Journal of Physics: Conference Series

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To cite this article: Petr Písařík *et al* 2015 *J. Phys.: Conf. Ser.* **594** 012008

Journal of Physics: Conference Series **594** (2015) 012008 doi:10.1088/1742-6596/594/1/012008

Influence of diamond and graphite bonds on mechanical properties of DLC thin films

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Abstract. Mechanical properties of diamond-like carbon thin films with various ratios of sp^3/sp^2 bonds were studied. The films were prepared in argon atmosphere (0.25 Pa) by laser deposition method for laser energy densities from 4 $J \cdot cm^{-2}$ to 14 $J \cdot cm^{-2}$. The sp^2 and sp^3 bonds were calculated by X-ray photoelectron spectroscopy. Films contained sp^3 bonds up to 70 %. Surface properties as roughness and atomic force microscopy topology were measured. Hardness (and reduced Young's modulus) were determined by nanoindentation and reached of 30 GPa (203 GPa). Films adhesion was studied using scratch test and was up to 12 N for biomedical alloy (titanium substrates - Ti-6Al-4V). Relations among deposition conditions and measured properties are presented.

1. Introduction

Diamond-like carbon (DLC) is a metastable form of amorphous carbon consists of hybridization in different percentage of sp^1 (acetylene-like), sp^2 (graphite-like), and sp^3 (diamond-like) bonding. DLC films are semiconductors with high mechanical hardness, chemical inertness, low coefficient of friction and optical transparency. In this work the characteristics of DLC films, possibilities of applications in orthopedics, cardiovascular surgery together with other medical field are presented [1, 2, 3, 4, 5, 6]. But adhesion of DLC films on biomedical alloy substrates (Ti-6Al-4V, Co-Cr-Mo and stainless steel) is poor [3, 7]. It is caused by stress in the film due to different hardness and different coefficient of thermal expansion of substrate and film. The content of sp^2, sp^3 bonds exhibits influence on optical, biological [8], electrical and mechanical properties [9]. Here is presented series of six samples with different ratio of sp^3 and sp^2 bonds and responsible mechanical properties.

2. Experimental details

2.1. Deposition

DLC films were prepared using KrF excimer PLD. Laser beam was focused onto a high purity graphite target with energy densities from 4 $J \cdot cm^{-2}$ to 14 $J \cdot cm^{-2}$. Substrate (Si 111 and Ti-6Al-4V) was placed in a distance of 45 mm from the target. The high purity graphite target was rotated (0.5 Hz). The number of pulses was adjusted to reach approximately the same film thickness (400 nm for films on Ti-6Al-4V substrate - ISO 5832-3 and 100 nm on Si 111 substrate). The base vacuum of the coating system was 1 x 10^{-4} Pa. Before deposition the substrates were RF cleaned (13.56 MHz) in 5 Pa of argon for two minutes. The films were deposited in argon ambient (0.25 Pa), with gas (argon) flow of 10 sccm. The DLC films were created at room substrate temperature [4, 6, 8]. Deposition parameters are summarized in Table 1.

Table 1 Deposition conditions of DLC films created by PLD. Carbon atoms sp^3 hybridization content measured by XPS (C 1s).

Sample (Substrate)	Laser energy density ($J \cdot cm^{-2}$)	PFM thickness (nm)	PFM Ra (nm)	AFM Ra (nm)	AFM RMS (nm)	XPS (C 1s)	
						sp^3	sp^3/sp^2
DLC-01 (Si 111)	4	111	4.0	0.381	1.110	58	1.38
DLC-02 (Ti-6Al-4V)		426					
DLC-03 (Si 111)	6	113	6.6	0.356	0.771	59	1.44
DLC-04 (Ti-6Al-4V)		380					
DLC-05 (Si 111)	8	125	4.1	0.712	1.612	65	1.86
DLC-06 (Ti-6Al-4V)		253					
DLC-07 (Si 111)	10	94	4.3	0.471	1.633	64	1.78
DLC-08 (Ti-6Al-4V)		315					
DLC-09 (Si 111)	12	91	2.5	0.580	2.261	67	2.03
DLC-10 (Ti-6Al-4V)		400					
DLC-11 (Si 111)	14	113	1.5	0.635	0.975	70	2.33
DLC-12 (Ti-6Al-4V)		402					

2.2. Ratio of sp^2 and sp^3 bonds - XPS
The percentage of sp^2 and sp^3 hybridized carbon atoms was estimated by XPS. The C 1s spectra were measured by an ADES-400 photoelectron spectrometer (VG Scientific, UK) using Mg Kα excitation (1253.6 eV) and a hemispherical electron energy analyser. Photoelectron spectra were recorded for wide-survey and narrow scans in C 1s and O 1s regions with a pass energy 100 eV or 20 eV (C 1s line) [8]. Inelastic electron background was subtracted using the Shirley`s procedure [10].

2.3. Thickness, film roughness and topology - PFM, AFM.
The film thickness and the roughness parameter Ra (arithmetic average values) were determined using an Alphastep IQ mechanical profilometer (KLA Co.). Topology was characterized using atomic force microscopy (AFM) type NT-NDT Solver Next P7LS.

2.4. Hardness and Reduced Young's modulus – Nano indenter
A system for nanomechanical testing (hardness, reduced Young's modulus) Hysitron TI TriboIndenter 950™ (Berkovich tip) was used for analysis of films on titanium [11, 12]. To minimize the influence of the substrate on hardness, the indentation depth was kept to less than 10 % of coating thickness

(~40 nm). Trapezoidal shape of loading curve was employed – loading, dwell, unloading segment time 5-2-5 seconds. It was indented in matrix 4x4 indent with separation of 5 µm.

2.5. Adhesion – Scratch tester

For determination of adhesions DLC films on Ti-6Al-4V substrate we used macro scratch tester (REVETEST Scratch Tester - CSM co.). The normal load of the indenter (Rockwell, diamond type, Radius – 200 µm) was linearly ramped from the minimum to the maximum during scratching. The critical loads Lc2 (edge spallation) and Lc3 (spallation inside the groove) were determined by optical microscopy after testing. Figure 1 shows the CCD micrograph of the scratch tracks. Here, the minimum load and the maximum load were 1 N and 30 N, respectively. In the test, the scratch length was 8 mm and the scratch speed was 2.76 mm/min.

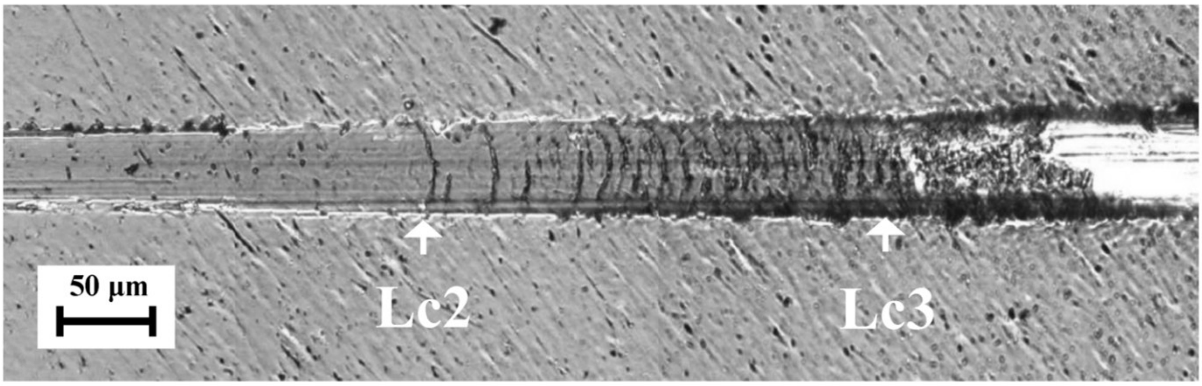

Figure 1 Optical micrograph of typical scratch tracks on DLC coated on Ti-6Al-4V substrate (The critical loads Lc2 - edge spallation and Lc3 - spallation inside the groove)

3. Results and discussion

DLC films were fabricated for laser energy densities of 4, 6, 8, 10, 12 and 14 J·cm^{-2}. Films prepared on Si substrates were used for thickness, AFM topology and XPS measurements. Films prepared on Ti-6Al-4V were used for determinated adhesion, hardness and Reduced Young's modulus.

3.1. Ratio of sp^2 and sp^3 bonds - XPS

The procedure are described in [6, 8] and the results are summarized in Table 1. The percentage of the sp^2 and sp^3 hybridized carbon atoms in the analyzed volume of the films was revealed from a peak-fit of the high-resolution C 1s spectra. As illustrated in Figure 2 three Gaussian lines correspond to the C sp^2 bonding peaked at 284.3 eV, C sp^3 at 285.2 eV, and the C-O at about 286 eV [8]. The percentage of the sp^3 bonds increased with increasing laser energy density. The maximum of sp^3 bonds (70 %) was measured by XPS for energy density of 14 J·cm^{-2}.

3.2. Thickness, film roughness and topology - PFM, AFM

Alpha-step profilometer with diamond tip (radius 5 µm, 60°) scanned the 2-mm film surface. With Gaussian filter (cutoff 250 µm) the arithmetic average of absolute values Ra parameter was calculated. Using AFM in noncontact regime the area of 10×10 µm was scanned and the roughness parameter Sq root mean squared (RMS) was determined. No distinct RMS changes were observed with changing deposition conditions, see Table 1. The films were generally smooth with rare droplets, usually tenths of nanometers in high, see Figure 3.

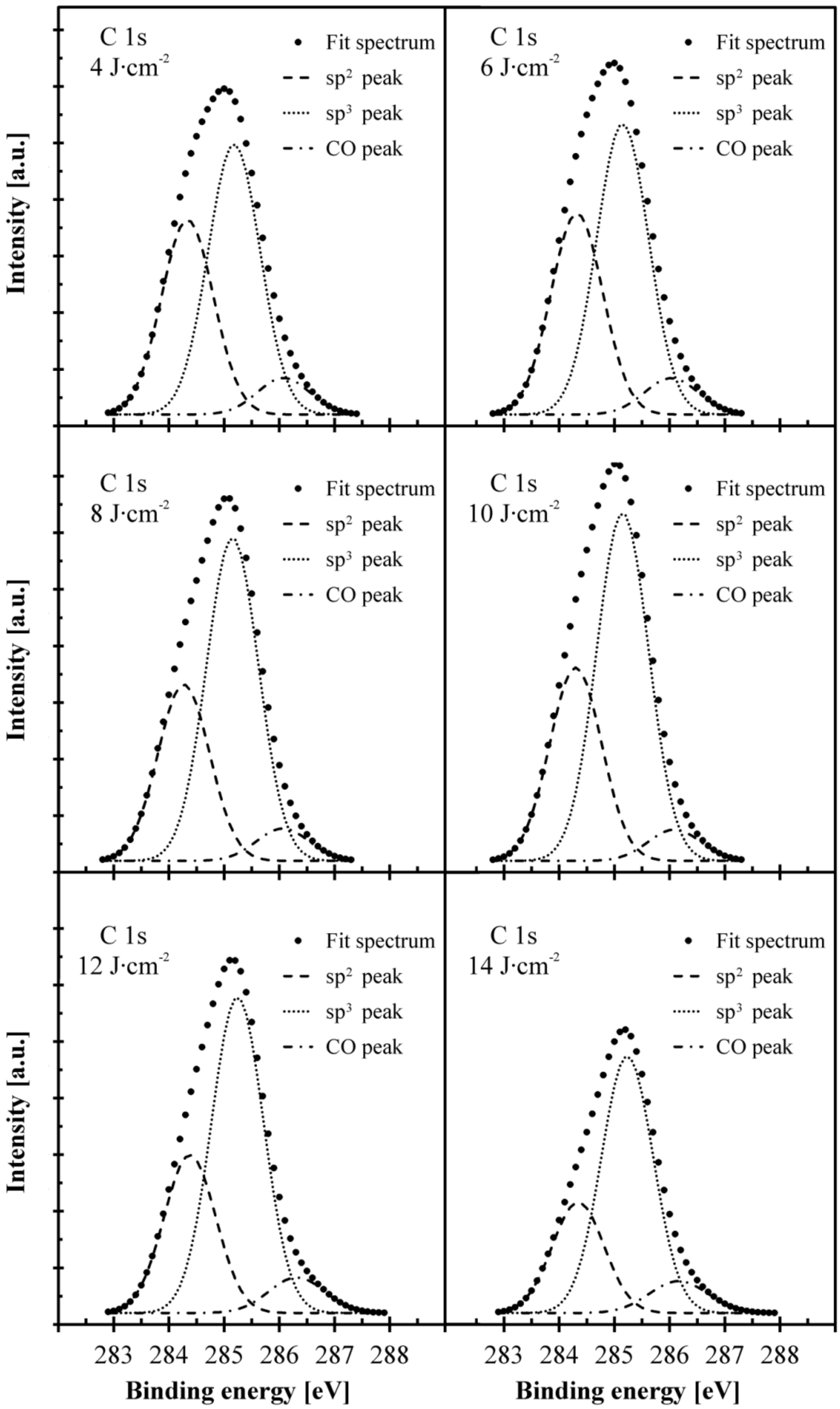

Figure 2 High-energy resolution C 1s peaks with illustration of peak fitting onto sp^2 at 284.2 eV, sp^3 at 285.2 eV, and C-O at 286.5 eV contributions for laser energy densities from 4 J·cm^{-2} to 14 J·cm^{-2}

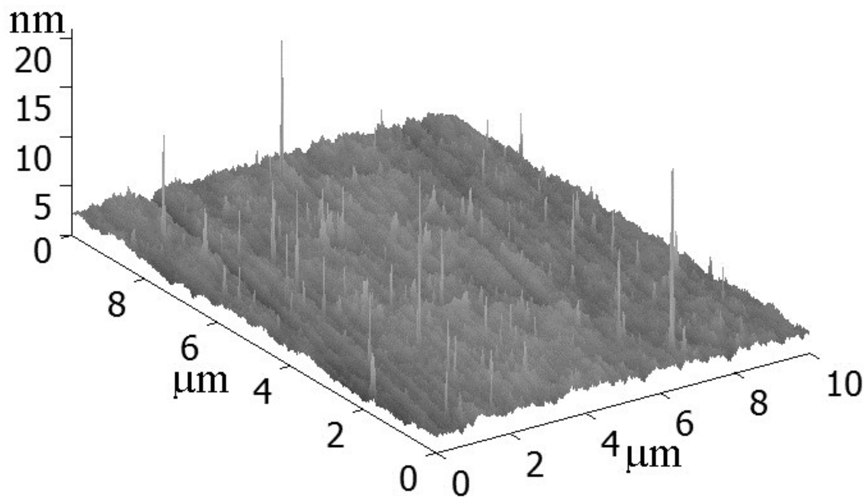

Figure 3 Typical AFM surface of DLC film (DLC-03 - energy density of 6 J·cm^{-2})

3.3. Hardness and Reduced Young's modulus – Nano indenter

Hardness and reduced Young's modulus of DLC films depends strongly on the deposition conditions and the type of deposition techniques. There are various values of hardness a and reduced Young's modulus reported in the literature [13, 14, 15, 16, 17, 18, 19], from units GPa to tens of GPa, from tens to hundreds of GPa respectively.

Hardness our layers grown from 0.8 GPa to 30.2 GPa, as a percentage of sp^3 bonds increased, as well as reduced Young's modulus of 17.8 GPa to 203.3 GPa - see Table 2. These results are similar to those of [13, 14].

Table 2 Hardness, reduced Young's modulus and adhesion (Lc2, Lc3) for laser energy densities from 4 J·cm^{-2} to 14 J·cm^{-2}

Sample (Ti-6Al-4V substrate)	DLC-02	DLC-04	DLC-06	DLC-08	DLC-10	DLC-12
Laser energy density (J·cm^{-2})	4	6	8	10	12	14
Lc2 (N)	8,3	5,5	9,1	5,5	7,6	6,8
Lc3 (N)	12,5	11,4	14,5	9,4	11,6	10,7
Hardness (GPa)	0,8	2,0	--	7,7	10,8	30,2
Reduced Young's modulus (GPa)	17,8	21,7	--	66,4	68,1	203,3

3.4. Adhesion – Scratch tester

The adhesion of DLC films on biomedical alloy substrates is poor [3, 7]. Sheeja found [20] that the critical load of the DLC films to silicon substrate was about 2.5 N. The higher value of the critical load in this study may be due to application of the Ti interfilm and control of the substrate temperature during deposition. Similar results were presented Baragetti [21]. DLC films on aluminium alloy exhibited critical load Lc3 about 3.5 N [21]. Jelínek [22] presented better results, the adhesion was about 14 N. This was probably caused by the use of RF cleaning and ion bombardment during growth of the layer.

Scratch test shows (Table 2) that the maximum critical load Lc3 of our DLC films was more than 14 N. This is a higher or same value published in the literature for similar DLC films (without buffer and doping). The same results as [22] is probably achieved by using RF surface cleaning before the deposition.

4. Conclusion

Diamond like carbon films with different content of sp^3 bonds were prepared by PLD using energy densities from 4 $J{\cdot}cm^{-2}$ to 14 $J{\cdot}cm^{-2}$. The percentage of the sp^3 bonds increased with increasing laser energy density. The maximum of sp^3 bonds (70 %) was measured by XPS for energy density of 14 $J{\cdot}cm^{-2}$. The films were generally smooth with rare droplets, usually tenths of nanometers in high.

Hardness our layers grown from 0.8 GPa to 30.2 GPa, as a percentage of sp^3 bonds increased, as well as reduced Young's modulus of 17.8 GPa to 203.3 GPa - see Table 2. These results are similar to those of [13, 14].

Scratch test shows (Table 2) that the maximum critical load Lc3 of our DLC films was more than 14 N. These results don't show any dependence with sp^3 content and adhesion.

Acknowledgements

This work was supported by the Grant Agency of the Czech Technical University in Prague, grant No. SGS14/096/OHK4/1T/17 and SGS14/168/OHK4/2T/17, the Grant Agency of the Czech Republic (grant P108/13-33056S).

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