Cr-DLC films deposited by dual pulsed laser ablation

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Abstract - Diamond-like carbon (DLC) and Cr doped diamond-like carbon (Cr-DLC) layers were studied for potential medical applications. DLC and Cr-DLC were deposited on silicon and titanium substrate by dual pulsed laser ablation using two KrF excimer lasers and two targets (graphite and chromium). The topology of layers was studied using scanning electron microscopy (SEM). The composition was analyzed using wavelength-dependent X-ray spectroscopy (WDS). Ethylene glycol, diodomethane and deionized water were used to measure their contact angles, which were used to evaluate the surface free energy.

Keywords - Chromium, Diamond-like carbon, Thin films, Surface morphology, Dual Pulsed laser deposition

1. INTRODUCTION

Diamond-like carbon (DLC) is thin film with high hardness, low friction coefficient, optical transparency in the visible and infrared regions, high electrical and thermal conductivities and high wear resistance [1--6]. DLC is a biocompatible material than can be used in prostheses or biological implant [3--6]. However, the practical applications of DLC films have been limited because of low adhesion on biomedical alloys and high internal stress. Several studies have shown that the internal stress in DLC films can be relieved reduced and their adhesion can be increased by doping elements into the DLC films.

One of the possibilities is doping with chromium. Cr-DLC layers were prepared by various techniques, mostly hybrid systems - radio frequency plasma enhanced chemical vapor deposition (RF-PECVD) and thermal evaporation techniques [7], plasma-assisted vapor/chemical vapor deposition (PVD/CVD) and magnetron sputtering [8, 9], linear ion source and DC magnetron sputtering [10, 11], intensified plasma-assisted processing and magnetron sputtering [12], dual-magnetron sputtering [13], dual-target cathodic art evaporation system [14].

The layers thus prepared were studied and effects of chromium doping on the mechanical properties (adhesion, hardness, Young's model, wear, friction coefficient) [7, 10--12, 15--20], optical properties (transmission) [7], structure (FTIR [7, 14], XPS [10--12, 14--16, 19], XAES [17], Raman [11, 15, 18, 21]) and electrical properties [7], surface morphology (AFM) [10, 11, 21] and contact angle [11, 22] were evaluated.

Adhesion of DLC films to biomedical alloy substrates (Ti-6Al-4V, Co-Cr-Mo and stainless steel) is poor [3, 23]. It is caused by stress in the layer due to different hardness and different coefficient of thermal expansion of substrate and layer. Sheeja found [24] that the critical load of the DLC films to silicon substrate was about 2.5 N. Similar results were presented Baragetti [25]. DLC films on aluminium alloy exhibited critical load about 3.5 N

[25]. One option to improve the adhesion is use of doping layer. Dai et al.'s study [15] revealed that the critical load of the Cr-DLC films is much higher than the DLC film. One the other hand, the hardness Cr-DLC films presented in [12] was increased by ~ 10 % by incorporating Cr into the DLC films, respectively ~ 30 % in [10]. On other hand, the results in [19] show that incorporation of Cr into DLC causes the hardness reduction.

In our contribution we concentrated on synthetize and study of DLC film and Cr-DLC films.

2. EXPERIMENTAL

2.1 Deposition

Silicon (100) wafers, titanium alloy (Ti-6Al-4V) and were used as substrates, which were cleaned ultrasonically in acetone, toluene, ethanol, then just cleaned with ethanol and dried in air before being put into the vacuum chamber. Cr-DLC films were prepared by dual PLD using a two KrF excimer laser (λ = 248 nm, τ = 20 ns). First laser beam was focused onto a high purity graphite target with energy densities of 8 J·cm^{-2} with repetition rate from 4 Hz to 12 Hz and second laser beam was focused onto a chromium target with energy densities of 5 J·cm^{-2} with repetition rate from 2 Hz to 10 Hz – see Table 1. Figure 1 shows the schematic diagram of the system used to prepare the Cr-DLC film samples. The numbers of pulses were adjusted to reach approximately the same layer thickness (350±50 nm) and different atomic chromium content 0-18 %. Substrate was in a distance of 45 mm from the targets. The targets were rotated (0.5 Hz). The Cr-DLC films were created at room substrate temperature. The base vacuum of the coating system was 5x10^{-4} Pa. The films were deposited in argon ambient (0.25 Pa) [4, 6].

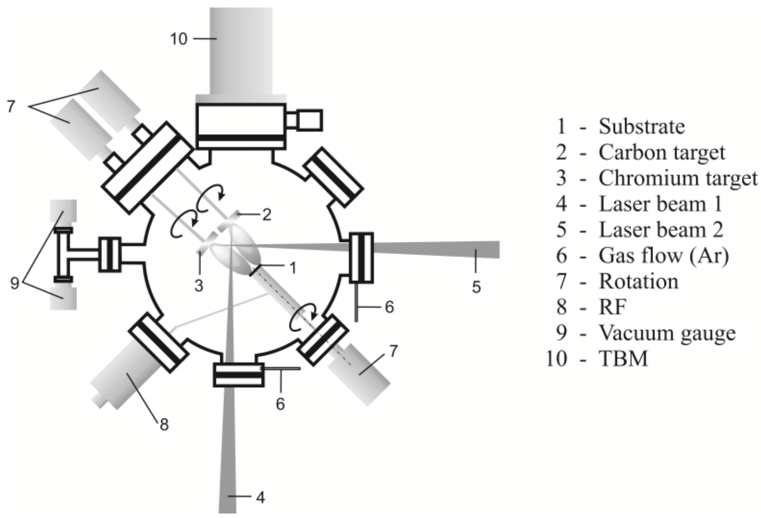

Figure 1 The scheme of dual PLD deposition system

2.2 Characterization of layers properties

The composition of Cr-DLC thin layers was determined by an electron microprobe using a wavelength dispersive X-ray spectroscopy (WDS). WDD was performed with JEOL 840. The energy of primary electrons was kept at 5 keV to minimize their penetration depth and the absorption of emitted X-rays. For this energy, an electron spot diameter was estimated to be in the range 1-2 μm, which gives information at a depth of about 0.5 μm. The accuracy of the measurement of Cr and C, using STRATA program [26] was better than 5 %. The surface morphology was observed at a magnification of 400.

Wettability studies were performed by static contact angle measurement. Using a contact angle meter (DSA100, Krüss Co.) and with combination of three liquids: demineralized water, diiodomethane and ethylene glycol. Measurement was arranged at room temperature and humidity 20 ± 5 % by the sessile drop method with drop volume approximately 0.75±0.25 µl. Surface free energy was calculated using the Fowkes method and dispersive (γ^{LW}) and polar (γ^{AB}) components were obtained. The component γ^{LW} summarizes long-range Lifshitz - van der Waals forces, and γ^{AB} describes short-range polar interactions.

3. RESULTS AND DISCUSSION

Cr-DLC films were synthesized using dual PLD of C and Cr target. In dependence with deposition conditions the Cr content moved from 0 at % to ~ 18 at % - see Table 1. The layers were generally smooth with rare droplets, see Fig. 2.

Contact angle (CA) of Cr-DLC for all liquids (ethylene glycol, diodomethane and deionized water) was higher compared the DLC film (CA $_{\text{Deionized water}}$ = DLC ~70°, Cr-DLC ~90°; CA $_{\text{Diodomethane}}$ = DLC ~41°, Cr-DLC ~52°; CA $_{\text{Ethylene glycol}}$ = DLC ~43°, Cr-DLC ~65°). Our measured for contact angles for water had the same trend as Cr-DLC layers reported by Ali [22]. Contact angles were used to evaluate the surface free energy (SFE). SFE of Cr-DLC for all liquids was lower than the DLC film (SFE $_{\text{Total}}$ = DLC ~43 mN/m, Cr-DLC ~33 mN/m; SFE $_{\text{Disperse component}}$ = DLC ~37 mN/m, Cr-DLC ~31,5 mN/m; SFE $_{\text{Polar component}}$ = DLC ~6 mN/m, Cr-DLC ~1,5 mN/m).

Table 1 Deposition conditions of Cr-DLC films created by dual-PLD

Sample (Substrate)	Laser 1 - Carbon	Laser 2 - Chromium	WDX
	Repetition rate (Hz)	Repetition rate (Hz)	Chromium (at. %)
DLC (Si 100 + Ti6Al4V)	12	0	0
Cr-DLC-1 (Si 100 + Ti6Al4V)	12	2	2.2
Cr-DLC-2 (Si 100 + Ti6Al4V)	9	3	4.1
Cr-DLC-3 (Si 100 + Ti6Al4V)	10	7	8.2
Cr-DLC-4 (Si 100 + Ti6Al4V)	4	7	17.9

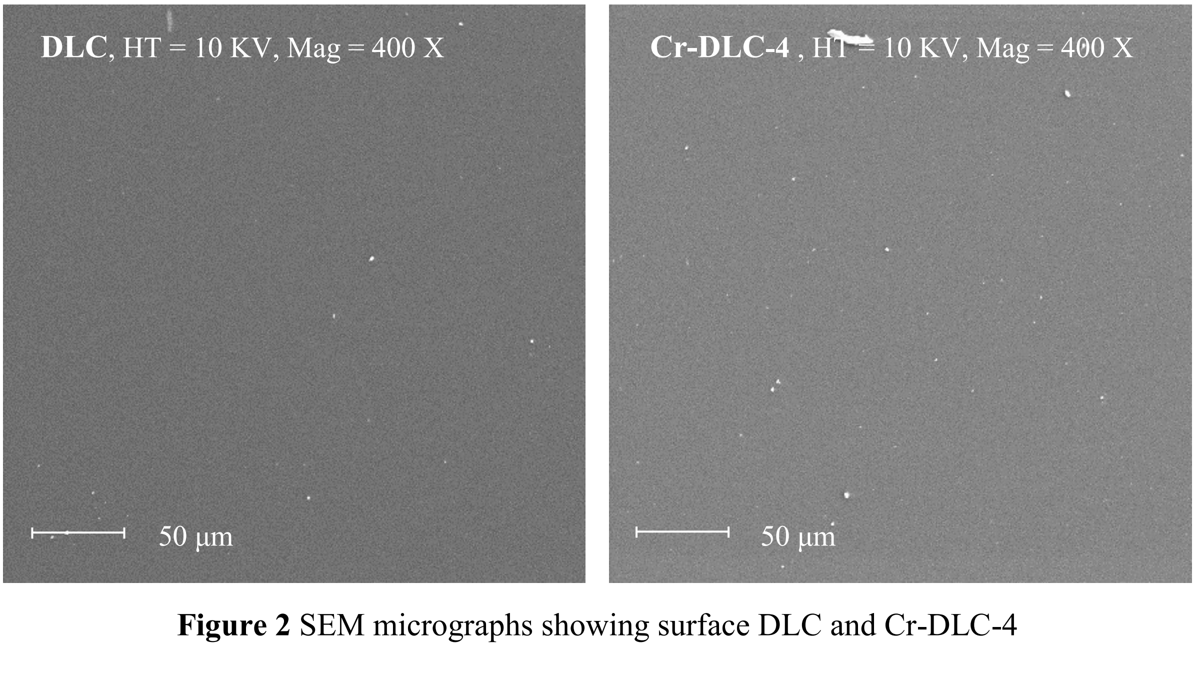

Figure 2 SEM micrographs showing surface DLC and Cr-DLC-4

4. CONCLUSIONS

This paper focuses on DLC and Cr-DLC films on silicon and biomedical alloy substrate (Ti-6Al-4V). The layers were prepared using dual Pulsed Laser Deposition (PLD) using two targets (graphite and chromium). The Cr content increased from 2.2 to 17.9 at. %. The layers were generally smooth with rare droplets. The contact angle measurements for water showed that the contact angle of Cr-DLC films (90°) was higher than DLC film (70°) and surface free energy of Cr-DLC films (43 mN/m) was lower than DLC film (33 mN/m).

ACKNOWLEDGMENTS

We thank the Institutional research plan AV010100522, grant of the Czech Technical University in Prague SGS12/167/OHK4/2T/17 and SGS12/088/OHK4/1T/17, and the Ministry of Education, Youth and Sports of the Czech Republic for grants COST LD12069.

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