Bulletin of the *Transilvania* University of Braşov • Vol. 8 (57) No. 1 - 2015
Series I: Engineering Sciences

OVERVIEW ON DLC LAYERS USED TO INCREASE THE TRIBOLOGICAL PROPERTIES

D.I. FELDIOREAN[1] **M.H. ŢIEREAN**[1]

Abstract: *Diamond-like carbon (DLC) deposition in thin films has known in the past decades a large development. There is a wide range of specific technologies of the DLC thin films deposition based on PVD (Physical Vapour Deposition) and CVD (Chemical Vapour Deposition) methods. Real processes may be different depending on the desired result. DLC thin coatings have various applications in microelectronics, aeronautics, automotive industry, medical technology, fine mechanics etc. This paper makes a review of the mechanical and tribological properties of DLC coating obtained through different technologies.*

Key words: *Diamond-like carbon (DLC) layer, CVD, PVD, tribology.*

1. Introduction

In order to achieve superior mechanical and tribological characteristics of the parts, heat treatments and thermochemical treatments have been applied to these days and are further applied. Shortcomings of these technologies are: high energy consumption, long process time, dimensional deviations, requiring subsequent finishing operations.

In the past years, amorphous Diamond-like carbon (DLC) coatings have increasingly caused a stir in the area of research and in the industrial practice all over the world. In some cases, they can be regarded as alternatives to the conventional heat treatments and thermochemical treatments procedures. The outstanding tribological properties, the low friction coefficient, high hardness, high corrosion resistance, the very good quality of the surface, as well as its unique feature to protect also the opposite friction surface by developing a transfer film (tribological film) [3], provide the difference between the DLC layers and the other types of coatings with hard layers becoming more attractive in industrial applications.

2. Morphology of DLC Films

Carbon crystallizes in two allotropic forms that are significantly different from one another: diamond and graphite. It also exists as coal with a structure resembling that of the graphite. The carbon atom falls under group IV in the periodic table of elements and has four valence electrons that enable it to establish simple σ type covalent chemical bonds with the neighbouring atoms when *s* type orbitals are interrelated, or *s* type orbitals with *p* type orbitals. The distribution of the 6 electrons in the carbon atom envelope is the following: there are 2 electrons on the

---

[1] Dept. of Materials and Welding Engineering, *Transilvania* University of Braşov.

first layer, which are located on orbital 1s^2, and there are two electrons with opposite spin on the second layer, which are located on orbital 2s^2, the other two electrons with parallel spin being located on orbitals 2*px* and 2*py*. Theoretically, the two electrons placed on orbital 2*p* must provide to the chemical bonds a bivalent feature, but actually, the electrons located on the upper orbitals 2*s* and 2*p* can be distributed on *sp* type hybrid atomic orbitals. The electrons' jumping from *s* orbital to the *sp* level is enabled by means of an engaging energy. Thus, the carbon atom becomes tetravalent and may feature three types of chemical bonds involving *s* type and *p* type orbitals:

a) Hybridisation of *sp* when an *s* type orbital is combined with a *p* type orbital and makes up two *sp* type orbitals with the angle between axes of 180° (Figure 1).

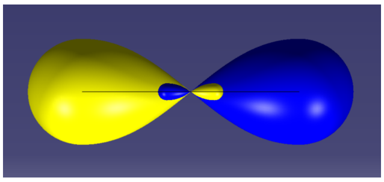

Fig. 1. *Hybridisation of sp*

b) Hybridisation of sp^2 when an *s* orbital is combined with 2 *p* orbitals and makes up three sp^2 orbitals, with the carbon atoms being placed on the peaks of a triangle with the angle between the axes of two orbitals of 120° (Figure 2).

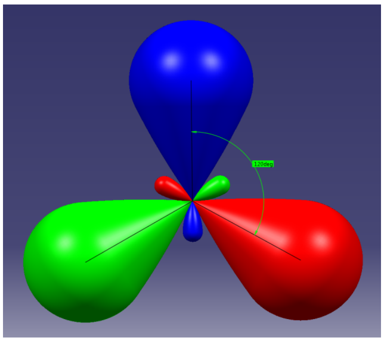

Fig. 2. *Hybridisation of* sp^2

c) Hybridisation of sp^3 when an *s* orbital is combined with 3 *p* orbitals and makes up four sp^3 orbitals, with the carbon atoms being placed on the peaks of a tetrahedron with the angle between the axes of two orbitals of 109°28’ (Figure 3).

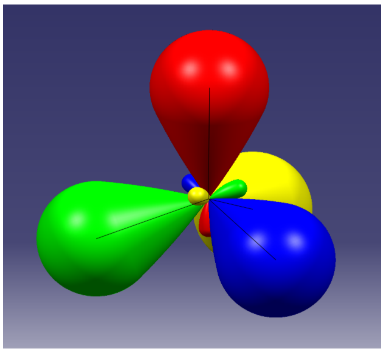

Fig. 3. *Hybridisation of* sp^3

The two forms of carbon crystallization, i.e. graphite and diamond, correspond to a sp^3 type hybridisation for the diamond, namely sp^2 for graphite. Diamond has the atoms arranged in the cubic crystalline lattice and graphite, in the hexagonal crystalline lattice.

The DLC film does not have a crystalline structure but rather an amorphous structure, consisting of cubic and hexagonal disordered alternating layers. For this reason, as there is no separation plan, there is no risk of the DLC layer to fissure. These layers may have different structures and properties based specifically on their construction.

The designation Diamond-like carbon was first used by Aisemberg and Chabot (1971) [1] for the amorphous carbonic materials deposited by ion beam deposition. Amorphous carbon is characterized by the mixture of certain sp^2 type structures with sp^3 type structures. These structures determine the physical and chemical properties of the material.

The DLC layer establishes ionic bonds with the substrate, being generally very adherent. However, the material in the substrate may have a strong influence on these bonds.

The ternary phase diagram (Figure 4) [10] enables the classification of the DLC thin coatings deposited by CVD (chemical vapour deposition) or PVD (physical vapour deposition) methods.

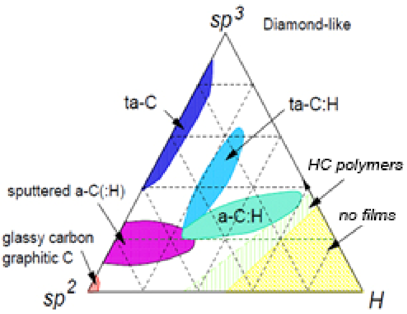

Fig. 4. *The ternary phase diagram depending on* sp^2, sp^3 *bonds and the hydrogen content of the various forms of DLC* [10]

Depending on the structural ratio of sp^2 bonds versus the sp^3 bonds, we encounter a large variety of DLC coatings. DLC films with predominantly sp^3 content are very hard and they have exceptional tribological particularities, resembling very much the diamond. A larger amount of sp^2 bonds results in relatively soft films, with a tribological behaviour resembling that of graphite.

Amorphous carbon may also contain up to 60% hydrogen, in addition to sp, sp^2, sp^3 bonds [4]. The structures of the hydrogenated amorphous carbon (a-C:H) are found in the centre of the ternary diagram. It has already been demonstrated that hydrogen in the composition of DLC layers plays an important role for the tribological properties thereof.

3. DLC Thin Layers Coating Technologies

The methods used to deposit thin films (max. 10 µm thickness) of material on a substrate, are PVD (Physical Vapour Deposition) and CVD (Chemical Vapour Deposition). Large ranges of specific technologies based on these two methods are used to produce the multifunctional thin films.

One of the applications of these thin coating technologies is “Diamond-like carbon” (DLC). This is the generic designation approved for hard carbon coatings. Properties of this type of coating are comparable with those of the natural diamond in terms of hardness, friction resistance, corrosion resistance etc.

Real deposition processes may be different: ion plating activated reactive evaporation, cathodic arc deposition, bias sputter deposition, ion-beam assisted deposition, dual ion-beam sputtering. If process parameters are changed, films with different structures and properties may be produced depending on the desired result.

Procedures to obtain thin coatings by chemical vapour deposition (CVD) may be with thermal activation, with plasma activation and with laser activation.

Subsequently have been developed PVD coating technologies. Physical vapour deposition procedures may be: thermal evaporation, sputtering, ion plating. The PVD technology is currently used at an industrial scale with the main purpose of depositing tribological films. Applications are diverse, as follows: cutters, tools for plastic deformation, bearings, parts in the automotive industry etc.

Unlike the CVD procedure, the PVD deposition of thin films has several considerable advantages: the source material is pure, the process temperature is noticeably lower, there is no risk of substrate oxidation, the range of materials that may be deposited is wider, the process is perfectly reproducible, low environmental impact, layer thickness may be more rigorously controlled, no effect of rounded edges.

Based on the process parameters changing, these thin layers may be: a-C (hydrogen-free DLC), a-C:H (hydrogenated DLC), ta-C (tetrahedral amorphous carbon), ta-C:H (hydrogenated tetrahedral amorphous carbon) [10]. Additional elements can be incorporated on the C-based layers, for example: metals Me-C:H (metal containing DLC layers), Si-DLC (silicon containing DLC layers).

The significant advantages of the DLC coating are: wear resistance, even at operation without lubricants, resistance to abrasion and tribological oxidation. The coating allows for surface pressures which would normally lead instantly to gripping and cold welding. Losses by friction are minimised. The good resistance to corrosion protects the substrate (part) from destruction.

4. Mechanical and Tribological Properties of Thin DLC Films

Gao, F., et al. [6], conducting research on the friction coefficient and the behaviour of hydrogenated DLC films to wear, using a tungsten carbide ball with the diameter of 6.35×10^{-3} m with an applied load of 0.98 N, under conditions of ultra-high vacuum and under partial pressure of water vapours, oxygen, nitrogen and hydrogen, have demonstrated that the presence of hydrogen in the DLC layer leads to a constant reduction of the friction coefficient, which was initially 0.15, to smaller values of 0.03 after about 30 sliding passes. Increasing the number of slides, the friction coefficient has increased to values close to 0.15 and this increase coincides with the decrease of the hydrogen content in the DLC film. Thus, hydrogen is confirmed to be the key element of the very good behaviour of the hydrogenated DLC films to friction.

Dalibon, E., et al. [2] have analysed the behaviour of DLC films (a:C-H-Si), deposited by the PACVD method on heat treated (hardened and tempered) martensitic stainless steels X20Cr13 (AISI 420). Before the DLC coating, part of the samples were subject to nitriding treatment (N+DLC), and part of them were subject to nitriding treatment and oxidation (N+O+DLC). The thickness of the deposited DLC film, which was determined by a scanning electron microscopy (SEM), ranges between 15 and 20 µm (Figure 5).

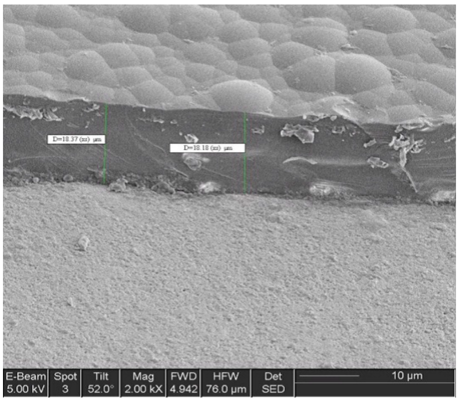

Fig. 5. *SEM image of the DLC film* [2]

During the sliding wear tests by loads of 4.42 N and 12 N, no significant difference has been observed between the DLC samples, i.e. N+DLC and N+O+DLC, but it was noted that the depth of the wear traces was much smaller than in untreated samples (Figure 6).

Hardness reached the value of 1500 $HV_{0.05}$, and the subsequent deposited film falls under the category of soft DLC films due to the high content of H_2.

Gangopadhyay, A., et al. [5] studied the potential of the DLC film to reduce friction by using the dynamic test stand of motor valves. The DLC film was deposited on a bucket tappet, made of 16MnCr5 steel and the period of the test was 1 hour. A decrease of the friction coefficient to the approximate value of 0.08 was noted in the absence of the lubricant.

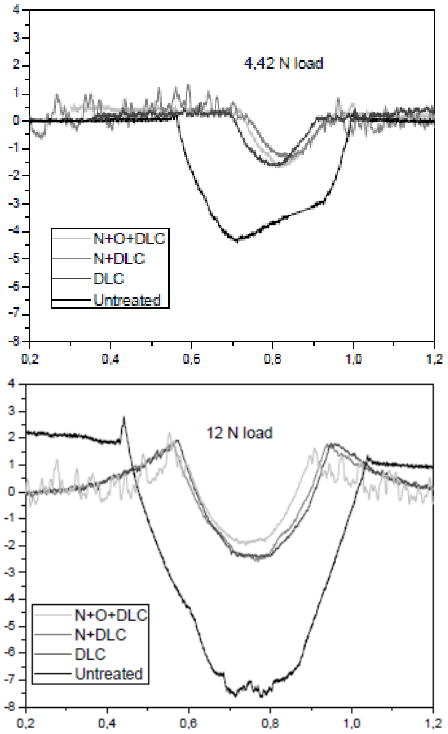

Fig. 6. *Profiles of wear traces for different loadings* [2]

Paskvale, S., et al. [9] assessed the tribological properties of double layers Cr/DLC deposited by ionic plating on bearings steel 100Cr6 with an anode layer source (ALS) using two different process gases, acetylene C_2H_2 and N_2, and compared them to those of double films TiAlN/DLC obtained by magnetron sputtering on the tool steel X153CrMoV12. It was noted that TiAlN/DLC coatings have a better behaviour only in terms of adherence. The Cr/DLC coatings performed better in the other properties: roughness, hardness, friction coefficient.

Yi, J.W., et al. [14] reviewed the tribological behaviour of DLC alternating films in various conditions of humidity. Alternating Si-DLC films were deposited (designated as sets) with DLC films. The tribological ball-on-disk tests were conducted in conditions of humidity: dry, 50% and 90% relative humidity. In dry air, the friction coefficient was very low (<0.05) and increased significantly for all samples in conditions of air humidity of 50% and 85%. From the tribological viewpoint, behaviour has improved by deposition of alternating layers Si-DLC/DLC, but was not influenced significantly by the number thereof.

Morita, T., et al. [8] showed on their study that the fatigue strength of an austenitic stainless steel JIS SUS316 (W 1.4401) can be improved with 53% through a hybrid surface treatment consisting of plasma carburizing (PC) as a pre-treatment and DLC (diamond-like carbon) coating (PC/DLC). Plasma carburizing increased the fatigue strength with 37% by forming a hardened layer with high compressive residual stress on the steel surface.

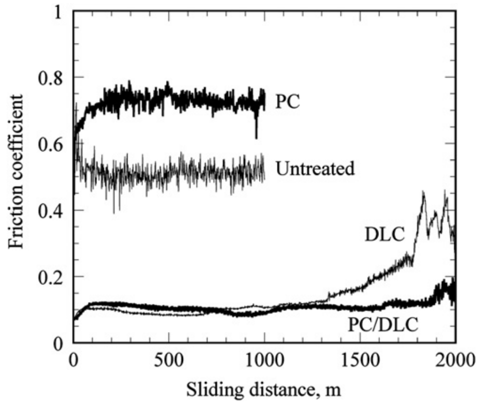

Fig. 7. *Relationship between the sliding distance and the friction coefficient* [8]

The high compressive residual stress was maintained and developed after DLC coating. On the other hand, they demonstrated that the hardened layer, formed by plasma carburizing, was effective also in improving the durability of the DLC layer. After a sliding distance of 1300 m, the friction coefficient of the DLC material started increasing while that of the PC/DLC material was stably maintained until 1900 m (Figure 7). Because of the relatively low process temperatures, the substrate mechanical properties were unaffected by plasma carburizing and DLC coating.

Yakabe, F., et al. [13] have made a comparative study between DLC films and TiN films deposited on JIS-SCr420 (20Cr4) steel. Mainly this steel is used in the automotive industry for transmission gears. Before de coating process the specimens were carburized, quenched, and tempered (CQT). DLC films were deposited by Plasma Chemical Vapour Deposition (PCVD), and TiN films were deposited by Plasma Vapour Deposition (PVD). They showed that resistance under Hertzian contact stress of 3.0 GPa was strongly improved by the DLC coating. The pitting resistance was strongly improved by the DLC coating compared to that of the uncoated specimen (CQT) and prolonged the life by 100 times. Pitting resistance of the TiN-coated specimen was slightly higher than or comparable to the JIS-SCr420 (CQT) specimen without coating. Difference between DLC and TiN coating could be attributed to the process temperature of the TiN coating (450 °C for 70 min) and DLC coating (230 °C for 150 min), compared to that of the CQT layer tempering (180 °C for 120 min). Due to this temperature difference, the surface strength of the substrate was smaller on the TiN coated samples.

Singh, R.K., et al. [11] prove that the final coating roughness of DLC coatings depends on the surface roughness of the substrate. Four samples from polished stainless steel 304 (W1.4301) with different relative mean surface roughness (Ra), S-12, S-35, S-78 and S-835 have been selected as substrate material in this study. The relative average roughness (Ra) of the substrates was measured using a profilometer (Mitutoya, Japan) equipped with a 5 μm tipped diamond indenter. It was shown on the samples with low relative roughness S-12, S-35 and S-78 that final coating roughness after DLC has increased relative to substrate roughness. On the other hand, in the case of S-835 sample, the deposited coating has smaller roughness than his substrate (Figure 8).

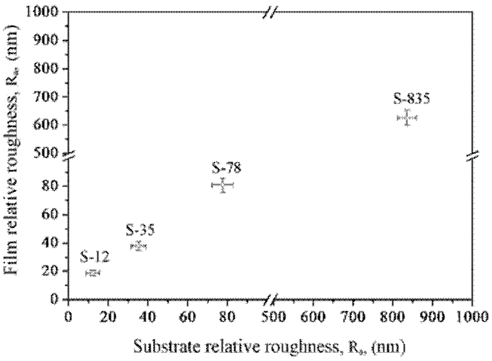

Fig. 8. *Variation of surface relative roughness (R_a) of coatings with their respective substrate relative roughness (R_a)* [11]

This phenomenon is explained by the fact that at the beginning, the coating relative roughness increases due to the faster deposition rate on the top of the peaks than on the valleys of the rough surfaces. After that, as the DLC layer thickness becomes thicker, surface roughness start to decrease. The layer grows laterally on the valleys and tends to fill them up, leading to a decrease in the final relative surface roughness. So that, in the case of S-835, the deposited coating has less roughness than that of its respective substrate.

Waseem, B., et al. [12] studied the wear and adhesion behaviour of DLC coatings on different substrates. Using the PVD technique, DLC coatings were deposited on medium carbon steel (0.403% C, 1.388% Mn, 0.312% Si), mild steel (0.193% C, 0.664% Mn, 0.258% Si), die steel (2.358% C, 0.563% Mn, 0.643% Si), and hard steel (0.951% C, 0.280% Mn, 0.233% Si). The adhesion of the DLC coating on the substrates was assessed by micro scratch testing using loads of 20 and 25 N; length of all scratches was 3mm. Analysing the optical micrographs of the scratches they have come to the conclusion that DLC layer has better adhesion to the harder substrate than to the soft one.

Mobaraka, RK, et al. [7] researched the tribological performance of (a-C:H) DLC coating lubricated with Canola oil. The study was focused on piston ring, the most friction prone part of engine. Balls and discs both made from 44 ^{0}C (W1.4125) stainless steel were used as samples for the experiment. From this type of steel is generally made the piston ring. The discs and balls were coated with a single layer of amorphous a-C:H DLC layer without doping elements. Cr-based adhesion promoting interlayer was deposited for this research. Samples of discs and balls were left uncoated for the tribological tests. Tests were conducted with the ball-on-flat reciprocating machine in the presence of Canola oil as lubricant. 1 GPa initial Hertzian contact pressure was applied, the stroke was 1 mm and the oscillating frequency 50 Hz, providing a 0.1 m/s means contact velocity. Experimental results demonstrated that the lowest value of the friction coefficient was submitted by, a-C:H/a-C:H, around 0.07 with Canola oil, followed by steel/a-C:H, around 0.08 and steel/steel, around 0.14. The friction coefficient of a-C:H coated material was approximately 42-50% lower than that of the uncoated material. Wear loss of the a-C:H/a-C:H combination, was approximately 9% higher than that for the steel/a-C:H combination. Steel/ a-C:H combination with Canola oil lubrication, presented a wear reduction more than 22% as compared to that of steel/steel. In this case, the significant improvement of the friction behaviour during the tribological tests, observed in SEM images, was due to the amorphous DLC transfer film from the coated surface to the steel surface. The friction coefficient and the wear loss were significantly reduced by the a-C:H DLC coating with Canola oil.

5. Conclusions

Compared to other types of hard thin films, DLC coatings are very diverse. Therefore they may be found in diverse applications: metallurgy, microelectronics, aeronautics, automotive industry, medical technology, fine mechanics, and packages for drugs or foodstuffs, with protective, hardening, tribological, reflective and decorative purposes.

Modern technologies of coating with DLC layers, not more than 10 microns thickness, enable to obtain products with high quality features: reliability, high performances in service, reducing environmental impact and resources saving. The properties of these films may vary depending on the CVD or PVD deposition technology, depending on the ratio of sp^2, sp^3 bonds in the layer, depending on the hydrogen content etc.

The studies and experimental research conducted so far have outlined the higher mechanical and tribological characteristics of the thin DLC films: high hardness rate, wear resistance in operation with or without lubricant, fatigue resistance, resistance to abrasion and tribological oxidation, reduced friction coefficient. In order to achieve optimal tribological results using these coating technologies, it is recommended to understand mechanism of the coating processes and this knowledge are very important because the deposition method have a strong influence on the tribological properties of DLC layers and the substrate.

Studies conducted so far shown also that the substrate has a substantial influence on the adherence, the friction coefficient, roughness and hardness of the DLC layers.

It still remains interesting to assess the influence that these layers have on the mechanical properties of the heat-treated steel substrate.

References

1. Aisenberg, S., Chabot, R.: *Ion-Beam Deposition of Thin Films of Diamondlike Carbon.* In: J. Appl. Phys. **42** (1971), p. 2953.
2. Dalibon, E.L., Brühl, S.P., Heim, D.: *Tribological behavior of DLC Films Deposited On Nitrided and Post-Oxidized Stainless Steel by PACVD.* In: Journal of Physics: Conference Series **370** (2012), 012029.
3. Erdemir, A., Donnet, C.: *Tribology of Diamond-Like Carbon Films: Recent Progress and Future Prospects.* In: Journal of Physics D: Applied Physics **39** (2006), R311.
4. Ferrari, A.C., Robertson, J.: *Interpretation of Raman Spectra of Disordered and Amorphous Carbon.* In: Physical Review B **61** (2000) No. 20, p. 14095-14107.
5. Gangopadhyay, A., Sinha, K., et al.: *Friction, Wear, and Surface Film Formation Characteristics of Diamond-Like Carbon Thin Coating in Valvetrain Application.* In: Tribology Transactions **54** (2010) Issue 1, p. 104-114.
6. Gao, F., Erdemir, A., Tysoe, W.T.: *The Tribological Properties of Low-Friction Hydrogenated Diamond-Like Carbon Measured in Ultrahigh Vacuum.* In: Tribology Letters **20** (2005) No. 3-4, p. 221-227.
7. Mobaraka, H.M., Chowdhurya, M.: *Tribological Performance of Hydrogenated Amorphous Carbon (a-C: H) DLC Coating when Lubricated with Biodegradable Vegetal Canola Oil.* In: Tribology in Industry **36** (2014) No. 2, p. 163-171.
8. Morita, T., Hirano, Y., Asakura, K., et al.: Effects of Plasma Carburizing and DLC Coating on Friction-Wear Characteristics, Mechanical Properties and Fatigue Strength of Stainless Steel. In: Materials Science & Engineering **A 558** (2012), p. 349-355.
9. Paskvale, S., Kahn, M., Čekada, M., et al.: *Tribological Properties of Diamond-Like Carbon Coatings Prepared by Anode Layer Source and Magnetron Sputtering.* In: Surface and Coatings Technology **205** (2011) Supplement 2, p. S99-S102.
10. Robertson, J.: *Deposition and Properties of Diamond-Like Carbon.* In: Material Research Society Symposium Proceedings **555** (1998), p. 291.
11. Singh, R.K., Xie, Z.H., Bendavid, A., et al.: *Effect of Substrate Roughness on the Contact Damage of DLC Coatings.* In: Diamond & Related Materials **17** (2008), p. 975-979.
12. Waseem, B., Alam, S., Irfan, M., et al.: *Optimization and Characterization of Adhesion Properties of DLC Coatings on Different Substrates.* In: Materials Science and Engineering **60** (2014), p. 012054.
13. Yakabe, F., Jinbo, Y., Kumagai, M., et al.: *Excellent Durability of DLC Film on Carburized Steel (JISSCr420) Under a Stress of 3.0 GPa.* In: Journal of Physics: Conference Series **100** (2008), p. 082049.
14. Yi, J.W., Kim, J.K., Moon, M.W., et al.: *Tribological Performance of Alternating-Layered Si-DLC/DLC Films under Humid Conditions.* In: Tribology Letters **34** (2009) Issue 3, p. 223-228.