Thin Solid Films 590 (2015) 60–63

Contents lists available at ScienceDirect

Thin Solid Films

journal homepage: www.elsevier.com/locate/tsf

Diamond-like carbon films deposited on three-dimensional shape substrate model by liquid electrochemical technique

Y.Y. He [a], G.F. Zhang [b], Y. Zhao [a], D.D. Liu [a], Y. Cong [a,*], V. Buck [c]

[a] Institute of Nano-photonics, School of Physics and Materials Engineering, Dalian Nationalities University, 116600 Dalian, China
[b] School of Materials Science and Engineering, Dalian University of Technology, 116024, Dalian China
[c] Thin Film Technology Group, Faculty of Physics, University Duisburg-Essen and CeNIDE, 47057 Duisburg, Germany

ARTICLE INFO

Article history:
Received 28 January 2015
Received in revised form 26 May 2015
Accepted 17 July 2015
Available online 21 July 2015

Keywords:
DLC films
Liquid electrochemical technique
Three-dimensional shape substrate model
Raman spectroscopy

ABSTRACT

Diamond-like carbon (DLC) films were deposited on three-dimensional (3D) shape substrate model by electrolysis of 2-propanol solution at low temperature (60 °C). This 3D shape model was composed of a horizontally aligned stainless steel wafer and vertically aligned stainless steel rods. Morphology and microstructure of the films were analyzed by scanning electron microscopy (SEM), atomic force microscopy (AFM) and Raman spectroscopy, respectively. The results suggested there were only differences in film uniformity and thickness for two kinds of samples. The hydrogenated amorphous carbon films deposited on horizontally aligned substrate were smooth and homogeneous. And the film thickness of DLC films gained on the vertical substrates decreased along vertical direction. It is believed that bubble formation could enhance nucleation on the wetted capillary area. This experiment shows that deposition of DLC films by liquid phase deposition on 3D shape conductive substrates is possible.

1. Introduction

DLC films have widespread applications in the fields of optical windows, magnetic storage disks, car parts, biomedical coatings and micro-electromechanical systems (MEM) because of their excellent physical and chemical properties, such as high mechanical hardness, low friction coefficient, wear-resistance and chemical inertness [1–5]. The practical applications usually request DLC films to be deposited on the substrates with complex surface or structure. Electrolysis of organic solution under atmosphere at low temperature (<100 °C) is a new method besides conventional vapor techniques. It becomes possible to deposit DLC films on 3D shape substrates because electrochemical reaction owns the advantage of employing complex substrates, such as spherical or cylindrical substrates. However, the publications about DLC films liquid phase deposition mainly concentrate on either one side or double sides of wafer substrates [6–9]. The research works about complex substrates deposition using liquid method is rarely reported. In this paper, we divided complex substrates into horizontal part and vertical part, investigating DLC films deposition on this simple 3D shape substrate model by liquid electrochemical technique.

2. Experimental details

The deposition system used in this work was self designed [10]. The substrates were placed in two ways. Fig. 1 is a schematic diagram displaying the relative position of anode and substrates. The horizontally aligned substrate is a stainless steel wafer ($13 \times 12 \times 0.5$ mm^3), facing to the graphite anode with a distance of 6 mm. The vertically aligned substrates were stainless steel rods in diameter of 3 mm and parallel to the anode with a space of 24.5 mm. Prior to deposition, the substrates were ultrasonically cleaned in 2-propanol and deionized water for 10 min, respectively. Analytically pure 2-propanol was chosen as electrolyte owing to its high dielectric constant, small viscosity and methyl bonding to the polar group, which is identified as ideal candidate reactant for liquid deposition of DLC films [11]. The deposition process lasted for 2 h under the applied potential of 1000 V (frequency 10 kHz, duty cycle 50%). Water cooling to the wall of a quartz reactor was used to control the solution temperature.

Dektak 6 M Stylus Surface Profilometer was used to measure film thickness. Surface morphology of the films deposited was observed by scanning electron microscopy (SEM) using Quanta 400 FEG and Hitachi S-4800. Atomic force microscopy (AFM) measurement was carried out with the help of Veeco 3100 using tapping mode. Microstructure of the DLC films was investigated using a micro-Raman system Jobin Yvon with a laser source wavelength of 514.532 nm.

* Corresponding author.
E-mail address: congyan@ciomp.ac.cn (Y. Cong).

http://dx.doi.org/10.1016/j.tsf.2015.07.031
0040-6090/

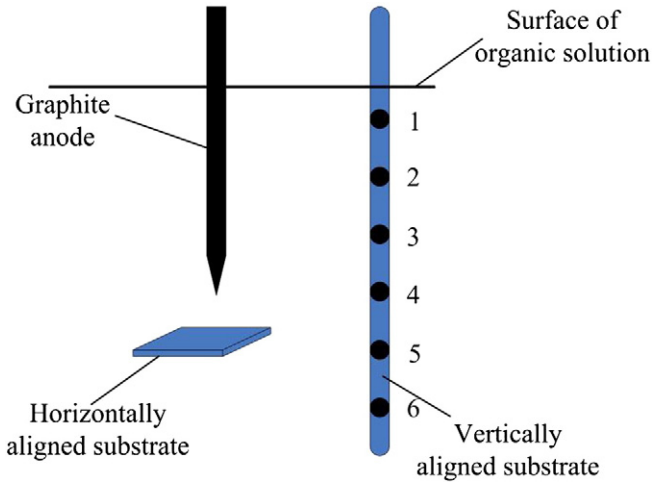

Fig. 1. Schematic diagram of 3D shape substrate in the liquid electrochemical deposition system.

3. Results

1) Horizontally aligned substrate
The horizontally aligned stainless steel substrate is covered with a gray film after deposition. The film thickness is 1300 ± 50 nm and the average film growth rate is approximately 650 nm/h. The film is continuous with uniform morphology under the observation of SEM. A typical image is given in Fig. 2a. In addition, AFM is applied to obtain more morphology information, as shown in Fig. 2b. The film has a homogeneous morphology, free of defects. The RMS (root mean square) roughness is 12.4 nm analyzed by software V531r1. From the morphology characterization it can be clearly indicated that a smooth film could be deposited on the horizontally aligned substrate.

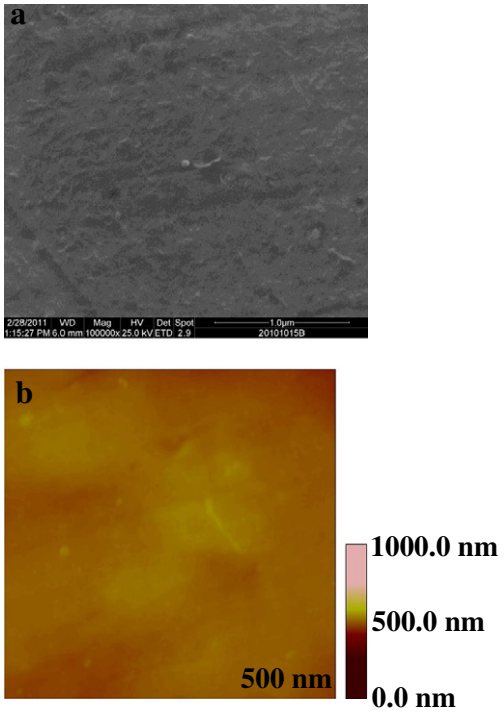

Fig. 2. SEM image (a) and AFM image (b) of films deposited on horizontally aligned substrate.

Raman spectroscopy is the most widely used technique to investigate the state of carbon [3]. Diamond has one sharp peak at 1332 cm^{-1}, and graphite has only one peak at 1580 cm^{-1}, called G peak. The disorder or fine graphite crystals have another peak at lower wave numbers around 1355 cm^{-1}, called D peak [12]. Raman spectra taken from different local areas across the films on the horizontally aligned substrate are quite similar. A typical Raman spectrum is shown in Fig. 3. On one hand, two broad peaks around 1335 cm^{-1} and 1595 cm^{-1} are related to D peak and G peak, respectively, indicating the existence of sp^2 amorphous carbon phases [13–15]. Raman scattering is more sensitive to sp^2 carbon phase than to sp^3 carbon phase, and the intensity of the sp^2 carbon phase is much larger than sp^3 carbon phase in the spectra excited by 514.5 nm [13]. Thus, the Raman spectra of the electrolysis carbon films mainly show graphite-like features in most cases, this phenomenon has also been observed by other researchers [7–9]. On the other hand, the slope of the photoluminescence background in visible Raman spectra can be used to estimate the H content [16]. According to the simple quantitative formula for the hydrogen content given by Casiragh [16], there is at least 20 atm.% bonded hydrogen in the film. This hydrogen must come from the liquid organic solution which contains plenty of hydrogen. Liquid electrochemical deposition of carbon films is a very complicated process, nevertheless, the film growth process contains several key steps. Certain chemical bonds are broken under high applied potential; organic molecules are polarized into positively charged and negatively charged groups; the positively charged groups tend to move towards cathode/substrate; the activated groups turn to carbon phase which will grow into continuous carbon film and other products through electrochemical reaction. Although part of hydrogen may form gas or water gets rid of the film, however, there is still a large amount of hydrogen bonded with carbon atoms, becoming bonded hydrogen. As a result, hydrogenated amorphous carbon films are deposited on the horizontal substrate.

2) Vertically aligned substrate
Meanwhile, the vertically aligned stainless steel rods were also covered with coatings. However, non-uniform film along vertical direction was easily visually observed. Color of the films nearby liquid level to the immersed part gradually changes from dark to light, and then almost bare at the bottom. In order to characterize the deposits on vertical substrate, six marks (No.1–No.6) in every 5 mm were chosen along the depth direction, as shown in Fig. 1. Fig. 4a, b and c provide morphology information at the marks of No.1, 3 and 5, respectively. The film performance changes a lot by comparison of SEM images. Continuous film with a rough surface is shown in Fig. 4a. The film with holes and slight scratches in Fig. 4b is not continuous. More deep scratches as can be seen in Fig. 4c come

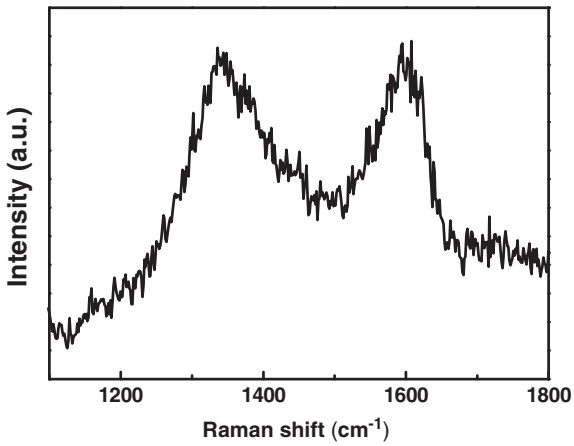

Fig. 3. A typical Raman spectrum (b) of films deposited on horizontally aligned substrate.

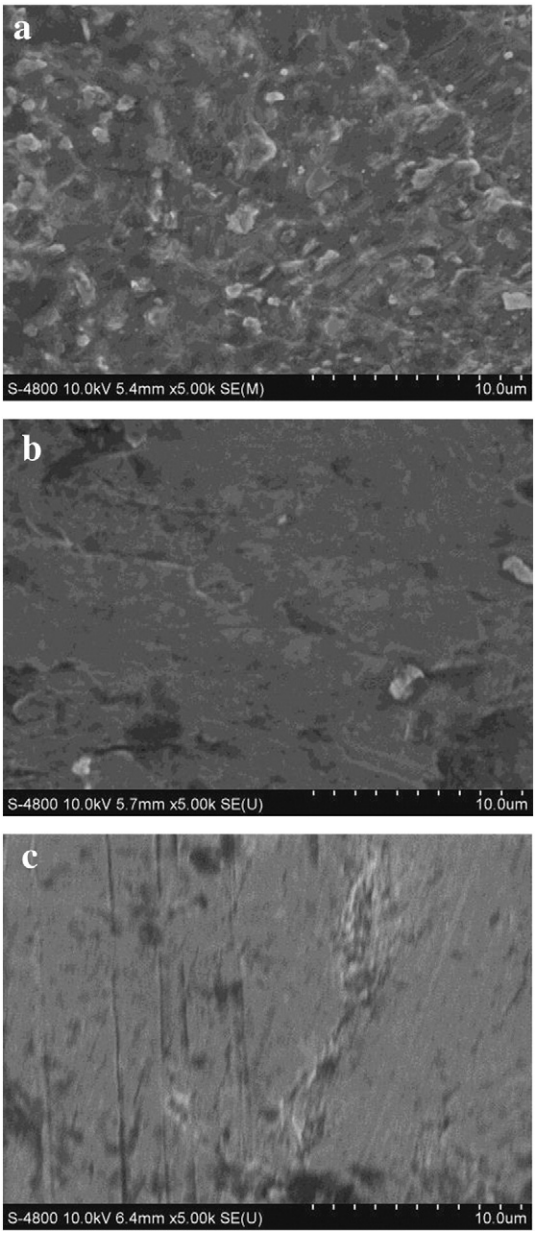

Fig. 4. SEM images on the vertically aligned stainless steel substrate, *a*, *b* and *c* are corresponding to mark No. 1, 3 and 5, respectively.

from the substrate. The film along vertical direction gets thinner from liquid level to the immersed part. Tonsin et al. [17] discovered similar phenomenon in their deposition system and discussed the near-wall boiling effect which can enhance nuclei near the liquid level, and decrease deposition to the immersed substrate. Bubbles and their attachment to the substrate surface were also observed during our deposition, so the film non-uniformity along vertical substrate should be caused by the same reason.

Raman spectroscopy was used to investigate the film microstructure. In Fig. 5, all the Raman spectra from No.1 to No.5 have two broad peaks which are corresponding to D peak and G peak, respectively, indicating DLC structure was gained on the vertically aligned stainless steel substrate. It is experimentally confirmed that DLC films could be deposited on the vertically aligned rod besides the horizontal wafer by electrolysis of organic solution. In addition, quite similar spectra were obtained at the same cross section on the vertically aligned rod, and thence uniform DLC films were deposited at the same depth inside the organic solution.

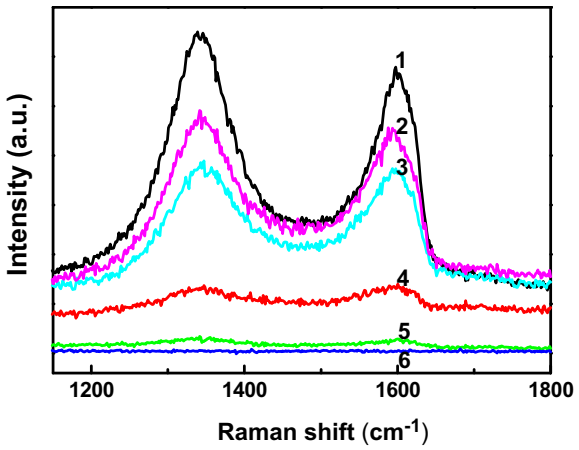

Fig. 5. Raman spectra of films deposited on different places of vertically aligned substrate, the numbers are corresponding to the marks in Fig. 1 on the vertically aligned substrate.

Carefully looking into the Raman spectra, the peak intensity reaches a maximum at No.1, and decreases along the vertical rod going into the solution. Neither D peak nor G peak is observed in the Raman spectrum of No.6. It is suggested that no significant DLC films signals are capable to be detected under the same detecting condition. The variation trend of peak intensity is consistent with the film thickness visual observation and morphology characterization described above. Thus, the change of peak intensity in Raman spectroscopy must be correlated to non-uniform film thickness distribution.

The region from 1150 cm^{-1} to 1800 cm^{-1} in all the Raman spectra were carefully Lorenz fitted on a linear background. The I(D)/I(G) ratio of each spectrum approximately is in the region of 0.98–1.16, and the G band position is in the range of 1585–1595 cm^{-1}. The I(D)/I(G) intensity ratio and the G band position obtained by Raman measurements are correlated with the sp^3/sp^2 ratio. A lower intensity ration is generally interpreted as corresponding to a higher sp^3 content [16,18].

Ferrari summarized the G position and I(D)/I(G) ratio vs sp^3 fraction for a-C:H from his deposition and other co-workers', as shown in Fig. 6a. The sp^3 fraction data were either directly measured or theoretically calculated [12]. In order to give a quantitative analysis of sp^3 content in the DLC films deposited, these data are exponential fitted into continuous "G peak position-sp^3 content" and "I(D)/I(G) ratio-sp^3 content" curves in Fig. 6b. The G peak position and I(D)/I(G) ratio of the DLC films at various positions are located on the curves for sp^3 fraction calculation, respectively. It is worth to point out that all the sp^3 content of four DLC films drawn from G position are about 20% lower than those drawn from I(D)/I(G) ratio. Poukhovoi [19] compared the calculation of sp^3 content in a:C–H films using both Raman and FTIR. The results from "I(D)/I(G) ratio-sp^3 content" and FTIR matched very well with each other. However, the sp^3 content calculated from G position is always lower, 10–20% depending on the deposition parameters. So the bonded sp^3 content gained from the I(D)/I(G) ratio is credible, in the range of 37–40%. From the point of calculated sp^3 content, the microstructure of DLC films along vertical substrate are quite similar at different depth. In addition, the calculated sp^3 content of DLC films deposited on the horizontal substrate is about 38%. The calculated results suggest that typical DLC films with similar sp^3 content were simultaneously deposited on the horizontally and vertically aligned stainless steel substrates in our deposition system.

4. Conclusions

Horizontally aligned stainless steel wafer and vertically aligned stainless steel rods were simultaneously imported into DLC film liquid

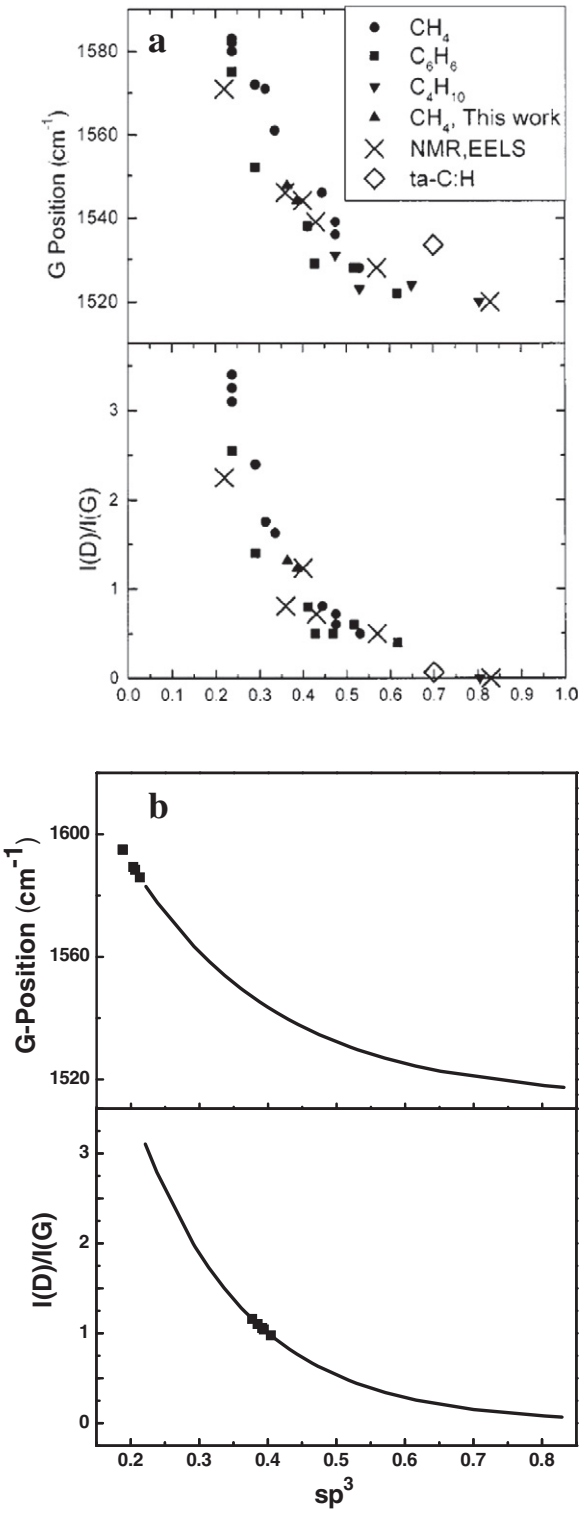

Fig. 6. a: G position and I(D)/I(G) ratio vs sp^3 fraction for a-C:H summarized by Ferrari [12]; b: exponential fitted "G peak position-sp^3 content" and "I(D)/I(G) ratio-sp^3 content" curves from the data in Fig. 6a, the points indicate the films deposited in this work.

electrochemical deposition system to make a simple model of 3D shape substrates. DLC films with quite similar sp^3 content were deposited on both substrates by electrolysis of analytically pure 2-propanol at low temperature (60 °C). Films on the horizontally aligned substrate appeared homogeneous in morphology and microstructure. The film distribution on the vertically aligned substrate was not ideal uniform due to boiling effect. The work of improving films uniformity and investigating films property should be carried out next step. Nevertheless, the attempt in this experiment has confirmed that liquid electrochemical technique is feasible to carry out DLC films deposition on conductive 3D shape substrates or complex surface which will be favored for industrial application of DLC films.

Acknowledgment

This project is supported by National Natural Science Foundation of China (Grant No. 11204024, 11204025, 21203179 and 61205178), Educational Committee Foundation of Liaoning Province (L2012475) and Technology Foundation for Selected Overseas Chinese Scholar (Ministry of Human Resources and Social Security of the People's Republic of China), the Fundamental Research Funds for the Central Universities (Grant No. DC201502080406 and DC201502080302) and Scientific Research Foundation for Doctor of Liaoning Province (Grant No. 20121073).

References

[1] A.A. Voevodin, M.S. Donley, J.S. Zabinski, Pulsed laser deposition of diamond-like carbon wear protective coatings: a review, Surf. Coat. Technol. 92 (1997) 42–49.
[2] Y. Lifshitz, Diamond-like carbon-present status, Diam. Relat. Mater. 8 (1999) 1659–1676.
[3] J. Robertson, Diamond-like amorphous carbon, Mater. Sci. Eng. R 37 (2002) 129–281.
[4] N. Paik, Field emission characteristics of diamond-like carbon (DLC) films prepared using a magnetron sputter-type negative ion source (MSNIS), Diam. Relat. Mater. 14 (2005) 1556–1561.
[5] H.B. Guo, Y. Qi, X.D. Li, Predicting the hydrogen pressure to achieve ultralow friction at diamond and diamondlike carbon surfaces from first principles, Appl. Phys. Lett. 92 (2008) 241921–2419213.
[6] B. Pandeya, P.P. Pala, S. Berab, S.K. Rayb, A.K. Kara, Effect of nickel incorporation on microstructural and optical properties of electrodeposited diamond like carbon (DLC) thin films, Appl. Surf. Sci. 261 (2012) 789–799.
[7] Y. Li, G.F. Zhang, X.D. Hou, D.W. Deng, Synthesis and tribological properties of diamond-like carbon films by electrochemical anode deposition, Appl. Surf. Sci. 258 (2012) 6527–6530.
[8] F. Niu, J.Y. Ma, L.G. Yu, P.Y. Zhang, Electrochemical deposition and characterization of diamond-like carbon films doped with surface-capped silica nanoparticles, Surf. Coat. Technol. 221 (2013) 77–87.
[9] R.S. Li, M. Zhou, X.J. Pan, Z.X. Zhang, B.A. Lu, T. Wang, E.Q. Xie, Simultaneous deposition of diamondlike carbon films on both surfaces of aluminum substrate by electrochemical technique, J. Appl. Phys. 105 (2009) 066107.
[10] Y.Y. He, Deposition of diamond-like carbon films by liquid electrochemical technique. Physics, University Duisburg Essen, Duisburg, 2011.
[11] H.S. Zhu, J.T. Jiu, Q. Fu, H. Wang, C.B. Cao, Aroused problems in the deposition of diamond-like carbon films by using the liquid phase electrodeposition technique, J. Mater. Sci. 38 (2003) 141–145.
[12] A.C. Ferrari, J. Robertson, Interpretation of Raman spectra of disordered and amorphous carbon, Phys. Rev. B 61 (2000) 14095–14107.
[13] R.J. Nemanich, J.T. Glass, G. Lucovsky, R.E. Shroder, Raman scattering characterization of carbon bonding in diamond and diamondlike thin films, J. Vac. Sci. Technol. A 6 (1988) 1783–1787.
[14] D.S. Knight, W.B. White, Characterization of diamond films by Raman spectroscopy, J. Mater. Res. 4 (1989) 385–393.
[15] W.A. Yarbrough, R. Messier, Current issues and problems in the chemical vapor deposition of diamond, Science 247 (1990) 688–696.
[16] C. Casiraghi, A.C. Ferrari, J. Robertson, Raman spectroscopy of hydrogenated amorphous carbons, Phys. Rev. B 72 (2005) 085401.
[17] M.C. Tosin, A.C. Peterlevitz, G.I. Surdutovich, V. Baranauskas, Deposition of diamond and diamond-like carbon nuclei by electrolysis of alcohol solutions, Appl. Surf. Sci. 144–145 (1999) 260–264.
[18] G. Irmer, A. Dorner-Reisel, Micro-Raman studies on DLC coatings, Adv. Eng. Mater. 7 (2005) 694–705.
[19] A. Poukhovoi, Abscheidung von amorphen wasserstoffhaltigen Kohlenstoffschichten mittels neuartiger hybrider RP-Plasma Quelle und deren spektroskopische Charakterisierung. Physics, University Duisburg Essen, Duisburg, 2011..