the influence of the count of impulses (Table 2) and bias voltage with various combinations of ion bombardment (Table 3) on the properties of DLC films and their Raman spectra were investigated. Experimental details are summarized in the respective tables.

Micro-Raman measurements of the DLC layers were performed using an ISA Dilor-Jobin Yvon-Spex Labram confocal system, where the excitation wavelength was supplied by an internal HeNe 20 mW laser.

Results and discussion

Investigation of Ar/N_2 flow rate influence

Raman spectra of DLC samples are shown in Fig. 1. In Fig. 1a, the influence of increasing Ar flow rate and on Fig 1b, the influence of increasing N_2 flow rate can be seen. From the spectra, some interesting facts can be concluded. Firstly, with increasing Ar flow rate during the deposition process, the D-band (rising from the limitation in the graphite domain size induced by grain boundaries or imperfections, such as substitutional N atoms, *sp*^{3} coordinated carbon and nitrogen atoms) increases; i.e., D-band at 1330 cm^{-1} increases at the expense of G-band at 1560 cm^{-1}, see Fig. 1a). Moreover, the third band present at 950 cm^{-1}, which is related to the second order of silicon and can be observed in the SiC phase, decreases with the increasing flow rate up to 30 cm^3 min^{-1} (thickness of the DLC film increases), but with a further Ar flow rate increase, this band also shows increasing character. This effect may be caused by higher ionization of carbon atoms penetrating deeper into the Si bulk substrate, in consequence of thicker carbide layer creation on the surface. Because of the increasing tensile strain in the DLC films with the increasing Ar flow there is a sizeable shift to the left both for D- and for G-bands. This shift is attributed to the stronger

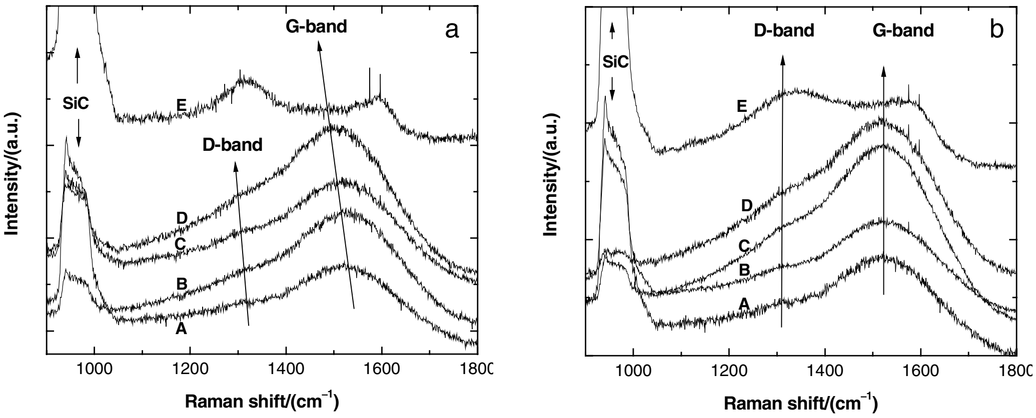

Fig. 1. Raman spectra of differently deposited DLC layers (a) by varying Ar flow rate (A: 0 cm^3 min^{-1}, B: 30 cm^3 min^{-1}, C: 50 cm^3 min^{-1}, D: 70 cm^3 min^{-1}, E: 100 cm^3 min^{-1}) at 0 cm^3 min^{-1} of N_2, and (b) by varying N_2 flow rate (A: 0 cm^3 min^{-1}, B: 30 cm^3 min^{-1}, C: 50 cm^3 min^{-1}, D: 70 cm^3 min^{-1}, E: 100 cm^3 min^{-1} of N_2) at 0–100 cm^3 min^{-1} of Ar.

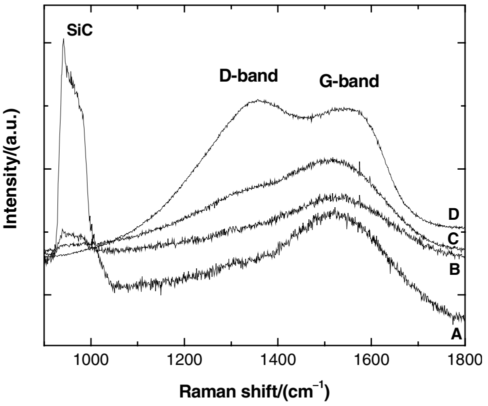

Fig. 2. Raman spectra of DLC layers deposited at different ratio of Ar to N_2 flow rate/(cm^3 min^{-1}): A: 0/0, B: 30/30, C: 50/50, and D: 70/70.

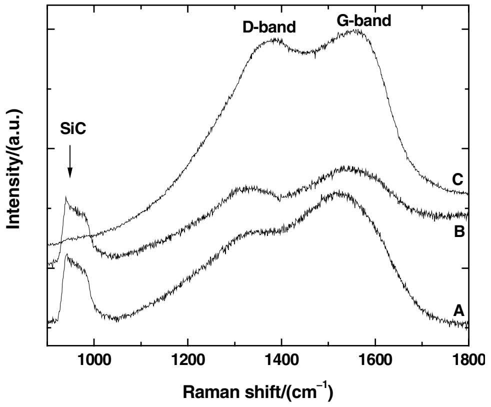

Fig. 3. Raman spectra of DLC layers deposited at various number of impulses: 1000 (A), 3000 (B), and 5000 (C).

graphitic character of the deposited films due to larger number or size of the carbon *sp*^{2} units. This fact was proven by other studies (Valentini et al., 2001; Jones et al., 2008). In addition, it was shown that higher Ar content in the gas mixture increases the D- to G-band intensity ratio, which also corresponds to the increase of the *sp*^{2} cluster size (Valentini et al., 2001).

This shift of G- and D-band does not occur in the second case, when varying the N_2 flow rate (Fig. 1b). In this case, with increasing N_2 flow rate, the D-band also increases and, in addition, the SiC band decreases. This is confirmed by the DLC film thickness increase (due to the sputtering yield enhancement) and by lower ionization of carbon atoms by nitrogen than by argon. However, after the N_2 flow rate increase to 100 cm^3 min^{-1}, the SiC band was markedly enhanced probably due to the carbon atom energy increase and deeper interdiffusion into the layer.

In Fig. 2, the influence of simultaneous increase of both Ar and N_2 flow rates is shown at the values of 0 cm^3 min^{-1}/0 cm^3 min^{-1}, 30 cm^3 min^{-1}/30 cm^3 min^{-1}, 50 cm^3 min^{-1}/50 cm^3 min^{-1}, and 70 cm^3 min^{-1}/70 cm^3 min^{-1}. The effect is reflected in the increase of the D-band and of the DLC layer thickness due to higher impact of ionized particles on the graphite target and hence in higher sputtering yield. The spectra are similar as in case of Fig. 1a with the increasing Ar content in the gas mixture; there is also the shift of the G- and D-bands to lower values due to the effect described above (e.g., increase of graphitic character of the deposited DLC films). For sample 11 (with the highest flow rates of 70 cm^3 min^{-1} for Ar and N_2), no SiC band was measured because of the thicker DLC film.

Investigation of impulse number and bias voltage influence

In Fig. 3, differences in the Raman spectra of DLC deposited at various impulse numbers of the pulse plasma source are shown. It can be concluded that increasing the impulse number (from 1000 up to 5000), the D- to G-band intensity ratio increases and the SiC band decreases. Higher number of impulses per minute

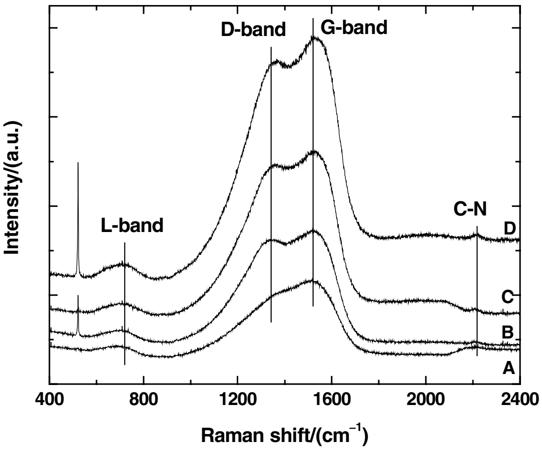

Fig. 4. Raman spectra of DLC layers. Investigation of bias voltage influence; A: without any ion bombardment (IB) and voltage, B: with IB and low voltage (50 V), C: with IB, low voltage, and high voltage (800 V), D: only with ion bombardment.

sputtered more particles from the graphite target, hence, the plasma density near the surface increased which is connected with the deposition of thicker DLC layers.

Four experiments were done to investigate the bias voltage influence described in details in Table 3. The first one was performed without any ion bombardment and bias voltage, the second one with Ar ion bombardment (further IB), the third one with IB and an application of low and high voltage, and the last one only with IB and low voltage. Raman spectra of the samples are shown in Fig. 4. By applying bias voltage to the substrate, the energy of incident ions bombarding the growth layer during the deposition increased and changes in the morphology occurred. The most suitable energy of incident ions to create sp^3 bonds in DLC morphology is, according to literature, 100 eV. This value is moderately differing depending on the used method and the type of the deposited layer (DLC or CN, e.g., carbon nitride with more nitrogen content). In general, at low bias voltage (< 100 V), the films are polymerlike, soft, with high hydrogen content; as the bias increases, the films become diamondlike, harder, with lower hydrogen content (Barklie et al., 2000). From the Raman spectra it can be concluded that the DLC layer without any bombardment and bias voltage had lower ratio of the D- to G-band intensity and thus, presumably, also the ratio of the sp^3/sp^2 bonds. This ratio slowly increased depending on the conditions applied. The highest ratio observed was that at the ion bombardment with low voltage (50 V) bias. This suggests that ion beam bombardment increases the ratio of the sp^3 bonds in the deposited DLC films, which is in agreement with earlier published works (Kim et al., 2007). Except the D- and G-bands, also a wide L-band (characteristic band for DLC layer) at approx. 700 cm^{-1} and a low peak at 2212 cm^{-1}, related to the C—N bonds, were observed. However, these bands were not significantly different from those of the various bias voltage and ion bombardment experiments.

Conclusions

In this study, Raman spectra of differently deposited diamond-like carbon (DLC) layers were investigated by varying (i) Ar and/or N_2 flow rate, (ii) number of impulses, and (iii) bias voltage during the growth process. It was shown that by increasing the Ar flow rate, a sizeable shift both for D- and for G-band appears, while in case of the N_2 flow rate, no shift was observed. In case of the Ar flow rate variations this is probably caused by the tensile strain increase in the material caused by a sp^3 bonds increase and the stronger graphitic character of the deposited films due to the larger number or size of the carbon sp^2 units. N_2 has no such strong influence on the DLC structure compared to Ar. By increasing the flow rate of both Ar and N_2 gases, the D-band and the thickness of the DLC layer increased due to higher impact of ionized particles on the graphite target and hence the higher sputtering yield. In case of different impulse numbers of the pulse plasma source, it was observed that with the impulse number increase, the D- to G-band intensity ratio increased and the SiC band intensity decreased, which is related to the DLC layer thickness increase caused by more carbon atoms being sputtered from the graphite target. And at last, the ion bombardment and bias voltage influence were shown as an easy way to enhance the sp^3 bond number and hence to improve the hardness of the DLC layers.

Acknowledgements. This work was done in the Center of Excelence CENAMOST (Slovak Research and Development Agency Contract No. VVCE-0049-07) and was financially supported by the grants of the Slovak Research and Development Agency No. APVV-0548-07, APVV-0628-06, LPP-0246-06, and of the Ministry of Education of the Slovak Republic No. AV 4/0124/06, VEGA 1/0857/08, 1/2040/05, and 1/3034/06.

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