ZAŁĄCZNIK NR 3

SUMMARY OF PROFESSIONAL ACCOMPLISHMENTS

IN ENGLISH

DR SŁAWOMIR KULESZA

1. **Name and surname:** Sławomir Kulesza
2. **Diplomas and degrees held – with name, place and year of their acquisition and the title of doctoral dissertation:**

2003 Ph.D. in physics
Faculty of Physics, Astronomy and Informatics
Nicolaus Copernicus University in Toruń
Doctoral dissertation: *Structure and electrical properties of thin diamond films*

1998 M.Sc. in physics
Faculty of Physics and Astronomy,
Nicolaus Copernicus University in Toruń
Thesis: *Deposition and measurement of selected properties of polycrystalline diamond films – pure and boron-doped*

3. **Information on the previous employment in scientific and research institutions**

2007-present	**assistant professor** Faculty of Mathematics and Computer Science University of Warmia and Mazury in Olsztyn
2013-present	**physics teacher** Zespół Szkół nr 3 im. Jana III Sobieskiego w Szczytnie
2013	**postdoctoral position** Department of Semiconductor and Carbon Physics Faculty of Physics, Astronomy and Informatics Nicolaus Copernicus University in Toruń
2012	**postdoctoral position** Laboratory of Molecular Materials and Nanosystems Eindhoven University of Technology, Netherlands
2009-2012	**physics teacher** III Liceum Ogólnokształcące im. Mikołaja Kopernika w Olsztynie
2005	**postdoctoral position** Laboratory of Molecular Materials and Nanosystems Eindhoven University of Technology, Netherlands
2004	**postdoctoral position** Institute for Materials Research, Hasselt University, Belgium
2003-2007	**assistant professor** Faculty of Physics, Astronomy and Informatics Nicolaus Copernicus University in Toruń
2002-2003	**assistant lecturer** Faculty of Physics, Astronomy and Informatics Nicolaus Copernicus University in Toruń
1998-2002	**doctoral student** Faculty of Physics, Astronomy and Informatics Nicolaus Copernicus University in Toruń

4. Indication of the achievement resulting from Article 16(2) of the Act on Academic Degrees and Scientific Titles and Degrees and Titles in Arts of 14 March 2003 (Journal of Laws [Dz. U.] of 2016 item 882 as amended in J of L [Dz. U.] of 2016 item 1311)

As the academic achievement indicated in accordance with the aforementioned Act, I selected a single-subject cycle of publications (in chronological order) under the shared title:

The research on the process of production and characteristics of spatial configuration of surfaces of thin diamond films and related structures

[D1] A 40 pts., IF 2.135, cited by (with/without self-citations): 12/11

S. Kulesza, J. K. Patyk, M. Daenen, O. A. Williams, W. Van de Putte, J. Fransaer, K. Haenen, M. Nesládek, "Structural investigations of protective polycrystalline diamond coatings on titanium substrates", *Surface and Coatings Technology*, 201 (2006) 203-207, DOI: 10.1016/j.surfcoat.2005.11.078

My contribution to the work included: planning measurements, performing diamond deposition process (co-operation M. Daenen), performing measurements: XRD, Raman, and SEM, processing of experimental data, preliminary analysis and conclusions, writing first draft of the manuscript, making corrections to the text suggested by the reviewers, leading scientific discussions, correspondence with the editorial board. My percentage contribution to the work is approximately 70 %.

[D2] A 35 pts., IF 1.318, cited by (with/without self-citations): 2/2

S. Kulesza, J. Szatkowski, E. Lulińska, M. Kozanecki, "Diamond-like carbon layers grown by electrochemical method – structural study", *Energy Conversion and Management*, 49 (2008) 2487-2489, DOI: 10.1016/j.enconman.2008.02.028

My contribution to the work included: planning measurements, performing diamond deposition process (co-operation E. Lulińska), processing of experimental data, preliminary analysis and conclusions, writing the manuscript, making corrections to the text suggested by the reviewers, leading scientific discussions, correspondence with the editorial board. My percentage contribution to the work is approximately 55 %.

[D3] A 30 pts., IF 1.884, cited by (with/without self-citations): 3/1

S. Kulesza, "Study of the moderate-temperature growth process of optical quality synthetic diamond films on quartz substrates", *Thin Solid Films*, 516 (2008) 4915-4920, DOI: 10.1016/j.tsf.2007.09.027

[D4] A 15 pts., IF 0.451, cited by (with/without self-citations): 1/1

J. Szatkowski, **S. Kulesza**, A. Korcala, M. Rębarz, M. Wojdyła, G. Trykowski, W. Bała, F. Rozploch, "Structural and photoluminescence study of diamond-like layers grown by electrochemical method", *Optoelectronics and Advanced Materials – Rapid Communications*, 2 (2008) 46-49
My contribution to the work included: planning measurements, performing diamond deposition process, writing the manuscript, making corrections to the text suggested by the reviewers. My percentage contribution to the work is approximately 30 %.

[D5] A 40 pts., IF 2.135, cited by (with/without self-citations): 1/1

S. Kulesza, "Infrared transmittance model for pyrometric monitoring of surface quality of thin diamond films", *Surface Coatings and Technology*, 206 (2012) 3554-3558, DOI: 10.1016/j.surfcoat.2012.02.047

[D6] A 15 pts., IF 0.541, cited by (with/without self-citations): 0/0

S. Kulesza, "The infrared transmittance model of a quartz/diamond/vacuum trilayer for in-situ monitoring of the deposition process", *Optica Applicata*, 3/42 (2012) 533-543, DOI: 10.5277/oa120309

[D7] A 35 pts., IF 2.538, cited by (with/without self-citations): 24/13

S. Kulesza, M. Bramowicz, "A comparative study of correlation methods for determination of fractal parameters in surface characterisation", *Applied Surface Science*, 293 (2014) 196-201, DOI: 10.1016/j.apsusc.2013.12.132
My contribution to the work included: main idea of the research, formulating research hypothesis, planning measurements, performing diamond deposition process, writing the part of the manuscript, making corrections to the text suggested by the reviewers, correspondence with the editorial board. My percentage contribution to the work is approximately 60 %.

[D8] A 30 pts., IF 2.331, cited by (with/without self-citations): 0/0

Ş. Ţălu, M. Bramowicz, **S. Kulesza**, A. Ghaderi, S. Solaymani, M. F. Kenari, M. Ghoranneviss, "Fractal Features and Surface Micromorphology of Diamond Nano-Crystals", *Journal of Microscopy*, (2016), DOI: 10.1111/jmi.12422
My contribution to the work included: performing statistical and fractal analyses of the AFM and SEM data, drawing conclusions, writing appropriate part of the manuscript, making corrections to the text suggested by the reviewers. My percentage contribution to the work is approximately 25 %.

The detailed list of published studies is included in Appendix 4, Appendix 5 contains the papers constituting the scientific achievements under consideration, while Appendix 6 contains the relevant declarations of the co-authors.
The cycle constituting the reviewed achievement comprises eight papers having an Impact Factor (IF) listed in the Journal Citation Reports (JCR) and in the A List of the Polish Ministry of Science and Higher Education. Three of them are articles with 100% own contribution and the remaining five are co-authored with own contribution at the level between 70% and 25%. The mean own contribution in the entire cycle of publications amounts to 67.5%, with the total number of points equalling 240 and the summary IF index of 13.333, while taking into account own contribution, respectively: 165.25 and 9.020.

4.1. Overview

Diamond is a two-faceted material: on the one hand, it has an enormous utilitarian potential, due to the combination of multiple extreme properties, and on the other – its properties are largely untapped, which begs the question regarding the reasons for such a dissonance. And there are many more doubts. Why has diamond not replaced silicon in microelectronics yet? Is it worth it to develop methods of metastable diamond synthesis when silicon technology has been perfected nearly to its full capacity? Should we look for applications of diamond-related materials, i.e. carbons of lower quality with structure close to diamond (e.g. diamond-like carbon (DLC) and tetrahedral amorphous carbon (ta-C)) – or develop the technology of nanostructured materials?

The cycle of studies invoked as my main scientific achievement in the habilitation process is the summary of almost 20 years which I have spent studying diamond and (to a lesser degree) other carbon materials. At first, my studies focused on the development of production processes under thermodynamic metastability conditions, then they were complemented with research regarding the shaping of selected properties of these structures by modifications in their surface condition. My contribution to the development of the entire academic discipline is twofold. Firstly, it is expressed by the numerous modifications of the synthesis processes of diamond thin films which significantly pushed forward the limits of possible growth of diamond on the phase diagram of carbon. Secondly, I have developed advanced methods of studying the geometrical structure of the surface layer which determines multiple significant properties of the entire crystal, e.g. tribological, electrical, optical, etc. The studies of surface properties of various materials attract huge attention. Despite numerous references, there is still a shortage of studies investigating the effect of the production process on the final parameters of the carbon material, determined by the specific surface geometry. This was my chief motivation to engage in the research resulting in the presented cycle of publications.

The use of carbon structures as an active component in modern technological appliances opens a great new area of applications. For many years, there have been attempts to introduce diamond as an alternative to silicon in high power and high frequency electronic systems, particularly – working at high temperatures [1]. Currently, however, we begin to understand that the similarities in the shape of the crystalline networks of these materials are not equivalent to the compatibility in their production technologies and therefore – does not translate to the number of applications, mainly due to the overestimated expectations regarding the performance of diamond devices and their productions costs – disproportionately high compared to the benefits. Because of this, there are significantly higher hopes regarding elements with active surface layer and nanostructured systems, based on which we can create electrochemical, dosimetric and mechatronic instruments of the next generation. In my opinion, they may meet the expectations regarding the speed of operation, efficiency and compactness from devices used in various areas of modern science and technology: from optoelectronics, through medicine, to renewable energy.

4.2. Scientific objective

The cycle of related publications presented for review puts into practice the chief scientific objective which was the **research of the growth processes of diamond and related carbon materials in the aspect of forming their specific surface geometry, determining the key physical properties of these structures.**

One property the studied carbons had in common was the fact that in normal conditions, they form a thermodynamically metastable phase and due to this fact, their production process is always a resultant of the kinetics of multiple accompanying reactions, such as: concurrent codeposition of carbon foreign phases, surface diffusion of defects and contaminants, closing of unsaturated bonds on the growth surface, etc. They all have a significant impact on the morphology of the surface of the emerging layer.

The subject of the studies was the determination of the relationship between the conditions for metastable growth of diamond or diamond-like materials and the morphology/properties of the emerging surface.

The implementation of the chief research objective was possible due to the achievement of the following specific targets:

- production of the thin films of diamond and related materials with various degrees of continuity and order of the crystalline structure,
- multi-aspect description of the geometric structure of the surface layer,
- linking the parameters of the deposition process with the geometric structure of the surface layer,
- linking the surface morphology of the surface layer with the selected material properties.

4.3. Results achieved

The most important academic achievement of the presented cycle is linking the specific stages of the process of growth of thin layers of diamond and diamond-like materials with characteristic changes of their surface morphology. It includes the following original research achievements, constituting significant development in the discussed academic discipline:

(1) research in the process of growth and the kinetics of the reaction of synthesis of layers with dominating sp^3 hybridisation which led to a significant decrease of the temperature of the process occurring in the gaseous phase and successful crystallisation of the diamond from the liquid phase in near-normal conditions,

(2) development of advanced methods of studying surface geometry for scientific and engineering purposes which enabled monitoring the formation of typical properties of layer surface morphology and relating them to the growth process parameters.

4.3.1. Production of diamond thin film structures and related structures

The studies of the growth process of layers with dominating sp^3 hybridisation listed among the most original scientific achievements are presented in papers: [D1], [D2], [D3], [D4] and [D8]. Study [D1] demonstrates the results obtained for polycrystalline layers on titanium substrates and study [D3] on quartz bars deposited using the microwave plasma method (MP-CVD). Papers [D2] and [D4] present unique results of experiments with the synthesis of diamond and diamond-like carbon nanostructures from the liquid phase, while the [D8] study – the results of experiments with the synthesis of thin nanocrystalline layers from the gaseous phase (hot filament method).

The most popular method of synthesising polycrystalline diamond layers is chemical vapor deposition (CVD) under a subatmospheric pressure proposed in early 1980s by Spitsyn [2]. This method takes into account the observation that the free enthalpy of carbon in graphite lattice is approx. 3 kJ/mol lower than in diamond lattice, which results in the fact that diamond heated to high temperatures without oxygen supply undergoes spontaneous graphitisation. On the other hand, this process does not occur in normal conditions, which means that both carbon phases must be separated by a high activation barrier. The key to success is, therefore, the production of free carbon atoms in the gaseous phase. These atoms can than sublimate in the diamond structure with a non-zero probability. Since graphite is the thermodynamically stable phase in the range of the applied pressures and temperatures, diamond is created somewhat randomly, as a structure that is metastable in these conditions [3]. This statement has multiple consequences which significantly affect the quality of the produced structures:

- concurrent growth of various structures resulting in the formation of visibly granular layers,
- low growth rate of the process, caused by the need to suppress the growth of foreign phases,
- formation of mechanical stress between the substrate and the layer, resulting from the high temperature required to create carbon vapours,
- unwanted chemical reactions between the substrate material and the activated constituents of the process mixture (e.g. deposition of carbides),
- incorporation of contaminants from the constituents of the process mixture.

In my earlier studies [4][6], I deposited thin diamond layers on silicon substrates using the hot filament method (HF-CVD), in which the decomposition of saturated hydrocarbons (propane, butane) occurs due to the high temperature produced by a tungsten wire heated to approx. 2200°C. Carbon media are a small fraction of the volume of the gas mixture (no more than several per cent) which is mostly composed of molecular hydrogen. The dissociated solution is a highly chemically active agent, etching the emerging carbon structures. One condition which is very favourable to the diamond growth process is the 50 times faster etching of the graphite phase compared to the diamond phase which significantly increases the thermodynamic metastability of diamond in the growth environment. Unfortunately, this method does not completely suppress the formation of non-diamond phases, so that the growing structures is polycrystalline with mosaic grains of various sizes and orientations.

In study [D3], I presented the result of research on producing thin layers of polycrystalline diamond on quartz substrates in low temperatures. This topic had significant application consequences due to the use of such structures for the construction of, for example: filters with surface acoustic wave (SAW), micro-electromechanical systems (MEMS), high power microwave instruments, protective coatings against UV and X radiation, UV detectors, electronic devices manufactured in the Diamond-on-Insulator technology and others. The lack of an intermediate layer of natural carbide enabled obtaining structures with high optical transmittance and low electrical conductivity. On the other hand, when carrying out the study, numerous details of the deposition process have been left unsolved, which translated to a low quality of the structures produced at the time. The more significant problems include:

- mismatch of the diamond and quartz thermal expansion coefficients, and consequently – high mechanical tension, impairing the adhesion of the layer to the substrate,
- trace self-nucleation which implies low crystal growth speed,
- high layer roughness,
- creation of structures with sp^3 hybridisation but short order range (ta-C, DLC).

I consider the meaningful development of the field of diamond growth on quartz resulting from the modification of the substrate preparation process and modification of the deposition process parameter to be my own and original scientific achievement, constituting a significant development in an academic discipline. In the study, I applied the microwave plasma (MP-CVD) method; however, before that, I decided to seed the quartz substrates mechanically for several hours, using an ultrasonic vibrator and diamond powder with the grain size of 250 nm. I considered this method to be a good alternative to implanting titanium ions [7] which leaves a thin intermediate TiC layer during the growth process, preventing any optical applications of the resulting structures, as well as to the application of diamond paste [8], which leaves chemical contaminants on the substrate. AFM measurements proved that the roughness of the substrate before seeding did not exceed 0.5 nm on a field with the scan length of 50 μm. The roughness increased slightly after seeding to 2 nm. At the same time, the comparison of the speed of growth and roughness of the layers deposited in identical conditions on a seeded and unseeded substrate show a clear benefit of the former. It can be suspected that during the mechanical interaction of diamond seeds with the quartz substrate, two processes occurred simultaneously: breaking down large diamond seeds from powder to smaller fragments and driving them into the substrate, together with the abrasion of the top layer of quartz increasing the density of surface defects which are also the potential nucleation centres for the growing crystal. Seeding resulted in the estimated nucleation density of $2 \cdot 10^8$ cm^{-2}, which proved to be a value sufficiently high for the creation of a closed layer of polycrystalline diamond with high optical quality.

The process of growth of thin layers was carried out in significantly lower substrate temperature, from the usual approx. 900-1000°C [9] to less than 500°C, as this was at the time considered to be favourable to the growth of diamond-like or even graphitised layers. The results of X-ray diffraction measurements (XRD) and Raman scattering proved the high quality of the growing structures beyond any doubt. When comparing the half-widths and heights of the 1332 cm^{-1} Raman line presented in studies [D3], [7] and [8] and applying them to the estimation of the composition of non-diamond phases in the structure in accordance with the formula proposed by Vorlicek et al. [10], the outcome was that they do not exceed 2%, which should be considered an outstanding result at the time.

My next own and original scientific achievement constituting a significant development to the academic discipline was the research of the process of incubation and closing of the layer based on the changes in the apparent temperature of the substrate measured using a dual wavelength pyrometer, also presented in study [D3]. The result showed the incubation period to last approx. 25 min. at 475°C and to be significantly shorter – 2 min. – at 800°C. It should be noted that these values are overestimated as they apply to the period of growth of a layer with the thickness of 151 nm, resulting from the occurrence of the first interference maximum in the record of the pyrometric measurement of substrate temperatures. Growth speed for the same extreme temperatures increased from approx. 0.5 μm/h to 3.6 μm/h (Figure 1), which should be considered a great accomplishment compared to the speeds of approx. 0.7 μm/h obtained with identical configurations for silicon-based processes, even at a slightly higher temperature (950°C) and under higher pressure (approx. 94 Torr) [9]. The observed difference is probably a result of the production of a thin layer of the SiC carbide on the surface of the silicon substrate in the beginning of the process which extends the incubation time for the diamond layer. We also must not forget that the growth speeds estimated in this manner are mean speeds after the entire process and so are, by definition, underestimated, while temporary speeds (as also illustrated in the [D3] study) increase asymptotically in the course of the process from zero to a certain stationary value. It should also be noted that the resulting growth speeds are at least twice as high as the results of other studies, e.g. [11], [12] (with approx. 1000-fold lower density of nucleation of the diamond layer). The Arrhenius plot (Figure 1) proves that the process activation energy amounted to approx. 320 meV which is a higher value compared to a similar process using silicon (200 meV [9]) and can indicate significantly different kinetics of the chemical reactions on the growth surface, particularly in relation to the value of the thermal activation barrier for the processes of activation of the diamond nucleation centres on the growth surface. On the other hand, this value is significantly lower than in the case of the hot filament process, estimated in my previous works at approx. 900-1300 meV [4].

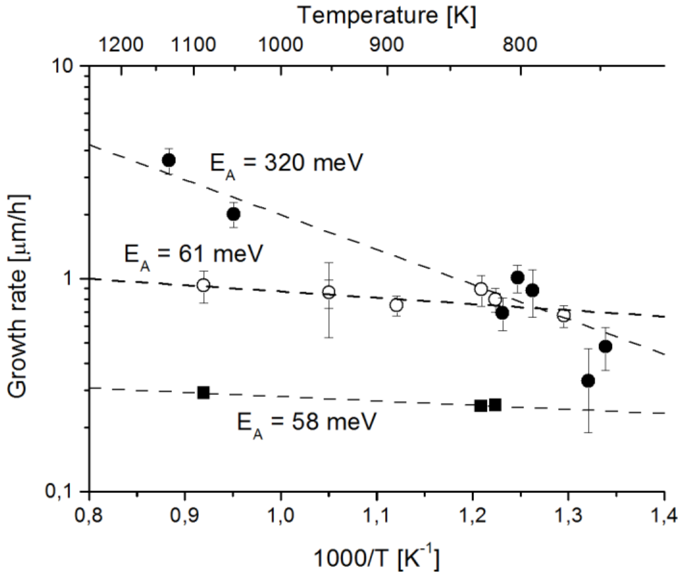

Figure 1. Arrhenius plots of the growth rate of thin layers of polycrystalline diamond as a function of reciprocal absolute substrate temperature: undoped and seeded layer (closed dots), boron-doped and seeded layer (open dots), boron-doped and unseeded layer (closed squares). The activation energies of the process amounted to, respectively: 320, 61 and 58 meV [D3].

Apart from the studies of the growth process kinetics, the study [D3] also includes an analysis of the effect of acceptor doping on the kinetics of the growth process. The source of boron dopants was trimethylborane (TMB) with the formula of $(CH_3)_3B$, of which the content per volume in the process mixture did not exceed 50 ppm. I noted several interesting and previously undiscovered relationships. Firstly, doping significantly reduced the growth speed compared to undoped layers deposited in identical conditions, but only in higher temperatures of over 800°C, increasing the duration of incubation and layer closing. In lower temperatures, between approx. 475 and approx. 630°C, the growth speeds on seeded substrates for doped and undoped layers were similar. Secondly, the growth speed of doped layers on seeded substrates proved to be a decreasing function of the concentration of the doping in the process mixture while the numerical fitting revealed a linear decrease tendency at the level of approx. 5 nm/h – this effect has never been observed before. This is surprising as the decomposition of TMB molecules resulted in the formation of additional CH_3 methyl radicals in the plasma (commonly believed to be diamond growth precursors) which should increase the growth rate. The experiment, however, has a contrary result. The explanation of this inconsistency is possible when we assume changes in the plasma chemistry, leading to a decrease rather than increase of the concentrations of methyl radicals, e.g. by their further decomposition with separation of hydrogen atoms or dimerization into ethane molecules. Thirdly, doping significantly reduces the growth process activation energy to approx. 60 meV, regardless of substrate seeding. The decrease of the thermal activation barrier means that the process enters into saturation, meaning that all the available growth precursors are activated. This seems to confirm the previous suggestion that doping reduces the content of methyl radicals in the plasma. Experimental data (Figure 1) shows a 3 times higher growth rate of doped layer on seeded substrates compared to unseeded substrates.

Study [D1] presents the results of research into the growth process of diamond thin films on titanium substrates. The purpose of this study was the optimisation of the process in the scope of protective coatings with the highest possible electrical conductivity and also resistant to strong oxidisers in order to use them for constructing electrodes for electrochemical sewage treatment. Three major obstacles had to be overcome during the experiments:

- weak adhesion of diamond to titanium due to a large difference of thermal expansion coefficients,
- substrate deformation in increased temperatures typical for the growth process, related to the release of residual stress generated in titanium during production using thermal and mechanical processing, including casting and cold rolling,
- diffusion of light elements (mostly carbon and hydrogen) from the growth area to the crystal, leading to the deposition of chemical contaminants: carbides and hydrides.

Ongoing modifications of the growth process were supposed to be a way to overcome these challenges. Even though the fundamental process parameters were similar to those in study [D3], the substrate preparation process was significantly modified. The own and original research achievement, constituting significant development in the academic discipline presented in this study is the comparison of the growth effects on:

- reference substrates, in the basic state resulting from previous thermal and mechanical processing during fabrication of the material,
- substrates subject to additional sandblasting,
- substrates with a thin layer of clean titanium with the thickness of approx. 1 μm applied using the magnetron sputtering method,
- substrates subjected to a two-stage deposition process, with the first stage of 15 min. consisting of strong substrate carburisation using a mixture with increased hydrocarbon content (15%) and the next part of the process carried out using a standard concentration mixture (5%).

The quality of the resulting layers was tested with Raman spectroscopy and X-ray diffraction. The analysis of the Raman spectra of unprocessed samples revealed the presence of sharp, distinct lines 1332 cm^{-1} typical for diamond, together with 1490 cm^{-1} and 1600 cm^{-1} lines characteristic for the structures of, respectively: curved graphene sheets (open carbon nanocages) and graphite. The Raman spectra of layers deposited in different temperatures also showed signs of line 1140 cm^{-1} – its presence is related to nanocrystalline diamond or C-H bonds on the borders of diamond grains. This will be discussed further in the paragraph. Phase purity calculations show that the optimum substrate temperature from this point of view is in the range 700-750°C, for which the content of non-diamond impurities in the structure does not exceed 12%. Increasing the substrate temperature causes the process to significantly increase its growth rate – from 1.4 to 7.6 μm/h with the temperature increase from 630 to 800°C. This, however, is accompanied by a reduction in the contents of the diamond phase, while in lower temperatures the content of diamond-like carbon increases at the benefit of lower contents of nanodiamond and nanocage structures. What is just as interesting, in the entire tested range of temperatures, the content of the sp^2 fraction remained nearly identical, while the expected effect was its rapid growth outside the optimum temperature range. This can be explained by blocking the formation of growth precursors for this phase (cyclic radicals) in the gaseous phase – a process unrelated to substrate temperature.

X-ray diffraction spectra are also interesting. The comparison of the spectra of the unprocessed and sandblasted sample revealed a three-layer structure: α-Ti/TiC/diamond, with similar intensities of individual lines – this warrants a conclusion that, outside of mechanical destruction of the substrate surface, sandblasting had no real effect on the growth process.

Another new information presented in study [D1] was the high variation in the growth processes on substrates with different oxidised layer thickness. The natural corrosion resistance of titanium is a result of the formation of the TiO_2 passivation layer on its surface, which is also known as a material intensifying diamond nucleation on those substrates which are not forming stable carbides [14]. After coating the previously unprocessed substrate with an additional layer of titanium with a thickness of approx. 1 µm, it turned out that despite the identical growth conditions, the growth of diamond on the part not coated with an additional layer of Ti progressed without major challenges, while on the section coated with fresh titanium, there was hardly any growth of carbon structures. The effect was described for the very first time and was highly surprising, since the previous assumption was that a strong enough carburisation of the substrate is the only necessary condition for growth initiation and that carburisation occurs always when the process gas contains carbon media. However, the result was a lack not only of the growth of carbon structures but also of the carburisation of the substrate coated with a fresh titanium layer – the surface remained bright metallic and shiny. It seems that the effect can be explained by the presence of highly chemically active atomic hydrogen in the gas mixture – immediately stripping the thin layer of fresh passivation but unable to remove the much thicker layer of oxide from the masked surface in the same amount of time. According to this observation, joining carbon to pure titanium would be much more difficult that to titanium oxide – this is an explanation for the noticed discrepancies. Study [D1] does not, however, pay attention to another possibility – emerging in the situation when the substrate is not made with pure metal, but rather its alloy. Its surface, in that case, would be a host to different chemical reactions, leading to the formation of a different intermediate layer. Then, the effect of the alloy composition of the substrate should be treated as catalytic influence, highly accelerating the formation of the intermediate carbide layer.

Study [D1] also contains an analysis of the effect of strong carburisation in the early growth phase on the quality of layers. For this purpose, the Raman spectra of two layers were compared: (1) layer deposited with the constant hydrocarbon content in the process mixture at the level of 5% and (2) layer deposited with the hydrocarbon content initially increased to 15% for 15 min. of the process and then 5% for the remaining deposition time. The purpose of increased carburisation was supposed to be forming a significantly thicker intermediate TiC layer for improved diamond adhesion. When comparing the spectra of the two layers, the situation with the 1332 cm^{-1} line seems interesting. In the case of the sample deposited at constant hydrocarbon concentration, the line is sharp and strong, however in the case of the initially carburised sample, the intensity decreases significantly and a clear split into two lines is visible: the actual diamond phase line (1332 cm^{-1}) and the 1340 cm^{-1} line with still uncertain origin. The latter is, on the one hand, always attributed to the discontinuities of the diamond structure, i.e. the presence of a disordered sp^3 phase[15] and on the other – breathing modes in small aromatic clusters present in the highly disordered sp^3 phase [16]. Apart from them, the presented spectra also show a broad 1330 line and weak 1140 and 1450 cm^{-1} lines. The first of those can be related to the presence of a disordered (defective and deformed) sp^3 phase, but the origins of the remaining two are not quite that simple – some studies attribute them to the presence of nanocrystalline diamond [17] and others – to the presence of C-H bonds at the edges of seeds [16]. In light of the results presented in study [D1], the origins of lines 1140 and 1450 cm^{-1} should rather be related to the presence of C-H bonds in seed borders, due to the increasing sp^3 phase contents signalled by increased intensity of the 1580 cm^{-1} line – with the decrease of the polycrystalline sp^3 phase contents, it is reasonable to expect a similar decrease in the contents of the nanocrystalline phase with the same hybridisation.

SEM images confirm the usefulness of the diamond layers grown on titanium substrates. They prove that the diamond layers adhere strictly to the substrate and are not subject to delamination, as is often reported in other studies. These images also prove that during the growth, the substrate with an applied layer is deformed, probably due to the difference of thermal expansion coefficients of both structures or the residual stress created in substrates during prior mechanical processing. In some applications, it may be a significant drawback, limiting the usefulness of this type of structures.

The experiments and measurements described above confirm the notion that CVD methods in the shape presented above exhausted their development potential in terms of significant improvements in the quality of the produced poly- and monocrystalline layers. Two clear directions for further research could be observed when carrying out the presented studies:

- development of entirely new methods of synthesis of diamond/diamond-like structures,
- application of CVD methods to the production of nanocrystalline diamond.

Studies [D2] and [D4] present the results of research into the first of the aforementioned directions – i.e. production (in design) diamond structures using a method of electrolysis of mixtures and solutions of liquid organic hydrocarbons. The first attempts in the field were made over 10 years earlier [18], but further work was quickly abandoned due to underwhelming results. The following circumstances made me carry out the research:

- low deposition temperature prevents the carburisation of the substrate and the formation of an intermediate carbide layer (pertains to, for example, silicon and titanium),
- low deposition temperature reduces the tension between the substrate and the deposited layer resulting from the difference in thermal expansion coefficients of both materials,
- lack of strongly aggressive reactants (atomic hydrogen),
- simple construction of the reaction chamber (compared to CVD methods),
- strong development of the surfaces of the produced structures with multiple application possibilities (carbon condensers, molecular sieves and adsorbents, etc.)

Of course, this method also required overcoming certain difficulties. Let us remember that diamond growth in CVD methods was possible due to the generation of free diamond growth precursors (e.g. methyl radicals) in direct proximity to the substrate. By analogy, in order to see growth of diamond structures from liquid, it was decided to select water solutions of ethanol with different concentrations. The original research hypothesis was the assumption that the electrolyte will be dissociated with the release of methyl radicals. Since the key issue was the breakdown of the C-C bond in the ethanol molecule, I tried to achieve this by using a catalyst – a platinum wire connected to a graphite electrode used as an anode and removed from the cathode – a monocrystalline silicon plate. Between the electrodes, I applied direct current from a high voltage source, additionally heating up the electrolyte. It had previously been shown that ethanol decomposition with the release of methyl radicals is the favoured reaction at around 700°C [19] – I therefore expected the catalyst to lower the temperature significantly.

The quality of the layers described in study [D2] was verified using scanning microscopy (SEM) and (micro-)Raman spectroscopy. The resulting layers are mostly black in colour which suggests a high content of the sp^2 phase. As the concentration of ethanol grows in the mixture, the structure morphology changed from continuous layers with fine DLC blooms with the diameter of no more than 10 μm, using sponge-like structures with highly developed surfaces, single microcrystallites of different shapes (rhomboidal, tetragonal, trigonal) with sharp edges to mixed morphology, consisting of layer with discontinuities, covered by irregular blooms and microcrystallites in the discontinuity areas.

Raman spectra confirmed the structural heterogeneity of the produced layers. Two wide lines are observed, typical for small cohesion areas for Raman scattering: 1355 and 1585 cm^{-1}, which were identified as layers of ta-C or DLC with mixed sp^2/sp^3 structure. The spectrum of the layer deposited at 10% ethanol concentration warrants the assumption that we have the amorphous carbon in this situation. In the case of a layer deposited at 66% alcohol concentration, the spectrum is taken from a single microcrystallite. Both the aforementioned lines here prove to be the narrowest and strongest amongst all the tested samples – this indicates the best structural properties. In addition, in this case we also see a weak 1450 cm^{-1} line which – as said before – can be indicative of the presence of nanocrystalline diamond or C-H bonds on seed borders. On the other hand, the 1140 cm^{-1} line, accompanying the 1450 cm^{-1} line in polycrystalline diamond layers, is lacking This is a strong suggestion of the presence of diamond nanocrystallites in the tested depositions – this was later verified in other experiments. This was the first ever reported successful attempt of synthesizing nanocrystalline diamond from the liquid phase. Then, the layer deposited at the highest ethanol concentration (90%) was identified as a typical DLC structure with high content of tetrahedral hybridisation carbon but with a short lattice continuity range. In the order category, this still is a higher quality structure compared to the amorphous carbon obtained with the lowest ethanol concentration (10%).

Study [D4], in turn, contains a detailed analysis of the structures forming at different points of a silicon substrate during an identical electrolytic process with the use of pure ethanol. The main difference comparing to the previously described experiment was the fact that due to the flow of the current and intense boiling of the electrolyte, a foam appeared on the air-electrolyte-substrate border – the deposition conditions in the foam were drastically different compared to the liquid itself. For this reason, the resulting structure was more diverse due to the hybridisation and order of its carbon material. It was also found that the deposited layer does not adhere completely to the substrate and even cracks in some places. Cracking – which had not been realised before – only appeared after drying the sample. We can, therefore, assume that alcohol molecules saturate the material, acting as a stabiliser and increasing its flexibility in a broad spectrum of deformations. After drying, the material becomes brittle, which requires the development of a conditioning method before further application.

The observations made using SEM and AFM proved that the structures forming in the ethanol foam area have the most interesting properties. The resulting layers are similar to a grainy sponge with a coarse and well-developed surface. Single grains of the sponge have irregular shapes and sizes not larger than 10 μm – they are composed of smaller crystallites with sharp edges and flat walls, with sizes below 100 nm. The latter were clearly identified as diamond nanocrystallites. What is interesting is the fact that on the surface of the substrate entirely immersed in the electrolyte, only DLC structures are formed, which is consistent with previous results regarding the deposition in electrolytes with various ethanol concentrations.

In one of the few studies on the topic published in this period, Tosin et al. [20] performed a similar experiment, using classic methanol (however, without the platinum catalyst). They attributed their results to "near-wall electrolyte boiling" effects. This phenomenon supposedly involves the formation of methanol bubbles which inhibit the diffusion of growth precursors, suppressing the crystalline lattice development process, i.e. the layer would grow slower in the immersed section and quicker above electrolyte level. In light if the results of [D4] this interpretation is not quite convincing. First of all, the molecules of the electrolyte passing into the gaseous phase during intense near-wall boiling have a rather high thermal energy, which they partly lose during ascension and adiabatic expansion, so they are less agitated when leaving the liquid. Secondly, their intensive movement towards the surface disturbs the liquid additionally and introduces locally turbulent flow streams, focusing the flow energy. In the third place, in the areas of the turbulent flow streams, conditions conducive to cavitation can form, causing the simultaneous implosion of gas bubbles and formation of ultrasound impact waves which should raise the substrate energy even more and favour their decomposition with the release of growth precursors below liquid level. Finally, the gas bubbles reaching the surface release their contents to the atmosphere, which should decrease the concentration of growth precursors in the area of contact with the air. On the other hand, we see the opposite phenomenon in the experiment – the most effective increase occurs in the foam area, at the border of the phases, due to which – in my opinion – the effect of the atmosphere should be taken into account, rather than just the boiling of the liquid. Therefore – the ethanol foam is an important element of the growth environment – it blocks diffusion and holds the precursors close to the substrate surface. In accordance with the second suggestion, another prerequisite for the growth of nanocrystalline diamond is free oxygen (absent from the liquid volume) which moves the thermodynamic stability towards structures with sp^3 hybridisation, similarly to what happens in CVD processes using the process mixtures with the addition of this gas as an etching agent.

The Raman spectra from sections immersed in electrolyte are typical for DLC structures and the one from the foam-covered section is similar in appearance to diamond. In this last case, a relatively narrow 1330 cm^{-1} line is accompanied with a distinct 1580 cm^{-1} line and a strong luminescent background emitted by carbon clusters. These spectra confirm earlier findings that the best conditions for diamond growth are found in the ethanol foam area. They both give hope for complete mastery of the process of low temperature diamond electrodeposition with liquid hydrocarbons.

Increasing interest and demand for nanostructured materials corresponded with the, previously mentioned, second direction of research in the scope of synthesis – i.e. the application of CVD methods for nanocrystalline diamond deposition. The [D8] study presents results of experiments using the hot filament (HF-CVD) method, with layers deposited on a silicon substrate with a pre-formed thin layer of gold, acting as a catalyst. Compared to other experiments, the most important modification was the use of a mixture of hydrogen and hydrocarbon without argon contents. For a long time, it was thought that the presence of argon is necessary to increase the concentration of electron in the plasma, which intensifies secondary nucleation, resulting in smaller, nanocrystalline diamond grains. Unfortunately, this type of plasma can be unstable – this resulted in an uneven growth of layers. Much better effects were achieved with pre-processing the substrate involving the application of a thin layer of nanocrystalline growth catalyst – in this case, gold. The [D8] study therefore demonstrated nanocrystalline diamond layers with grain diameters of 300–400 nm, clustered however into larger structures with sizes reaching several micrometres – as created on silicon substrates covered with a gold layer with grain diameter of approx. 90 nm. Other modifications are: reducing substrate temperature to approx. 600°C, pre-etching the Au layer in an atomic hydrogen flux and enriching the process mixture to 8% hydrocarbon content. The presence of the tetrahedral carbon phase was confirmed with measurements of Raman scattering and X-ray diffraction.

4.3.2. Research of surface geometry evolution during the growth of layers

Mentioned as the second part of the scientific accomplishment and an important development of the academic discipline – progress towards advanced methods of surface geometry research – was presented in studies: [D1], [D3], [D5], [D6], [D7] and [D8]. And so, study [D1] presents the results of studies of the three-layer Ti/TiC/Diamond system texture measured with X-ray diffraction. Study [D3] presents the results of research of the quartz-deposited polycrystalline diamond surface structure compared with the measurements of optical transmittance in the UV-VIS-IR range. Similar layers are examined in studies [D5] and [D6] in the aspect of capturing the characteristic changes in their surface morphology observed making use of the changes in the pyrometric signal occurring during the growth process. These studies also present a unique model of transmittance in the IR scope of optical three-layer (substrate/layer/vacuum) systems, taking into account the roughness of the deposited layer. Study [D7], in turn, analyses the thin layers of polycrystalline diamond using fractal analysis in order to establish the characteristic changes in fractal characteristics occurring during the growth process. Finally, study [D8] presents the results of comparative fractal analysis of the nanocrystalline diamond structures, based on AFM and SEM images in order to capture the differences between the two methods.

The surface treated as a structural discontinuity of the solids and liquids determines many of their physical properties. In previous studies, I investigated this effect in terms of surface electrical properties of carbon materials [4], [21], [22] and in the works included in the described academic achievement – also based on optical, tribological and micromechanical properties of thin diamond layers. Furthermore, the discovery of links between a surface geometry with specific properties and the character of the growth process seems far more important than a pure description of the surface configuration – this would provide a possibility of their formation by controlling the growth process and further processing.

If the surface is treated as a dense set of points, then one can sample and discretise it using appropriate tools (SEM and AFM microscopes or profilometer), resulting in a series of numbers which locally approximate the actual height. In the following, these data can be processed numerically in order to extract the parameters describing specific spatial aspects of surface configuration. In studies included in the described academic achievement, I focused on three groups of parameters, defined in the ISO 25178 standard:

- statistical parameters describing the features of the probability distribution for a sequence of samples, e.g. mean squared roughness, skewness, kurtosis, autocorrelation coefficient, surface anisotropy ratio,
- fractal parameters describing the behaviour of a set of topography samples when changing the spatial scale, e.g. fractal dimension, topothesy, corner frequency,
- functional parameters describing the features of the cumulative probability distribution of a sequence of samples, e.g. surface layer core thickness, reduced peak heights, reduced valley depths etc.

The advantage of the statistical description is the simplicity of setting parameters in surface geometry description. On the other hand, one should remember that statistical description is ambiguous and the surface formation process itself – nonstationary, meaning that the results are highly dependable on, for example, measurement conditions. When it comes to the fractal description, the allometric scaling law enables the separation of specific geometrical patterns which are the "fingerprint" of surface processing methods. The only drawback of this method is its calculation complexity and partial dependence of the results on the selection of the calculation algorithm. On the other hand, the description with functional parameters shows surface features that are important for tribological applications: friction, abrasion wear, penetration of process fluids, transmission of stress, etc. The downside of this description is a large diversification of the parameters and a lack of clear relations between the processing activities with end values of these parameters.

The next own and original scientific achievement in the described cycle, and an important contribution to the academic discipline, I consider to be the research of the time evolution of diamond surface configuration, as presented in studies [D5] – [D7]. The results are unique not only because of the lack of similar studies in the discipline, but also due to the fact of contrasting series of data collected using different methods: ex-situ using AFM and in-situ from pyrometric measurements of apparent substrate temperature changes recorded during crystal growth. For multiple reasons, especially the second method is interesting:

- there are no comparative data regarding in-situ evolution of diamond roughness in growth processes to be found in literature,
- for purposes of in-situ determination of the roughness and thickness of the growing layer, I proposed an original nomogram method based on own-build model of optical transmittance in the quartz-diamond-vacuum three-layer system, derived from Fresnel coefficients for the amplitude of repeatedly reflected waves crossing media boundary,
- the model was used to simulate the process of crossing for two waves with lengths within the infrared range emitted by a quartz substrate, treated as a perfectly grey body.

The aforementioned model of optical transmittance in a three-layer system and radiation emission by a perfectly grey body was described in detail in studies [D5] and [D6]. I make an assumption there that the quartz-diamond boundary is smooth and the diamond-vacuum boundary – rough, making the model itself non-linear which, in turn, implicates huge difficulties with numerical fitting to experimental data. In order to solve this problem, I proposed the use of nomograms binding the thickness and surface roughness of the layer in connection with the system transmittance analysis. Knowing the parameters of local transmittance extremes in the function of the current thickness of the layer, one can assign them to specific roughness values. This, in turn, enables the reconstruction of the time evolution of layer thickness and roughness and, consequently – growth rate. The validity of the method and applied model was verified by comparison of the "pyrometric" roughness results with AFM results and the layer thickness and growth rate – with results measured by the profilometer.

Obtained results are very interesting. There is no surprise in the fact that the growth rate increases asymptotically to a constant value (as confirmed by ex-situ measurements, e.g. in study [D7]); however, the evolution of roughness presented in [D5] seems more intriguing. The study shows that roughness decreases suddenly during growth – this is probably related to breaking the growing layer due to increasing mechanical stress. The possibility to make such an observation proves the great usefulness of the proposed method, for example to provide ongoing monitoring of the layer growth process. In further works, I built more models of the rough diamond surface in order to extract the roughness based on the measurements of

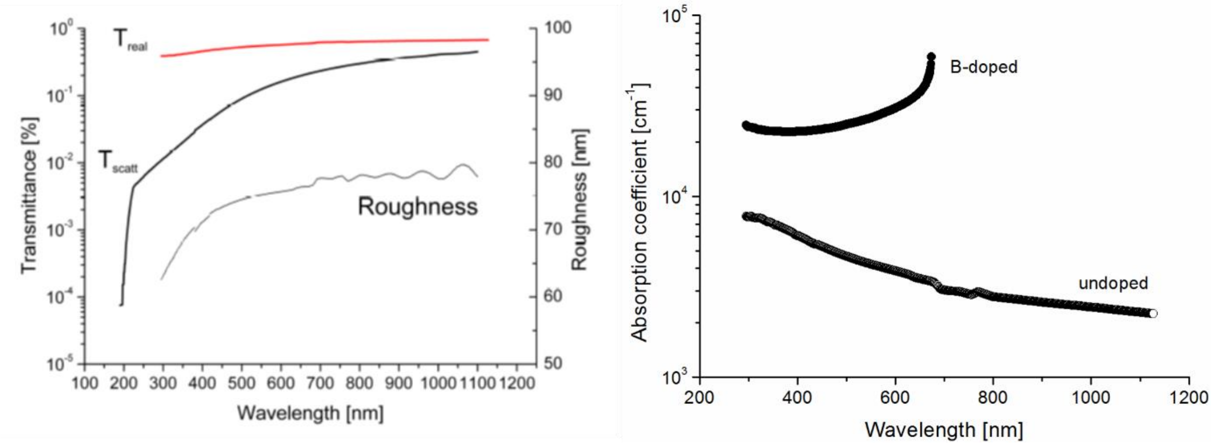

Figure 2. (A) Results of calculations of the roughness (thin black line) of the polycrystalline diamond layer based on total (thick red line) and scattered (thick black line) transmittance measurements in the UV-VIS range, (B) Estimation of the absorption coefficient for thin layers of polycrystalline diamond: without doping and with heavy boron doping. The most interesting is the sudden increase in the absorption coefficient of the doped layer for waves longer than 650 nm, which corresponds to the dopant energy level of approx. 1.9 eV.

the coefficient of total and scattered transmission of light in the UV-VIS range (Figure 2A) and the spectrum of light absorption coefficient in doped layers using self-consistent iterations (Figure 2B). They proved to be in line with the results obtained using the pyrometric and AFM methods.

Study [D7] presents an entirely new approach to the problem of researching the time evolution of the geometric structure of the surface, using fractal and statistical analysis which describe characteristic aspects of geometry of the thin layers of diamond on quartz: roughness and anisotropy on the one hand and fractal dimension and corner frequency on the other. In the scope of statistical parameters, I found that they evolve in two ways: roughness increases asymptotically to a constant value while the anisotropy ratio at first increases from a very small value to approx. 0.9 and then asymptotically decreases to approx. 0.5. The initial increase of the surface texture anisotropy ratio can be linked to diamond nucleation, then surface closing and concurrent growth period, in which a substrate with highly directional features becomes covered with regular, fine diamond grains. These, at first, grow freely only to merge at one point and start competing for growing space. As soon as the secondary nucleation ceases, when the dominant grains topography stabilises, the anisotropy starts decreasing again due to the formation of ever larger walls and longer edges of the crystallites, reaching the value typical for the crystal habit dominant in the given conditions.

Fractal parameters appear to evolve in a different manner. It is worth mentioning that, since there are at least several methods of determination of fractal parameters, e.g. surface roughness method, cube counting, power spectrum density function, auto-correlation function and structure function, the first requirement was to verify the numerical estimations provided by these methods. For this purpose, a series of virtual surfaces with certain fractal characteristics was generated – the results were tested. The analysis showed that the method based on surface roughness is the most reliable, followed by the structure function method. The auto-correlation method turned out slightly worse and the least accurate was the cube counting method which failed entirely, especially in the scope of high values of the fractal dimension, meaning – in the case of highly developed surfaces. Since many surface representations with changing scan length are required for the roughness method, further research uses the structure function method – details are described in studies [D7] and [D8]. The non-monotonic relationship between fractal dimension and scan length observed in study [D7] is worth mentioning. This relationship is a result of the growing surface scanning step and the order length typical for the surface, which provide the maximum value of the determined fractal dimension after equalisation.

Fractal analysis showed the process of diamond layer growth on quartz in an entirely new perspective in relation to statistical parameters. The calculations show that the fractal dimension at first increases rapidly until the layer is completely closed. From this point, it starts to decrease asymptotically to a value approx. 20% lower than the initial value. What is interesting is the fact that despite the differences in estimations of all the aforementioned methods, the trend and amplitude of changes were similar. Strong correlation between fractal dimension and layer closing degree was observed for the first time, not only in relation to diamond, but to thin films in general. A multi-faceted analysis of the changes of fractal and statistical parameters over time provides a possibility of making a clear distinction between growth process phases, with particular focus on layer closing and damping concurrent growth.

In the case of quartz, study [D3] also presents unique results regarding the change in surface roughness as a function of increasing acceptor doping (ex-situ measurement). It shows that layers with increasing boron doping have lower surface roughness, decreasing by approx. 0.3 nm per 1 ppm of increasing doping amount. Having in mind almost constant size of diamond grains in tested layers, the observed relationship can signify that light doping atoms fill in structural defects, possibly due to the higher surface mobility of these atoms. This effect is not fully understood and its practical application for producing smooth optical structures can be problematic due to the greatly increased light absorption in highly doped layers.

The next own and original scientific achievement of the author and an important contribution to the academic discipline is the determination of the effect of mechanical processing of the surface on the texture of the created polycrystalline layers, as researched in study [D1]. For this purpose, the polar charts of diffraction peaks were taken and compared for all three materials: substrate, intermediate carbide layer and diamond – which are all located in the range of close diffraction angles, changing from 40 to 45°. Then, their shapes were compared for unprocessed and sandblasted substrates. In the first case it turned out that a distinct mosaic was observed, together with a similarity in the polar charts of the diffraction lines of the substrate and the intermediate layer, while in the second case, there is visible similarity between the polar figures of the intermediate layer and diamond. This obviously shows that sandblasting destroys the initial substrate texture made with previous mechanical processing but also, depending on the degree of substrate surface damage, the intermediate layer reflects the privileged substrate texture or forces its own texture on the surface diamond layer.

Study [D8] involved researching the changes in the geometries of nanocrystalline surfaces of diamond structures occurring during their growth by using numerical analysis of AFM and SEM images. The main problem to be solved during the described studies was the development of a method for the reconstruction of three-dimensional surface topography based on the information coded in the grey scale of SEM images which are, in fact, projections of the actual surface on the imaging plane. I decided to apply the simplest solution and linearly assigned values from the range between 0 (black) and 1 (white) to individual pixels, without knowing the actual height of the surface in these points. I assumed that even though this does not provide the possibility to determine the values of parameters describing the absolute surface configuration, on the other hand – this has no bearing on the fractal parameters determined based on allometric scaling laws.

The comparison of AFM and SEM images for similar areas of tested layers showed a fundamental difference between the observed structures which is reflected in fractal characteristics. Specifically – SEM images showed a cluster, cauliflower-like structure, i.e. grains of fine diamond crystallites converging into larger bunches. On the other hand, AFM images showed more or less flat surfaces covered with regular diamond nanocrystallites. The probable reason for the differences was the application of the AFM images flattening procedure – a standard process implemented in order to eliminate long-wave surface components (waviness) and to bring out the short-wave components (roughness). The described observations were confirmed by the selected fractal characteristics of the tested layers: bifractal for SEM images and monofractal for AFM images. In the case of bifractal images, the fractal dimension related to shorter distances describes the dynamics of surface variability inside the clusters while the dimension related to longer distances – describes the surface height variations of entire clusters. Comparing the two fractal dimensions shows that the surfaces inside clusters are less developed than secondary configuration of the entire clusters. These two dimensions fluctuate slightly with elapsed deposition time, however it is difficult to notice any clear trends in their behaviour.

Corner frequencies, which divide individual scaling law variability ranges, can be identified with typical sizes of objects within a given substructure or with an order range of a particular grade. The analysis of SEM images confirmed that individual clusters have dimensions of about 1 μm and decrease as the growth process lasts longer, while their order spans virtually the entire imaging area. This could testify to the high regularity of the resulting structures as in the contrary case, the correlation would quickly decrease to zero. Similar estimates based on AFM images provided a result of 250 nm, i.e. 4 times lower than SEM, however similarly unchanging with increased deposition times.

Apart from typical fractal parameters, the study also described the mean size of grains determined based on the rate of decay of the autocorrelation function in AFM images. It so happens that this dimension is close to corner frequency and does not exceed several hundred nanometres – it is, therefore, lower than it would appear from SEM images and characterizes the size of typical nanocrystallites in the layer. What is interesting is the fact that this size changes with deposition time. The resulting values of anisotropy coefficients also suggest large differences between the primary and secondary structures. The anisotropy ratio from SEM images has low values, typical for structures with a defined surface texture and practically does not change with the growth time. On the other hand, the anisotropy ratio from AFM images reaches values near one, i.e. typical for isotropic structures. This testifies to the large regularity of the created monostructures, both in terms of size and shape and also – distribution on the surface.

4.4. Summary

The single-subject cycle of publications presented for evaluation is devoted to the studies of producing thin layer diamond and related structures as well as of the geometrical spatial characteristics of their surface layers. During the experiments, I used the following deposition techniques: hot filament (HF-CVD), microwave plasma (MP-CVD), electrodeposition from the liquid phase and magnetron sputtering, the phase purity of the resulting structures was determined using Raman spectroscopy and X-ray diffraction (XRD), surface topography measurements were made using atomic forces microscopy (AFM) and scanning electron microscopy (SEM).

In my opinion, the most important results obtained and presented in the evaluated cycle of publication, shown for the very first time on a global scale, are:

- production of continuous layers of optical quality of polycrystalline diamond on transparent substrate using microwave plasma in temperatures below 500°C,
- demonstration of the high differentiation between the growth rate on titanium surface, depending on its oxidation and presence of alloy ingredients contributing to an additional catalytic effect,
- production of diamond nanocrystallites from ethanol foam using the electrodeposition method,
- creation of a model of optical transmittance for rough three-layer substrate/diamond/vacuum structures and its application to the *in-situ* determination of diamond surface roughness,
- comparison of the time evolution and geometric configuration of surfaces of various diamond and related structures with distinguishing characteristic thin layer growth stages (*in-situ* and *ex-situ*), using statistical and fractal analysis,
- comparison of the surface configuration analysis results of SEM and AFM images.

The completed studies and obtained results show great promise for the future of diamond structures in science and technology. The indisputable advantage of these materials is their still extreme physical and chemical properties, predestining them for multiple practical applications. The demonstrated possibilities in the scope of new method of production are grounds for consideration of mass production of nanocrystalline structures, due to a significant reduction in production costs and technological requirements. We can have especially high hopes for the liquid phase deposition processes which enable the production of the required nanostructures even directly in their operation location.

As of today, my academic activity concentrates on the studies of the surfaces of various materials by means of AFM techniques. These studies are generally aimed at determining surface properties after physicochemical processing. The subjects are not only carbon materials, but also an entire range of materials used, for example, in implantology (titanium alloys, polymers), biotechnology (functionalised nanoparticles and enzymes), medicine ("smart" drugs, carriers for the active substance in drugs, tissues) and others. The completed measurements enable imaging not only the classic, dipole edge-surface forces, but also electrical, magnetic effects, friction and adhesion forces, and many others. Combined with a multi-faceted numerical analysis of the images in order to isolate statistical, fractal and functional properties of the configuration of studied surfaces, we are provided with a powerful tool for researching the surface condition of various materials. For this reason, devices with active surfaces are likely to find even more numerous application in modern science and technology.

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5. Elaboration on other scientific and research achievements

5.1. Description of academic activity before obtaining a doctoral degree (Ph.D.)

I began my academic research activities in the fall of 1996, as a fourth-year student of physics specializing in “Physical foundations of microelectronics” at the Faculty of Physics and Astronomy of the Nicolaus Copernicus University in Toruń, as an integral part of my master’s thesis written under the supervision of Prof. dr. hab. Franciszek Rozpłoch in the Division of Radiospectroscopy and Carbon Physics. The subject of my thesis was the production of thin, polycrystalline diamond layers using the hot filament method on foreign substrates (silicon, quartz, copper). The main goal of the study was to streamline the polycrystalline layers’ growth process due to the specific structural properties tested with the following methods: Raman scattering, X-ray diffraction (XRD) and scanning electron microscopy (SEM). The determined parameters included, among others: biaxial mechanical stresses in the layer, mosaic grain size (domains with coherent diffraction of X-ray beams), crystallographic orientation of the grains, texture, structural purity of the material, foreign phases contents, etc. I defended my thesis successfully in 1998.

After completing my master’s degree, I started doctoral studies on the Faculty of Physics and Astronomy of the Nicolaus Copernicus University in Toruń. In 2002 I was offered a position of assistant lecturer in the Division of Radiospectroscopy and Carbon Physics. At the same time, I continued my scientific endeavours under the academic supervision of Prof. dr. hab. Franciszek Rozpłoch – with the theme of production and researching the properties of diamond thin films. The areas of my research were then mostly focused on explaining the controversies surrounding surface electrical conductivity in diamond and especially their modification via mechanical reaction of the polycrystal and the surface (change in the concentration of charge carriers in the intermediate area between crystals due to lack of structural continuity) and chemical reactions between the layer and its surrounding environment (saturation of structural defects by gas particles heavily affected the surface electrical conductivity of the layer). For the purpose of this research, I designed and built an appliance for testing electrical conductivity of thin layers in the temperature range from room temp. to 1000 ^{0}C, and in vacuums of up to 10^{-6} Pa.

In addition to researching carbon structures, I also engaged to a limited degree in measurements of the crystalline structure of neodymium doped yttrium aluminium garnet

(YAG) layers made using the laser ablation method (PLD). In order to determine the significant parameters of the crystal, such as: crystallographic orientation, lattice constants, stress values, foreign phase inclusion contents, etc., I used X-ray diffraction, similarly as in the case of diamond structures.

I successfully defended my doctoral dissertation: “Structure and electrical properties of diamond thin films” in 2003 at the Faculty of Physics, Astronomy and Informatics of the Nicolaus Copernicus University in Toruń. My scientific activity before obtaining the doctoral degree includes:

- 5 articles in peer-reviewed scientific journals,
- 3 post-conference articles in peer-reviewed scientific journals,
- 7 appearances at national and international level conferences.

5.2. Description of academic activity after obtaining a doctoral degree (Ph.D.)

After defending my dissertation, I was offered a position of assistant professor in the Division of Radiospectroscopy and Carbon Physics. My academic activity was at first the continuation of my previous interests, i.e. in the direction of studying the electrical conductivity mechanisms in polycrystalline diamond layers. For this purpose, I made a qualitative refurbishment of my measurement apparatus, resulting in a much wider temperature range (from -200 to +1200 ^{0}C) and adding the possibility of adjustment of the composition of the measurement atmosphere. Thanks to this fact, it became possible to study the electrical conductivity mechanisms also for low-dimensional carbon materials, e.g. bundles or sheets of nanotubes.

When researching low-dimensional carbon structures, I became interested in the production of nanocrystalline layers of diamond and diamond-like carbon (DLC) by methods of catalytic electrolysis of liquid hydrocarbons. The results I published were then among the very first to confirm the possibility of using this method to produce not only diamond-like (DLC) layers, which are essentially a mixture of carbon clusters with three basic hybridisations: tetrahedral, trigonal and linear, but also diamond layers of pure sp^3 hybridisation and short order range (nanocrystals).

In 2004, I spent 2 months on a post-doctoral internship at the Institute for Materials Research, Hasselt University in Belgium, where under the supervision of Prof. Milos Nesladek and Prof. Ken Haenen, I contributed to the optimisation of the process of heteroepitaxial growth of optical quality polycrystalline diamond layers on quartz substrates and diamond depositions on active titanium electrodes used for electrochemical treatment of sewage. These studies were part of the project: “Quantum Size Effects in Nanostructured Materials” (IAP-V/01) and the programme: “DRIVE” Marie Curie Research Training Network (MRTN-CT-2004-512224). In 2005, in turn, I took a 2-month post-doctoral position at the Laboratory of Molecular Materials and NanoSystems, Technical University in Eindhoven in the Netherlands, were under the supervision of Prof. Kees Flipse, I carried out the AFM measurements of nanocrystalline diamond layers and STM measurements of thin iridium layers.

I greatly extended the experience in the field of the AFM gained throughout my works so far, when in 2007 I was offered a position of assistant professor on the Faculty of Mathematics and Computer Science of the University of Warmia and Mazury in Olszyn, where I engaged in the studies of crystalline nanostructures and their topographical, magnetic, electrical and tribological properties. Materials under investigation involved, among others:

- thin carbon layers,

- abrasion surfaces of tool steels,
- construction steel surfaces with increased abrasion resistance,
- titanium surgical implants coatings,
- surfaces of polymer surgical implants,
- biological materials (stem cells, nail plates, hair),
- powders with active substances (medical tablets, sorbents, catalysts),
- sediments of noble metals nanoparticles from biotechnological synthesis,
- nanofunctionalised enzymes and others.

The studied materials were obtained due to intensive academic cooperation with numerous Polish research groups, representing: Faculty of Technical Sciences of the University of Warmia and Mazury (UWM) (abrasion-resistant tool steels), Medical University of Silesia in Katowice (powders with active substances), Faculty of Medical Sciences UWM (biological materials), Faculty of Food Sciences UWM (biotechnological materials), Faculty of Physics, Astronomy and Informatics of the Nicolaus Copernicus University in Toruń (carbon materials), Institute of Physics of the Kazimierz Wielki University in Bydgoszcz (nanostructured carbon materials). The AFM research was partly financed from my participation as a contractor in the internal UWM grant: “Description and analysis of select photon and soliton spectra” (UWM grant no. 1310.0801). For my outstanding academic achievements, I was granted The University of Warmia and Mazury Rector Award in 2008.

In 2014, I began a scientific cooperation with ChM sp. z o.o. in Lewickie, Poland – a leading European manufacturer of implants and tools for surgery and traumatology with the purpose of studying the surface layer of titanium and polymer implants for resistance to organic etching and tissue osseointegration. It is a highly applicable branch of research with direct effect on improving company products, however due to the trade secrecy limitations, not all results of these studies can be published in journals and are not fully visible in the list of my academic accomplishments.

Apart from national cooperation, I also conduct studies in cooperation with foreign institutions. Since 2014, I have cooperated with groups in: Technical University of Cluj-Napoca (Romania) and Islamic Azad University in Teheran (Iran) in the scope of analysis and numerical processing of AFM measurements of functionalised thin-layer nanostructures. In 2014, I also started a cooperation with a group in the National Institute for Optoelectronics, Bucharest (Romania), for which I provide analysis and numerical processing of AFM measurements of biomedical materials. The effect of this cooperation is the invitation to participate in the international project “Nanofunctionalisation to induce osseointegration and to reduce the risk of infection”, implemented by a consortium of 6 scientific institutions: (1) National Institute for Optoelectronics, Bucharest, Romania, (2) Consejo Nacional de Investigaciones Científicas y Técnicas, Argentina, (3) Latvian Institute of Organic Synthesis, Riga, Latvia, (4) Riga Technical University, Latvia, (5) Sao Paulo State University, Brasil, (6) University of Warmia and Mazury in Olsztyn, within the project: ELAC2015/T08-0496 (Surinfect).

In 2012, I spend two weeks on a post-doctoral internship at the Laboratory of Molecular Materials and NanoSystems, Technical Inversity in Eindhoven in the Netherlands. In 2013, I spend 2 weeks on a similar internship at the Department of Semiconductor and Carbon Physics of the UMK in Toruń, where I improved my expertise in the field of AFM research.

Apart from strictly physical applications, since 2007 I have also contributed to the applications of the dynamic systems theory to modelling price trends in real estate markets. These studies are part of the so-called econophysics, in which sequences of economic data are treated as samples for system states – their dynamics is analysed by comparison to natural phenomena (turbulence, chaos, equilibrium). For the purpose of this research, I took part in the scientific workshops – Advanced School on Numerical Solutions of Partial Differential Equations: New Trends and Applications, Universitat Autònoma de Barcelona, in Spain. Furthermore, I was a holder of the NCN grant: “Application of the non-linear transitions theory to modelling and diagnosis of the Polish real estate market” (DEC-2012/07/B/Hs4/03267), implemented from 1 July 2013 to 30 June 2015.

My plans for the nearest future are related to the development of the AFM methods and their application to studying surfaces of materials, particularly biomedical ones. I have high hopes for the comparative studies using the AFM methods and NMR relaxometry to research current carriers of active ingredients in drugs and studies of stem cells. I wish also to continue my advanced studies of functionalised nanoparticles and enzymes produced using biotechnological synthesis methods. One of my priority endeavours is further development of my cooperation with ChM sp. z o.o. in Lewickie in the studies of the surfaces of implants and international cooperation in the scope of processing and analysis of the surface images for various materials.

After obtaining the doctoral degree, I was a reviewer of the scientific articles for the following scientific journals enlisted in the Web of Science database:

- Applied Physics A (IF 1.444, 25 pts. (A)),
- Microsystem Technologies (IF 0.974, 15 pts. (A)),
- Optical and Quantum Electronics (IF 1.290, 20 pts. (A)),
- Processing and Application of Ceramics (IF 0.944),
- Journal of Inorganic and Organometallic Polymers and Materials (IF 1.308, 20 pts. (A)),
- The International Journal of Advanced Manufacturing Technology (IF 1.458, 30 pts. (A)).

In summary, my academic accomplishments after obtaining the doctoral degree includes (as at 10 January 2017):

- a number of articles in peer reviewed scientific journals: **49**,
- a number of lectures during international and Polish conferences and during invitation scientific seminars: **45**,
- summary Impact Factor: **65.714**,
- Hirsch index: **7** (Web of Science), **10** (Google Scholar), **7** (Scopus),
- number of citations (all / without self-citations): **136/90** (Web of Science), **249/165** (Google Scholar), **136/91** (Scopus).

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Sławomir Kulesza