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# The effect of deposition parameters on the properties of gradient a-C:H/Ti layers

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**Properties**

## ABSTRACT

**Purpose:** During the last 20 years DLC (diamond-like carbon) layers became a very attractive material in many medical and engineering applications. While the layer's stress and adhesion were always a concern, several adhesion improvement methods have been proposed. A majority of those methods consists of either the deposition of an adhesion promoting interlayer or the application of a gradient of chemical composition. In whatever way this reduces the internal stress and improves the adhesion of carbon layers, it also affects the properties of the carbon layer. The aim of this study was to investigate the physicochemical properties of gradient carbon layers manufactured by RF PACVD/MS method at different process parameters.

**Design/methodology/approach:** The a-C:H/Ti gradient layers were deposited onto silicon wafers using a hybrid deposition method which combines PVD and CVD processes in one reaction chamber. Surface topography, adhesion and coefficient of friction (COF) were measured at a nanoscale using Atomic Force Microscopy, Nanoindentation, and Nanotribometry.

**Findings:** The result of this investigation has demonstrated that gradient interlayer deposition parameters affect roughness and tribological properties of outer carbon layer.

**Research limitations/implications:** Presented investigation was performed with mirror-polished silicon wafers to prevent possible interferences caused by variations in surface topography of other typical substrates during polishing. However, the adhesion of carbon layer measured for the silicon substrates can be noticeably different from that measured for metal substrates. Thus, new adhesion investigations have to be done when using these layers on application-specific substrates. Also, additional friction and wear resistance measurements performed under wet conditions (biological serum) should be conducted in a case of medical applications.

**Originality/value:** There are several reports available on the properties of carbon layers deposited subsequently onto the adhesion promoting interlayer. Present work is an attempt to understand and describe influence of adhesion promoting interlayer deposition parameters on the properties of interlayer - layer system as a whole.

**Keywords:** Wear resistance; Friction coefficient; Adhesion; DLC

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# 1. Introduction

Since early 70's after a pioneering work of Aisenberg and Chabot, the DLC (*amorphous diamond-like carbon)* layers have become more and more attractive material in many fields of science and industry [1-4]. High hardness, low friction coefficient, good wear resistance, chemical inertness and biocompatibility are the most popular characteristics quoted by many authors [3-5]. A unique combination of chemical and physical parameters makes DLC a perfect choice for such applications like protection against wear and corrosion or improvement of biotolerance or lubricity [5-10]. The combination of properties is strongly connected with the ratio of $sp^3/sp^2$ hybridized electrons, which tells us about diamond ($sp^3$) and graphitic ($sp^2$) bonding in the layer's structure [3,4]. The physical phenomena related to the DLC properties have been well understood and described in the literature. However, the high stress and poor adhesion strength of coating with a substrate are still the critical issues for the most industrial applications. A number of different approaches have been developed to address the DLC stress and adhesion on various substrates, e.g., doping of DLC layers, deposition of nanocomposite and/or gradient layers, etc. [11-13].

In this work, in order to improve the adhesion and reduce the internal stress of diamond-like carbon films, gradient a-C:H/Ti layers were deposited onto silicon wafers using RF PACVD method combined with magnetron sputtering technique. Good corrosion parameters such as a-C: H/Ti layers have been observed in the earlier work [14]. In present study we investigated the influence of the negative bias voltage on the surface topography, coefficient of friction (COF), and adhesion of a-C: H/Ti layers.

# 2. Experimental details

## 2.1. Samples preparation

Considering the goal of the paper and the used analytical methods, the experiments were conducted with polished Si wafers to ensure the same surface roughness of the substrate in each experiment. Samples were cleaned ultrasonically in acetone and dried by compressed air just before the deposition process.

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## 2.2. Film preparation

A hybrid RF PACVD/Magnetron Sputtering (MS) system was employed to manufacture the gradient carbon coatings. The system consists of a cylindrical chamber 290 mm in diameter and 190 mm high, with water cooled bottom electrode connected through a feeder-box to the radio frequency 13.56 MHz power generator, and with a magnetron equipped with 60 mm Ti cathode, mounted in the centre of the chamber top cover. The vacuum system employs one rotary and one diffusion pump which make it possible to reach $10^{-4}$ Pa residual pressure. The samples mounted on the r.f. electrode were etched in argon plasma for 10 minutes at a -720 V self-bias voltage prior to the layers synthesis. Then, during MS deposition of adhesion improving Ti interlayer, methane gas was progressively added into the reaction chamber to obtain a gradient of chemical composition. Thickness of such interlayer was 150 nm. Two different self bias voltages -150 V and -300 V were applied during the MS process. After that, DLC layer synthesis was conducted by RF PACVD process with methane gas at a constant flow rate of 30 sccm. Negative self- bias voltages during PACVD were set at -300 V, -600 V and -800 V, respectively. The deposition was stopped after desired 1 $\mu$m thickness of carbon layer was reached. Such a diversity of bias voltages applied during the deposition process allowed to investigate their influence on adhesion and surface topography of the gradient reactive magnetron sputtered interlayer, and on roughness parameters and coefficient of friction of DLC layer deposited on the top.

## 2.3. Characterisation

Surface topography analysis was made in two steps. First, after the MS process, samples were taken out and influence of self-bias voltage on roughness parameters of the interlayer were investigated. The analysis was performed using *Veeco MultiMode Scanning Probe Microscope* operated in contact with AFM mode. Second, the influence of self-bias voltage on the surface topography of PACVD DLC layer was studied. For that purpose, new samples were coated with a-C:H/Ti gradient layer. Roughness parameters of a-C:H/Ti gradient layer were measured using *Veeco Explorer SPM* also working in contact AFM mode. After these measurements, correlation between surface topography of the interlayer and deposited film was evaluated.

During adhesion measurement special emphasis was put on adhesion of the interlayer and influence of negative self bias voltage on this parameter. Adhesion of the films was investigated using G 200 NANOINSTRUMENTS nanointender equipped with diamond tip (curvature radius of 0.98 µm and an angle of 87.70). Scratch tests were performed under increasing load from 0 to 80 mN in a distance of 1200 µm. During the measurement the coefficient of friction (COF) was recorded, and the drastic change of this parameter was a signal of discontinuity between the layer and the silicon substrate. At least 5 scratches were made for each sample and the results were averaged.

The coefficient of friction was measured using CSM INSTRUMENTS NANOTRIBOMETER and employing a UHMWPE (polyethylene) ball of 3 mm in diameter as a counterpart. The choice of the UHMWPE is based on the fact that it is a common material for biomedical applications mainly for the sliding couples in the hip joint prosthesis. Dry friction conditions were applied during our preliminary experiments. The main reason for these experimental conditions was to investigate the differences in the coefficient of friction for two materials presenting diverse mechanical properties (hardness, Young's modulus). The investigations were performed in linear reciprocating mode with 0.5 mm amplitude under load of 100 mN and sliding speed of 4 mm/s during 5000 cycles.

# 3. Results and discussion

Considering a wide range of deposition parameters using our hybrid RF PACVD and MS process, significant variations in surface roughness, adhesion, and tribological properties of a-C:H/Ti gradient layers have been expected and observed in our experiments.

Table 1.
Roughness and coefficient of friction of DLC layers deposited under different process parameters

| Sputtering bias [V] | a-C:H layer deposition bias [V] | Ra [nm] | CoF against PE |
|---|---|---|---|
| 150 | 300 | 0.665 | 0.09 |
| 300 | | 0.738 | 0.11 |
| 150 | 600 | 0.960 | 0.11 |
| 300 | | 0.753 | 0.13 |
| 150 | 800 | 0.792 | 0.1 |
| 300 | | 0.633 | 0.12 |

Adhesion measurements prove that the negative bias voltage has the influence on the topography of Ti – C interlayer. Besides, despite of almost the same roughness parameters of -150 V and -300 V interlayers, the different shape of protrusions can be observed in Fig. 1 a) and b). Sharper peaks occur on Fig 1 a).

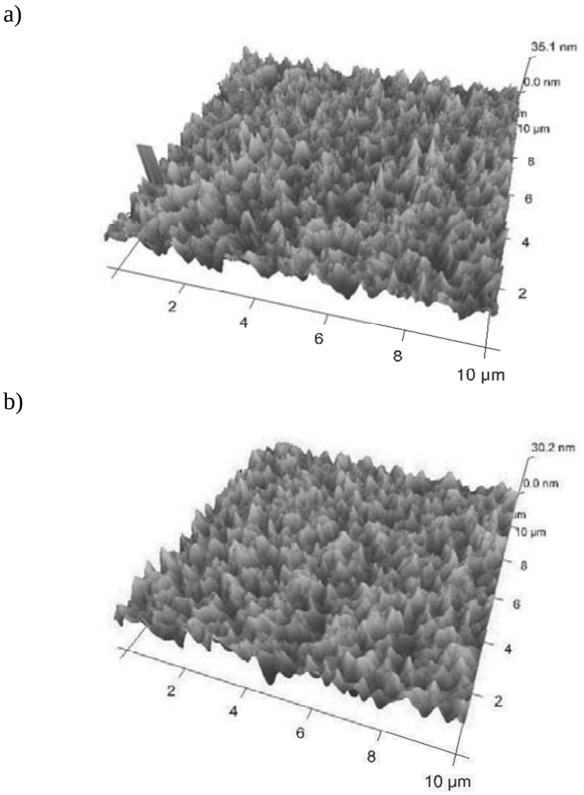

Fig. 1. Surface topography of the Ti – C interlayers deposited under self-biases of: a) 150V and b) 300V

During the reactive magnetron sputtering process titanium carbides can be formed, and the layer's topography can be strongly affected by the growth character and structure of TiC inclusions. The increased bias voltage results in higher energy of ions impinging on surface of the substrate, thus leading to enhanced diffusion and self-patterning of the growing layer.

The grain size and their orientation are also affected by the ion energy, thus causing the changes in the surface topography. Strong reduction of the interlayer's deposition rate with increased negative bias was observed assuming the dominating effect of sputtering. However, the Ra parameter measurements did not show significant changes. Its value was 3.85 nm and 3.6 nm for biases of 150V and 300V, respectively. The measured values of Ra parameter and the coefficient of friction are presented in Tab. 1.

Roughness parameters of a-C:H/Ti layers are presented on Fig. 2. The behaviour of DLC layers deposited under bias of 300V was slightly different from other samples.

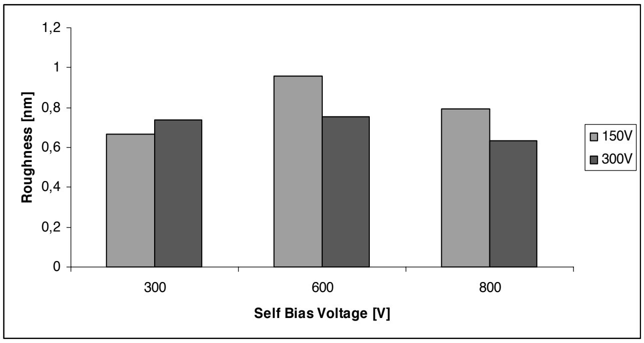

Fig. 2. Ra parameter investigation results

Despite of slightly higher roughness of the interlayer manufactured at bias voltage of 150V, the final Ra parameter is higher for DLC layer deposited subsequently on the interlayer sputtered under bias of 300V. We suggest that the growth character of DLC layer under lower self bias is different from that observed for higher biases.

Surface topography for both coatings is smoother than that of gradient interlayers (Fig. 1). However, despite of opposite trend in roughness parameters, for the DLC layer synthesized onto interlayer deposited under bias of 300V, the topography of the layer in Fig. 2 b) seems to have a better quality than that presented one on Fig. 2 a). Although, the latter surface is significantly smoothened by the amorphous carbon layer, a few randomly distributed protrusions are visible. Those protrusions are the probable reason for higher Ra parameter recorded during the measurements.

For DLC layers deposited under biases 600V and 800V the situation is different and expectable. Higher roughness is observed for the samples where the Ti-C interlayer was deposited under bias 150V. As it was shown earlier, Ra parameter for this bias was higher and the sample's surface was rougher than that deposited under bias of 300V. Lower Ra parameter value obtained for layer deposited under 800V is the consequence of higher temperature and deposition/etching rate ratio.

Surface topography of both layers is presented in Fig. 3 a),b).

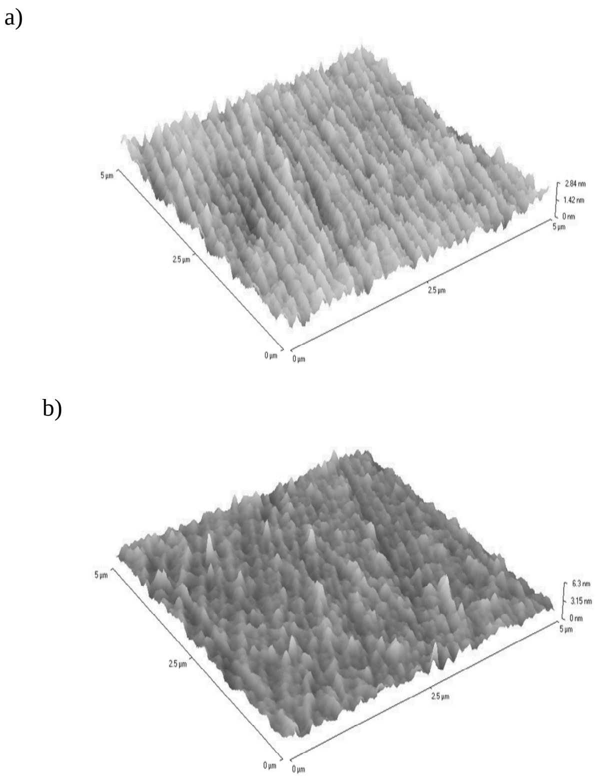

Fig. 3. Surface topography of DLC layer deposited under bias of 300V onto interlayers manufactured under biases of: a) 150V and b) 300V

From the adhesion measurement results presented in Figs. 4–5 it can be stated that the negative bias voltage has no influence on adhesion strength of the layer on the silicon substrate. Adhesion values and their standard deviations presented in Fig. 6 are very close to each other and no significant difference can be observed.

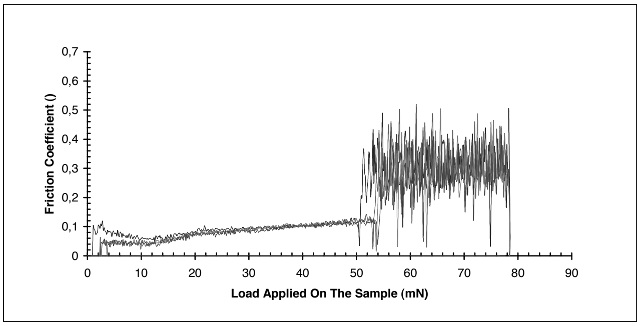

Fig. 4. Adhesion measurement results for sample sputter deposited at -150 V negative bias voltage

Titanium does not form any compounds with the surface of silicon substrates, thus the temperature and acceleration voltage can only affect the growth character and structure of the layer (Fig. 6). Within the used bias voltages range, this parameter seems to have little effect on the stress in the interlayer.

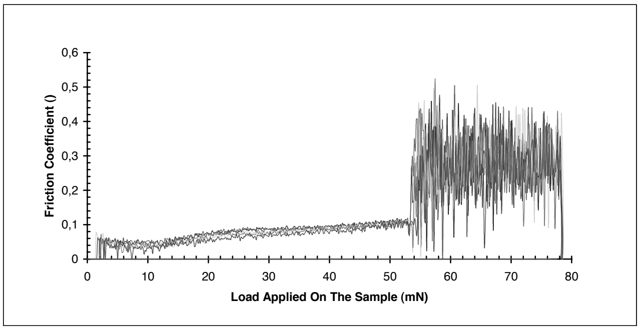

Fig. 5. Adhesion measurement results for sample sputteted under -300 V negative bias voltage

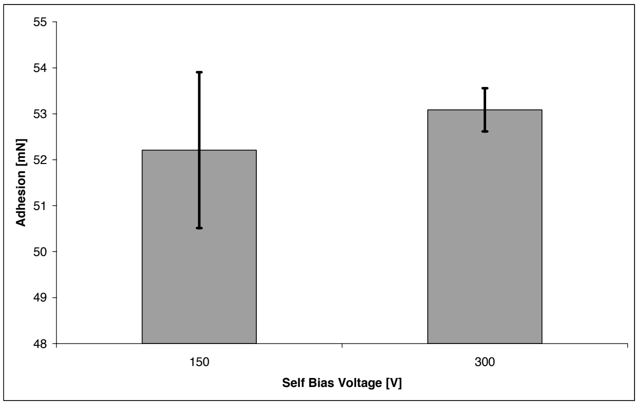

Fig. 6. Adhesion strength of a-C:H/Ti layers as a function of negative self bias voltage applied during the gradient interlayer deposition

The results of the coefficient of friction measurements are presented on Fig. 7. It is clearly visible that self-bias applied during the reactive sputtering process has some influence on friction coefficient of a-C:H/Ti layers. The lowest values of these parameters were obtained for the coatings where the gradient interlayers were manufactured under self bias of 150V. The tendency of the COF values for both biases is the same, and it follows the trend in the surface roughness changes.

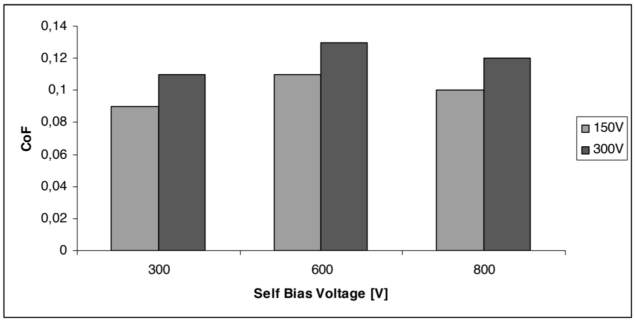

Fig. 7. Coefficient of friction of UHMWPE ball against a-C:H/Ti layers deposited under 300V, 600V and 800V onto gradient interlayer sputtered under biases of 150V and 300V

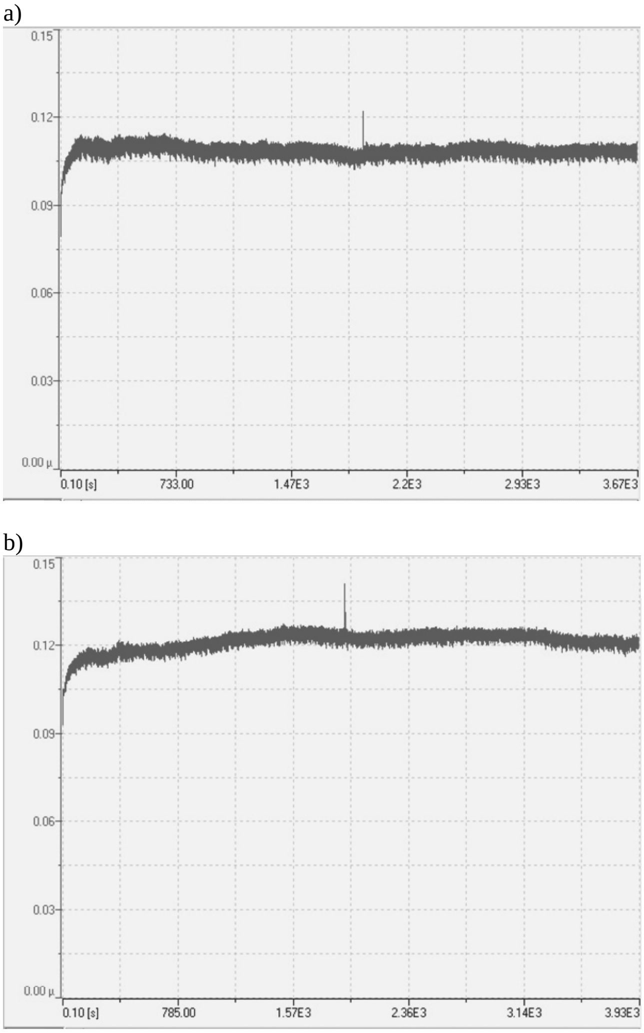

Fig. 8 Examples of COF vs time graphs obtained for layers deposited under different parameters; a) sputtering bias -150V, DLC deposition bias -600V, b) sputtering bias -300V, DLC deposition bias -800V

According to the surface topography of the interlayers, it was expected that the interlayer manufactured under 300V self bias, would have a positive impact on the tribological properties of the DLC layer (i.e. lower coefficient of friction was expected for DLC layers deposited on this interlayer). However, the opposite trend can be caused by many reasons like the structure and phase composition of the gradient interlayer or the additional stress generated during the synthesis process. These issues certainly need further investigations. During all our examinations, the value of the coefficient of friction was stable and did not change significantly (see Fig. 8). The lack of spikes in the COF vs time graphs also indicates that the layers have good adhesion, at least for these test parameters.

Different values of COF obtained for various negative self biases can also be related to different hydrogen content in the DLC layers, and to $sp^3/sp^2$ ratio. Both hydrogen content and diamond/graphitic bonding ratio and their influence on the coefficient of friction is well understood and widely described in the literature. Although the same gas atmosphere during each deposition process, the acceleration voltage can strongly affect the structure as well as the chemical composition of the layer. In particular, different ratio of atoms with $sp^3/sp^2$ electron's hybridization can be obtained.

## 4. Conclusions

Well-adherent a-C:H/Ti gradient layers were successfully deposited onto silicon substrates. Self-bias voltage applied during the reactive magnetron sputtering process allowed to control the surface topography of layers. The results of adhesion measurement confirm that self-bias voltage applied during the reactive sputtering process does not change the adhesion, thus considering very small difference between the roughness parameters of both types of interlayers and much lower deposition rate for bias of 300V, the most optimal bias for silicon substrates seems to be 150V. However, different situation can be possible for steel or other alloy substrates (not discussed in this paper). Final roughness of a-C:H/Ti layers strongly depends on the self-bias applied during the reactive magnetron sputtering process. For all deposition parameters the Ra parameter was below 1 nm. The coefficient of friction of a-C:H/Ti gradient layer against UHMWPE ball was as low as 0.1. The lowest value of this parameter was obtained for 150V bias applied during the magnetron sputtering process and 300V bias applied during carbon layer deposition. During our experiments, the highest deposition rate of DLC layer was observed for the negative bias of 600V. However, at this bias the highest values of roughness and COF were also registered for this layer.

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## References

[1] S. Mitura, A. Mitura, P. Niedzielski, P. Couvrat, Nanocrystalline diamond coatings, Nanotechnology in Materials Science 10 (1999) 2165-2176.
[2] S. Aisenberg, R. Chabot, Ion-Beam deposition of thin films of diamond-like carbon Journal of Applied Physic 42 (1971) 2953-2956.
[3] H.O. Pierson, Handbook of carbon, graphite, diamond and fullerens, Properties, processing and application, Noyes Publications, New Jersey 1993.
[4] J. Robertson, Diamond-like amorphous carbon, Materials Science and Engineering R 37 (2002) 129-281.
[5] NANODIAM. New technologies for medical applications: studying and production of carbon surfaces allowing for controllable bioactivity, in: S. Mitura, P. Niedzielski, B. Walkowiak (red.), PWN, Warszawa, 2006.

[6] J. Grabarczyk, D. Batory, P Louda, P. Couvrat, I. Kotela, K. Bakowicz–Mitura, Carbon coatings for medical implants, Journal of Achievements in Materials and Manufacturing Engineering 20 (2007) 107-111.

[7] W. Kaczorowski, D. Batory, Carbon and titanium based layers for wood-based materials, Journal of Achievements in Materials and Manufacturing Engineering 27/1 (2008) 187 -190.

[8] A. Erdemir, O.L. Eryilmaz, I.B. Nilufer, G.R. Fenske, Synthesis of superlow-friction carbon films from highly hydrogenated methane plasmas, Surface and Coatings Technology 133-134 (2000) 448-454.

[9] R. Hauert, An overview on the tribological behaviour of diamond-like carbon in technical and medical applications, Tribology International 37 (2004) 991-1003.

[10] Z. Rożek, W. Kaczorowski, D. Lukas, P. Louda, S. Mitura, Potential application of nanofibre textile covered by carbon coatings, Journal of Achievements in Materials and Manufacturing Engineering 27/1 (2008) 35-38.

[11] M. Cłapa, D. Batory, Improving adhesion and wear resistance of carbon coatings using Ti:C gradient layers, Journal of Achievements in Materials and Manufacturing Engineering 20 (2007) 415-418.

[12] C. Donnet, Recent progress on the tribology of doped diamond-like and carbon alloy coatings: a review, Surface and Coatings Technology 100-101 (1998) 180-186.

[13] W.J. Yang, T. Sekino, K.B. Shim, K. Niihara, K.H. Auh, Deposition and microstructure of Ti-containing diamond-like carbon nanocomposite films, Thin Solid Films 473 (2005) 252-258.

[14] D. Batory, T. Balaszczyk, M. Clapa, S. Mitura, Investigation of anti-corrosion parameters of Ti:C gradient layers manufactured In hybrid deposition system, Journal of Materials Science 10 (2008) 3385-3391.