- First name and last name:
Kazimierz Paprocki

- Diplomas and scientific degrees with the name, place and year of obtaining them and the title of the doctoral dissertation:
  
  - January 2013  PhD in physical sciences, Faculty of Technical Physics and the Applied Mathematics Lodz University of Technology, title of the monograph: "Optical and electrical properties of diamond and nanodiamond layers", supervisor: prof. dr hab. Kazimierz Fabisiak,
  

- Information on previous employment in scientific and didactic units
  
  - 2013-now  assistant Professor, Institute of Physics, Kazimierz Wielki University in Bydgoszcz
  
  - 2007-2013  assistant, Institute of Physics, Kazimierz Wielki University in Bydgoszcz
  
  - 2005-2007  senior technician, Department of Kazimierz Wielki University in Bydgoszcz
  
  - 2000-2005  individual economic activity, photography
  
  - 1993-2000  technologist specialist, VigoTor Sp. Z o.o. in Toruń
  
  
  - 1987-1990  assistant-technologist, Electronic Research and Development Center Specialized Systems Mera OBREUS in Torun
A. Indication of the achievement resulting from art. 16 sec. 2 acts

A.1. Title of achievement

As a scientific achievement obtained after receiving the PhD degree being a significant contribution of the author to the development of a specific scientific discipline, I am indicating a series of 12 publications related thematically under the collective title:

„Influence of the amorphous carbon and defects on the electrical conductivity mechanisms as well as electrochemical and dosimetric properties of thin polycrystalline diamond layers”

A.2. List of publications being one thematic collection:

A.2.1. Mosinska, L., Fabisiak, K., Paprocki, K., Kowalska, M., Popielarski, P., Szybowicz, M.,

*Undoped CVD diamond films for electrochemical applications,*

Electrochimica Acta, 2013, **104**: 481-486.

(IF=4,086)

A.2.2. Fabisiak, K., Kowalska, M., Szybowicz, M., Paprocki, K., Popielarski, P., Wrzyszczyński, A., Mosińska, L., Zhusupkalieva, G.K.,

*The undoped CVD diamond electrode: The effect of surface pretreatment on its electrochemical properties,*


(IF=1,508)

A.2.3. Kowalska, M., Fabisiak, K., Wrzyszczyński, A., Banaszak, A., Szybowicz, M., Paprocki, K., Bała, W., Bylicki, F.,

*CVD diamond layers for electrochemistry,*


(IF=0,444)

A.2.4. Kowalska, M., Fabisiak, K., Wrzyszczynski, A., Szybowicz, M., Paprocki, K.,

*Electrochemical impedance spectroscopy studies of HF CVD diamond films,*


(IF=0,525)

A.2.5. Dychalska, A., Popielarski, P., Franków, W., Fabisiak, K., Paprocki, K., Szybowicz, M.,

*Study of CVD diamond layers with amorphous carbon admixture by Raman scattering spectroscopy,*

Materials Science-Poland, 2015, **33**(4): 799-805.
A.2.6. Dychalska, A., Fabisiak, K., Paprocki, K., Makowiecki, J., Iskaliyeva, A., Szybowicz, M.,

*A Raman spectroscopy study of the effect of thermal treatment on structural and photoluminescence properties of CVD diamond films*.

Materials & Design, 2016, **112**: 320-327.

(IF=4.364)

A.2.7. Banaszak-Piechowska, A., Paprocki, K., Fabisiak, K., Dudkowiak, A., Szybowicz, M., Staryga, E.,

*Structural and electrical characterization of undoped diamond layer grown by HF CVD*.


(IF=0.469)

A.2.8. Paprocki, K., Fabisiak, K., Dychalska, A., Szybowicz, M., Dudkowiak, A., Iskaliyeva, A.,

*Impedance study of undoped, polycrystalline diamond layers obtained by HF CVD*.


(IF=1.455)

A.2.9. Paprocki, K., Fabisiak, K., Bogdanowicz, R., Gołuński, Ł., Staryga, E., Szybowicz, M., Kowalska, M., Banaszak-Piechowska, A.,

*Charge-based deep level transient spectroscopy of B-doped and undoped polycrystalline diamond films*.


(IF=2.599)

A.2.10. Banaszak-Piechowska, A., Fabisiak, K., Staryga, E., Paprocki, K.,

*Electrical properties and Mott’s parameters of polycrystalline diamond films synthesized by HF CVD method from hydrogen/methanol gas mixture*.


(IF=0.610)

A.2.11. Paprocki, K., Winiecki, J., Kabacińska, R., Przęgętka, K., Szybowicz, M., Fabisiak, K.,

*Thermoluminescence properties of undoped diamond films deposited using HF CVD technique*.


(IF=0.610)

A.2.12. Kabacińska, R., Winiecki, J., Przęgętka, K., Szybowicz, M., Fabisiak, K., Paprocki, K.,

*Chemically vapor deposited diamond films as dosimetric material for potential clinical applications*.
Statements by all co-authors of the publication, confirming their individual contribution to the published articles, are included in Annex 5.

B. Description of achievement

B.1.1. Introduction

A series of scientific papers under a collective title: *The influence of amorphous carbon phase and defects on the electrical conductivity mechanisms and electrochemical and dosimetric properties of thin polycrystalline diamond layers*, which I pointed out as the main scientific achievement in habilitation, is the result of my long-term research on the electrical, electrochemical and dosimetric properties of thin polycrystalline diamond films. Mechanisms responsible for electric transport phenomena, kinetics of heterogeneous electron transfer reactions through the interface of the diamond layer and ionic solution, as well as excitation and stimulation of optical transitions are still poorly recognized, which results from a small amount of basic research devoted to this issue.

Taking it into account, my motivation was to investigate the impact of the amorphous carbon phase and defects in the thin layers of polycrystalline diamond on their physical properties. The choice of the diamond was not accidental. It resulted from the possibility of controlling morphological properties, phase composition and doping of thin films during the CVD growth process. The understanding the phenomena occurring in polycrystalline diamond is an excellent reference point for understanding phenomena occurring in other thin polycrystalline films.

The carbon belongs to the same group of the periodic system as silicon and germanium, however, it is a much smaller atom than the other atoms from the same group, which enables the formation of C-C bonds with sp$^1$, sp$^2$ and sp$^3$ hybridizations. Si and Ge crystalize in the structure called a diamond structure. In the case of carbon, we know such crystalline forms as graphite, diamond, fullerene, nanotubes and graphene. The crystal lattice of the diamond (sp$^3$ hybridization bonds) is identical to that of Si and Ge crystal lattices, with a lattice constant (0.31 nm) which is much smaller in comparison to the lattice constants Si (0.543 nm) and Ge (0.566 nm).
Short C-C covalent bonds in the diamond structure determine its extraordinary physical properties. This crystal belongs to the hardest minerals, it is an excellent electrical insulator (energy gap is 5.45 eV), it is an excellent heat conductor (thermal conductivity 5x greater than Cu), is transparent in the entire spectral range from UV-VIS to infrared, it is characterized by the index of refraction (n = 2.42), it is chemically inert, etc. Due to such unique properties, this crystal has become the object of interest not only of jewelers but also of physicists and material engineers.

The creation of natural diamonds is probably the result of crystallization from alkaline magma, at great depths in the Earth at temperatures above 1000°C, at a pressure of several GPa [1]. Because it impossible to find two indentical natural diamond crystals is the main reason for the low usefulness of natural diamonds in applications other than mechanical work, where their hardness (the highest for minerals), excellent thermal conductivity (22 W/cmK) and Younge module at 1140 GPa [2] are most important properties.

Since the discovery that a diamond is a crystalline form of carbon (Lavoiser 1796), attempts have been made to synthesize it in laboratory conditions. Historically, 1955 was the year when synthetic diamonds were first obtained using the HP-HT method (High Pressure and High Temperature), based on the conversion of graphite into diamonds [3].

However, the real breakthrough, was the development in 1982 when HF CVD (Hot Filament Chemical Vapor Deposition) reactor was used for diamond synthesis where hot tungsten fiber (HF) was used to dissociate hydrogen and hydrocarbons [4-7]. There was the possibility of producing polycrystalline diamond layers, a material similar in parameters to the natural diamonds, but, what is very important, these layers were produced in laboratory conditions during a well-described technological process, which in theory could guarantee their repeatability.

The following years the works were proceeding in two different but dependent directions. On the one hand, we tried to refine the technology of layer synthesis (Physical Vapor Deposition, low pressure CVD, plasma assisted CVD, thermally activated CVD), and the second direction was the use of this material as a replacement for existing solutions (diamond electrodes for electrochemistry applications, cold emitters electrons, SGFET transistors).

The problem was and is, to correlate both directions of research, because only the purposeful design of the synthesis of layers for specific applications may lead to the actual development of applications based on diamond layers.
B.1.2. Research goal

The main aim of my study was to determine the effect of the presence of the amorphous phase, defects and a hydrogenation on the properties of the electrical transport, the rate of heterogeneous reaction of electron transfer and the dosimetric properties of thin polycrystalline diamond layers. To achieve this goal, it was necessary to undertake studies on the correlation of technological parameters of the process of diamond layers synthesis with their physical properties.

An undoped diamond single crystal is a dielectric with a wide energy gap of around 5.45 eV. This means that at room temperature (RT) this material does not conduct electricity. Doping of diamond to obtain semiconductor properties is possible, but because of the degree of packing of the diamond network and the size of the lattice constant, doping atoms with elements larger than the carbon ionic radius is very difficult. Natural admixtures of the diamond, due to the size of the atoms, are nitrogen (type Ia and Ib) and boron (type IIa and IIb).

Natural nitrogen is the most popular admixture in natural diamonds, however, donor states related to nitrogen are located around 1.7 eV below the minimum of the conductivity band, so their role in electrical conductivity is very limited, even at temperatures much higher than room temperature [8], which determines the low usefulness of this kind of doping. In laboratory practice, diamonds are usually doped with boron which forms acceptor levels at a distance of 0.37 eV above the edge of the valence band [9]. Boron-doped diamond becomes a p-type semiconductor, however, also in this case, the hole conductivity associated with the admixture of boron, plays a role at temperatures higher than 450 K.

CVD technology for depositing diamond layers and applied research methods

All CVD methods are based on the discovery by J.C. Angus [10], on the role of atomic hydrogen which etches almost 20-30 fold faster graphite phase compared to the diamond phase. This feature of atomic hydrogen is extremely important in the case of diamond synthesis from the gas phase. The synthesis of diamond using CVD methods takes place in metastable conditions for this carbon phase and takes place in the area of stability for the graphite phase. It should be expected, that in the process of diamond synthesis, the simultaneous growth of graphite-like phase, will be unavoidable. The CVD process should be carried out in such way that the growth rate of the diamond phase is greater than the growth rate of the graphite-like phase.

In contrast to a single diamond crystal, which is a material with a strictly defined crystal
structure, the polycrystalline diamond layer is composed of densely packed diamond crystallites containing on the surface an amorphous carbon layer with sp² hybridization, which results from the character of the CVD process.

Above leads to fact that in the polycrystalline undoped diamond layer, hole-type surface conductivity is observed, showing the features of a p-type semiconductor.

The synthesis of diamond layers was carried out using a CVD reactor operating in a hot filament configuration (HF CVD), which is shown in Figure 1.

Fig. 1. On the left: reaction diagram of the CVD synthesis of the diamond layer [11], on the right: HF CVD large area reactor (IF UKW).

The HF CVD method can produce diamond layers with very different morphology, as illustrated in Figure 2.

Fig. 2. Different morphologies of undoped diamond layers: a) morphology (400), b) dominance of structures (111), c) ball-like type “crystallites”, d) nanodiamond structure (own work).
The structural properties of diamond layers and their morphology were characterized using the following methods as:
  - X-ray diffraction,
  - Raman scattering spectroscopy,
  - Scanning Electron Microscopy (SEM).

I determined electrical properties based on:
  - Temperature dependencies of current-voltage characteristics (I-V-T) (DC measurements),
  - Temperature AC characteristics (impedance measurements),
  - Cyclic voltammetry.

The spectroscopy of defects:
  - Cathodoluminescence (CL),
  - Thermoluminescence (TL),
  - QDLTS methods (*Charge Deep Level Transient Spectroscopy*).

The above experimental methods allowed for full characterization of the obtained diamond layers and for solving the problems described in further parts of the self-review.

The presented scientific achievement is based on the solving four problems presented below:

**Problem I**

*As growth parameters influence the structure of diamond films?*

In order to determine the relationship between synthesis parameters and structure, morphology, electrical and optical properties, I made a series of diamond layer samples deposited on a Si-type substrate with a thickness $d=0.2$ mm. In experiments, I focused on two synthesis parameters: (1) the pressure of working gases in the reactor changed from 20 mbar to 100 mbar and (2) the concentration of methanol vapors in the working gas changed in the range from 2.3% to 3%. Growth time, as well as other parameters of the synthesis process were kept at a constant level.

I determined the layers thickness of the based on SEM measurements of cross-sections of samples. The ratio of the content of the carbon phase $sp^2$ to $sp^3$ ($f=sp^2/sp^3$), I estimated, based on the integral intensities of the diamond Raman line and the G band from the $sp^2$ phase in the Raman spectrum using the dependence [12]:
\[
f = \frac{100I_G}{75I_{diam} + I_G}, \tag{1}
\]

where: \(I_{diam}\) is the integral intensity of the diamond line and \(I_G\) is the integral intensity of the G band.

The size of crystallites (in the direction perpendicular to the analyzed plane) was determined on the basis of X-ray diffraction spectra using the Debye-Scherrer formula [13]. The texture factor was determined using the formula [14]:

\[
TC_{(hkl)} = \left( \frac{1}{n} \sum I_{(hkl)} / I_{0(hkl)} \right)^{1/n}
\tag{2}
\]

where: \(TC_{(hkl)}\) is the texture factor for the plane \((hkl)\), \(I_{(hkl)}\) is the intensity of the diffraction peak corresponding to the reflection from the plane \((hkl)\), \(n\) - is the total number of identified peaks in diffraction spectrum of the layer. \(I_{0(hkl)}\) is the intensity value of the diffraction maximum of the reference material (result from the JCPDS-ICDD (or ASTM) base for the powder).

![Fig. 3](image)

**Fig. 3.** (a) Comparison of the quality changes of the test layers \(f\) - expression (4)). (b) Dependence of thickness of deposited diamond layers on pressure and CH\(_3\)OH vapor concentration \([B.10.13]\).

![Fig. 4](image)

**Fig. 4.** (a) Comparison of microcrystalline size changes for the examined layers. (b) Percentage of crystallites \(\{111\}\) in the test layers \(\text{changes in the texture ratio } Tc_{\{111\}} \) \(\text{formula (5)}\) \([B.10.13]\).

The simultaneous influence of the pressure of working gases and the concentration of methanol on the content of the sp\(^2\) phase in the obtained diamond layers was presented in Fig.
3a. The results obtained by me clearly indicate, that the content of the sp² phase grows fast, if
the concentration of methanol vapor exceeds ~2.7%, as well as the pressure of the reaction
gases is greater than ~25 mbar. On the other hand, both of these parameters are directly
proportional to the deposition rate of the diamond layer (Fig. 3b).
The dependence of the size of diamond microcrystallites on the working gas pressure and
methanol concentration is presented in Fig. 4a. At higher working gas pressures and higher
CH₃OH concentrations, microcrystalline sizes are reduced. At the same time, the texture factor
$TC_{(hkl)}$ decreases. In conclusion, I showed that both the growth rate of diamond layers as well
as their quality (sp² phase content, microcrystalline size, texture) can be effectively controlled
by the pressure of reaction gases in the reactor and the concentration of carbon (CH₂OH)
source. At the same time, the increase of conductivity is associated with increase of sp²
hybridized amorphous carbon content.

Another problem which should be solved was to find the correlation between the degree of
ordering carbon phases in the sp² and sp³ hybridizations in the diamond layers. To solve this
problem, I synthesized a series of 13 diamond layers on Si substrate with methane
concentrations ranging from 1% to 2.5%. The results of these experiments were published in
[A.2.5.]. The basic technique used for determination the diamond layers quality was Raman
spectroscopy. The Raman scattering spectra were deconvoluted into following components:
the diamond line, the D and G bands of the sp² phase and the photoluminescent background
(Fig. 5).

![Fig. 5. An example of the deconvolution of the Raman scattering spectrum for the polycrystalline HF CVD layer, visible components of the diamond, the D line and the G line from the carbonaceous sp² phase [A.2.5.].](image)

Because the polycrystalline diamond layer is a set of diamond microcrystallites (sp³ phase)
coated by amorphous carbon layer of sp² hybridization, I it is expected that it will be a
correlation between the ordering of the sp³ and sp² structures.
Figures 6a, 6b and 6c confirm the statistical consistency of the character of changes in the half-width and position of the maximum band G from the ratio of and ratio of intensities $I_D/I_G$, for diamond layers which in agreement with literature reports on amorphous carbon [15, 16]. The most important result obtained in this series of experiments is the relationship between changes in the diamond half line width (FWHM) and the $I_D/I_G$ ratio presented in Fig. 6d. The FWHM decreases with the $I_D/I_G$ increase, while the FWHM minimum is observed for the $I_D/I_G = 1.4$ value and the probable increase of FWHM with the increase of the $I_D/I_G$ value is expected. This means that the more ordered the structure of diamond microcrystallites in the layer, the more amorphous the nature of sp$^2$ carbon surrounding microcrystallites. In conclusion, I found an inverse relationship between the quality of the sp$^3$ diamond phase and the graphite sp$^2$ phase in the thin CVD diamond layers.

In the process of diamond layers synthesis, the admixture of the amorphous carbon phase with the sp$^2$ C-C hybridization is always present. Literature reports [17-20] indicate its participation in electrical conductivity. The analysis of Raman scattering spectra for both non-doped and boron-doped diamond layers indicated the presence of the G-band associated with the presence of amorphous carbon (Figure 7). In addition, for the different hydrocarbon concentrations in the working gas mixture, the intensity of the G line (with max. about at 1520 cm$^{-1}$) may vary (Figure 8).
Fig. 7. Comparison of Raman spectra for boron-doped diamond layers (Ax767-3, Ax768-3) and non-doped layer (Dpk18). The Raman line for the diamond is 1332 cm\(^{-1}\), 1570 cm\(^{-1}\) - the G-band (sp2) [A.2.9.].

Fig. 8. Raman spectra of non-doped layers with different concentrations of methane in the reaction gas: a) 3%, b) 2.3% [A.2.8.].

The query of scientific databases indicates that most reports on the electrical properties of polycrystalline diamond layers refer to boron doped layers. An example can be the cyclic active electrodes covered with a diamond layer, used in voltammetry measurements.

Obtained results of the performed studies gave the basis for the controllable synthesis of diamond layers with requested physical properties, i.e. the necessary knowledge was obtained allowing for predictable control of technological parameters.

It should be noted that all technological work related to the synthesis of diamond layers were performed by me personally at IF UKW.

Problem II

What is the relationship between the structure of thin diamond layers and their electrochemical properties?

The set of next performed experiments were concerned on the application possibilities of
undoped polycrystalline diamond layers in electrochemistry. The subject of my interest was both the ranged from of electrochemical stability for aqueous ion solutions to sensitivity activity. For this purpose, of the cyclic voltammetry measurements have been done and the results of which were published in the paper [A.2.1.]. Fig. 9a shows cyclic voltammograms obtained for two diamond layers used as a working electrode, which are different due to their in structural quality and phase composition. Electrode I: FWHM = 5,1 cm\(^{-1}\) and amorphous phase content \(\Phi_{am} = 0.00358\), electrode II: FWHM = 16,8 cm\(^{-1}\) and \(\Phi_{am} = 0.023\). For comparison, a voltammogram were recorded also on a platinum electrode. As it was observed, the width of the electrochemical window for the electrodes coated with undoped diamond layer is on average two times higher than that for a typical platinum electrode.

The performed measurements of the electrochemical response in 0.1 M aqueous KCl solution, which served as the basic electrolyte. As a redox couple the \(\text{Fe(CN)}_6^{4/-3}\) with a concentration of 0.01 M was used. Voltammograms obtained for different potential sweep rate \(v\) recorded on the diamond electrode are presented in Fig. 9b. The insert shows linear dependence of the maxima of reduction and oxidizing peaks current vs. \(v^{1/2}\), which proves that the Randles-Sevcik equation is satisfied, i.e. the reaction is reversible [21]. The impedance analysis of the tested diamond electrodes (Nyquist graphs) shows that they differ in series resistance, with the electrode resistance (I) being much smaller. At this point one can conclude that the electric conductivity of an undoped diamond layer is related to the presence of the amorphous carbon layer and can be controlled during the synthesis process, as it was discussed earlier.

The results obtained clearly indicate that doping diamond layers is not a necessary condition for the redox reaction which can occur on the diamond electrodes. The presence of the carbon with \(sp^2\) hybridizations results from the role of hydrogen in the CVD process [4], while the formation of subsurface conductive layer (ca. 10 nm) of p type conductivity, is due to
hydrogen termination [22]. It seems that the concentration of adsorbed hydrogen is mainly related to the sp² phase.

The results published in [A.2.3.] confirm this hypothesis. Table 1 presents examples of Raman spectrum analysis results for three selected diamond layers (WC-0.5%, WD-2.3% and WF-4.74%) synthesized at different concentrations of methanol.

Table 1. Parameters of Raman analysis for WC, WD, WF samples [A.2.3.]

<table>
<thead>
<tr>
<th>Electrode</th>
<th>Diamond Raman line position [cm⁻¹]</th>
<th>Diamond Raman FWHM [cm⁻¹]</th>
<th>Φ_{am}, 100 %</th>
</tr>
</thead>
<tbody>
<tr>
<td>WC (a)</td>
<td>1332.2</td>
<td>6.1</td>
<td>0.3576</td>
</tr>
<tr>
<td>WD (b)</td>
<td>1333.6</td>
<td>12.8</td>
<td>0.5211</td>
</tr>
<tr>
<td>WF (c)</td>
<td>1334.4</td>
<td>13.7</td>
<td>1.3208</td>
</tr>
</tbody>
</table>

Table 1 shows that the decrease of the quality of diamond layers (increase in the FWHM value for the diamond line) is accompanied with an increase in amorphous phase concentration Φ_{am} in the layer. At the same time, an increase in internal stresses is observed, which results in a shift of the Raman diamond line. This problem is discussed in detail in [B.1.20.].

Performed cyclic voltammetry measurements allowed to determine the symmetry coefficients of the charge transfer electrode kinetics, the standard constant heterogeneous transfer reaction $k_0$ for Fe(CN)$_6^{4-/3-}$ (defining the reaction kinetics rate) and the potential difference $ΔE_p$, where there are oxidation and reduction peaks, being an indicator of the reversibility of the reaction ($ΔE_p$=60 mV - perfectly reversible reaction).

![Polarization curves for the WF electrode and various concentrations [Fe(CN)$_6^{4-/3-}$ in a solution of 0.5 M H$_2$SO$_4$. Concentrations of I - 0.001 M, II - 0.005 M, III - 0.020 M [A.2.3.]](image)

In Table 2 are collected the values of $ΔE_p$, the symmetry coefficient $α$, and the standard constant $k_0$ for the electrodes with different contents of graphite phase sp². The results clearly
show, that the content of the sp\(^2\) phase **positively affects** the reversibility of the redox reaction (\(\Delta E_p\) decreases), the symmetry of the reduction and oxidation peak, and the kinetics of the electron transfer reaction.

Table 2. Reaction parameters for the tested electrodes (electrode designation as in table 1) [A.2.3.]

<table>
<thead>
<tr>
<th>Electrode</th>
<th>(\Delta E_p) [mV]</th>
<th>(\alpha)</th>
<th>(k_0) [cm/s]</th>
</tr>
</thead>
<tbody>
<tr>
<td>a</td>
<td>140</td>
<td>0.34</td>
<td>2.4 (10^{-4})</td>
</tr>
<tr>
<td>b</td>
<td>136</td>
<td>0.36</td>
<td>4.9 (10^{-3})</td>
</tr>
<tr>
<td>c</td>
<td>128</td>
<td>0.37</td>
<td>6.8 (10^{-3})</td>
</tr>
</tbody>
</table>

It is assumed that for metallic electrodes, the symmetry value of the cathodic/anodic reaction is constant and amounts to \(\alpha=\beta=0.5\). For doped electrodes, the symmetry coefficients are usually different from 0.5. For p-type semiconductor electrodes, in the ideal case should be: \(\alpha=0\) and \(\beta=1\). The obtained values \(\alpha\) may indicate a high density of surface sites that are involved in electrochemical reactions in accordance with the model proposed by Martin and others [23]. In this model (for electrochemical applications of diamond electrodes) diamond crystallites are treated as an inactive matrix in which there are conductive amorphous carbon paths (grain boundaries inside the layer).

In order to identify possible mechanisms of charge transport in diamond layers, the impedance measurements were performed in a wide range of frequencies (0.1 Hz to 1 MHz) [A.2.4.] The examples of the results of impedance measurements for two different diamond layers, whose Raman spectra parameters are collected in Table 3, are shown in Fig. 11a.

Table 3. Parameters of Raman spectra for the measured samples [A.2.4.]

<table>
<thead>
<tr>
<th>Sample</th>
<th>FWHM Diamond [(\text{cm}^{-1})]</th>
<th>Diamond peak position [(\text{cm}^{-1})]</th>
<th>FWHM D-band [(\text{cm}^{-1})]</th>
<th>(D)-peak position [(\text{cm}^{-1})]</th>
<th>FWHM G-band [(\text{cm}^{-1})]</th>
<th>(G)-peak position [(\text{cm}^{-1})]</th>
<th>Quality factor (f_g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>7</td>
<td>1332</td>
<td>110</td>
<td>1337</td>
<td>160</td>
<td>1331</td>
<td>0.999</td>
</tr>
<tr>
<td>B</td>
<td>21</td>
<td>1333</td>
<td>299</td>
<td>1390</td>
<td>120</td>
<td>1554</td>
<td>0.975</td>
</tr>
</tbody>
</table>

In Fig. 11 I presented the impedance spectra in the form of Nyquist diagrams with the equivalent circuit used to determine the electrical parameters of the layers. The proposed equivalent circuit is used for simulation of the impedance characteristics of the diamond layers, consists of ohmic resistances connected in series (R1) and three Voigt elements. The first of them \(Z1(R2/CPE1)\) represents the contribution of diamond microcrystallites (grain interiors) to the impedance, the second \(Z2(R3/CPE2)\) defines the contribution of grain
boundaries to the impedance, the third $Z_3(R_4/C_1)$ describes the impedance properties of the interfacial surface diamond electrode and electrolyte. In the case of impedance of diamond microcrystallites and grain boundaries, a simple model of a flat-parallel capacitor is not enough, therefore it was replaced by the special capacitor called CPE (constant phase element) whose complex impedance ($Z = \text{CPE} \cdot (i\omega)^{-\alpha}$) it is described by the CPE factor and the parameter $\alpha$. For the ideal capacitor $\alpha=1$, the CPE factor is the meaning of the capacitance.

Fig. 11. (a) Nyquist graphs for diamond layer samples with a quality coefficient of 0.999 (sample A) and 0.975 (sample B). (b) Substitute circuit used to model the impedance characteristics of the layers [A.2.4.]

The numerical simulation, using equivalent circuit, of the experimental results of impedance spectra, have been summarized in Table 4.

Table 4. Parameters of numerical matching of replacement circuit elements for tested electrodes [A.2.4.]

<table>
<thead>
<tr>
<th>Sample</th>
<th>$R_1$ [\Omega]</th>
<th>$R_2$ [\Omega]</th>
<th>$R_3$ [\Omega]</th>
<th>$R_4$ [\Omega]</th>
<th>$C_1$ [F cm$^{-2}$]</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>310</td>
<td>$2.03 \times 10^4$</td>
<td>$3.8 \times 10^{-10}$</td>
<td>0.79</td>
<td>2.1 $\times 10^4$</td>
</tr>
<tr>
<td>B</td>
<td>140</td>
<td>$514 \times 10^4$</td>
<td>$4.5 \times 10^{-6}$</td>
<td>0.99</td>
<td>122 $\times 10^5$</td>
</tr>
</tbody>
</table>

Obtained results shows significant differences in the values of the coefficient $\alpha$ of the CPE$_1$ parameter (impedance of diamond microcrystallites) between layers with different quality. The value of $\alpha$ is closer to unity for the diamond layer with a lower quality factor, which is related to the microcrystalline size and FWHM of the diamond line (Table 3). For CPE$_2$, associated with impedance at grain boundaries, factor $\alpha$ approaches unity and shows poor dependence on the quality factor.

Analysis of changes in conductance as a function of frequency for both layers shows high agreement in the low frequency range. Up to a certain value of $\nu_c$, conductance is not dependent on frequency, and above this value it can be described by formula [24]:

$$G(\theta) = G_0 \left[ 1 + \left( \frac{\theta}{\theta_c} \right)^n \right] + A\theta^m$$

where: $A$ is a temperature-dependent coefficient, $n$ is in the range $0<n\leq 1$, $m \geq 1$, $G_0$ is associated with direct current conduction through the layer structure, taking into account grain
boundaries.

Obtained results for lower frequencies confirmed the hypothesis on the hopping conduction mechanism in diamond layers [A.2.4].

From applications point of view, the properties of the hydrogenated surface of the diamond layer mentioned in [A.2.1.] and [A.2.3.] are essential. The analysis of the role of hydrogen termination level of the diamond surface and its electrochemical properties were presented in [A.2.2.].

The electrode electrochemical properties can be changed after "processing" in the form of cathodic pretreatment and anodic pretreatment. Cathodic treatment leads to an improvement of the degree of hydrogen termination, while the anodic treatment to convert the diamond surface from hydrogen termination surface with to the oxygen termination associated with etching the amorphous carbon phase [25]. The results are presented in Figure 12. It is assumed that the concentration of hydrogen in the diamond layer is proportional to the concentration of the carbon phase of sp² hybridization [26], thus removing the sp² phase from the surface of the diamond layer can lead to the loss of electrical conductivity.

![Figure 12](image)

*Fig. 12. The cyclic voltammetry (CV) curves obtained on a diamond electrode for a Fe(CN)_6^{4/-3} depolarizer in a basic electrolyte consisting of a 0.5 M aqueous solution of H_2SO_4. Curve 1 was measured on unmodified diamond electrode, curve 2 on the diamond cathode electrode pre-treated (5 min), curve 3 after anode treatment (5 min), curve 4 after cathodic treatment (40 min) [A.2.2.]*

This phenomenon was also observed in the case of diamond layers doped with boron [27]. So I showed that correctly functioning diamond electrodes can be obtained on the basis of undoped diamond layers. Since most scientific reports related to the use of diamond layers in electrochemistry refer to boron-doped layers (about 98% according to the "Scopus" base), it can be considered an interesting result also from application point of view.
My original achievements in this area include:

- determining that doping with boron is not a necessary condition for proper operation of diamond electrodes [A.2.1.], [A.2.2.], [A.2.3.].
- determining that the key parameter affecting the electrocatalytic activity of electrodes is the concentration of the amorphous carbon phase [A.2.1.], [A.2.2.].
- demonstration that with increasing amorphous content in the diamond the kinetics of the electrode reaction are improved, but at the same time the width of the electrochemical window is reduced [A.2.3.].
- demonstration that in the case of undoped diamond layers a compromise between the appropriate quality (good quality - wide electrochemical window) and electro-catalytic activity (good quality - low $k^0$ constant) is necessary [A.2.3.].
- proposing a concept for the description of the physical mechanism of conductivity in undoped polycrystalline diamond layers used in electrochemistry [A.2.3.], [A.2.4.].

Problem III

As the structure of thin films of diamond affect the electrical transport properties?

As shown in the previous paragraphs, the electrochemical properties of diamond electrodes are strongly dependent on the carbon graphite phase (sp$^2$) content, thus also with the concentration of chemically adsorbed hydrogen on the surface of the diamond layer. Therefore, it seemed advisable to undertake research on the problem of thermal stability of the diamond surface hydrogen termination.

I published the results in [A.2.6.]. The methodology for testing the concentration of hydrogen in the layers was based on the analysis of the slope of the photoluminescent background occurring in Raman spectra (Figures 13 and 14). The Raman spectrum of single diamond crystal is flat (free of luminescent background) and temperature independent (Figure 13, spectrum for single crystal SC) [28]. The luminescent background for CVD diamonds, whose slope $S$ is determined using the formula (4), is associated with the presence of amorphous carbon and chemically adsorbed hydrogen [29]:

$$S = \frac{m}{I_G} \text{ [μm]},$$

where: $m$ - slope of the luminescence background expressed in μm, $I_G$ - integral intensity of the line G band.
Fig. 13. Comparison of the luminescence background inclination for the tested samples at different temperatures. SC - CVD single crystal [A.2.6.]

Fig. 14. Changes of the slope the luminescence background (parameter S described by the dependence (2)) in the temperature for the analyzed CVD layers [A.2.6.]

For room temperatures, the relationship between the slope of the luminescence background of the Raman spectrum and the hydrogen content in the structure studied determines the empirical dependence [30]:

\[
H[\%] = 21.7 + 16.6 \times \log(S[\mu m])
\]  

(5)

where: \(H[\%]\) is the percent fraction of hydrogen in the amorphous carbon phase, \(S\) is the slope of the luminescence background defined by the formula (2) described above.

Analysis of Figures 14a and 14b, and taking into account the dependence (3), leads to the conclusion that heating up to 600 K does not change the concentration of hydrogen contained in the sp\(^2\) phase. The observed differences are unimportant within the error (<1%), although some minor corrections of hydrogen distribution cannot be excluded as a result of migration and the probable increase of order in amorphous carbon phase [26, 31].

The obtained results indicate on the potential of application diamond layers. Diamond-based devices can also work at higher temperatures.

Another issue, which has been solved, concerned the finding of relationships between the
structure of diamond and the pressure of working gases controlled in growth process on the electrical properties of resulting diamond layers. The results of these studies are published in [A.2.7.]. In Tables 5 and 6, are collected the characteristics of the samples obtained on the basis of Raman spectra and X-ray diffractograms.

Table 5. Structural parameters determined from Raman measurements: m - the slope of the luminescence background, H - content of hydrogen in the amorphous carbon phase of the amorphous layer [A.2.7.].

<table>
<thead>
<tr>
<th>Sample</th>
<th>Pressure [mbar]</th>
<th>FWHM [cm⁻¹]</th>
<th>sp² / sp³ [%]</th>
<th>m [cm]</th>
<th>H [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Kf 221</td>
<td>20</td>
<td>7.2</td>
<td>0.30</td>
<td>1.9</td>
<td>7.5</td>
</tr>
<tr>
<td>Kf 230</td>
<td>60</td>
<td>7.5</td>
<td>0.49</td>
<td>7.1</td>
<td>11.6</td>
</tr>
<tr>
<td>Kf 217</td>
<td>100</td>
<td>8.8</td>
<td>0.53</td>
<td>10.2</td>
<td>21.6</td>
</tr>
</tbody>
</table>

Table 6. Structural parameters estimated on the basis of XRD measurements: d - interplanar distance, D - size of crystallites, Tc_{(hkl)} - texture factor [A.2.7.].

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Kf 221</td>
<td>43.98</td>
<td>2.0587</td>
<td>36.09</td>
<td>75.34</td>
<td>61.11</td>
<td>95.1</td>
</tr>
<tr>
<td>Kf 230</td>
<td>43.97</td>
<td>2.0594</td>
<td>30.16</td>
<td>75.35</td>
<td>56.30</td>
<td>84.0</td>
</tr>
<tr>
<td>Kf 217</td>
<td>44.04</td>
<td>2.0559</td>
<td>28.26</td>
<td>75.39</td>
<td>40.03</td>
<td>64.7</td>
</tr>
</tbody>
</table>

Fig. 15 presents examples of constant current characteristics of I-V of the Al-diamond-Si-Al heterojunction. They show a straightening character.

Fig. 15. Constant current characteristics of layers at RT temperature (Kf 221 - (a), Kf 230 - (b), Kf 217 - (c)) [A.2.7.].

In general, current-voltage characteristics (I-V) can be described using the relationship:

\[ I = N_V q \mu_p V \frac{V}{d} + \frac{9 \varepsilon \varepsilon_0 \theta \mu_0}{8 \varepsilon_0} \frac{V^2}{d^3} \]  

(6)

where: \( N_V \) - effective density of states in the valence band, \( \Theta \) - is the ratio of free carriers to those trapped at a given temperature, \( \mu_0 \) - mobility of holes, \( d \) - thickness of the diamond layer, \( \varepsilon \) - dielectric constant.

In the voltage range from 0 V to approx. 0.7 V, the I-V relationship is ohmic and is described
by the first part of the equation (6). Above 0.7 volts, the I-V relationship describes the second part of the equation (6). This means that in this voltage area, the current flow is controlled by a space charge limited current (SCLC).

The determined values of conductivity $\sigma_{300}$ and density of states near the Fermi level $N(E_F)$ in the SCLC area, according to the Den Boer model [32], I presented in table 7.

*Table 7. Determined values of conductivity and density of states at the Fermi level for the tested samples [A.2.7.]*

<table>
<thead>
<tr>
<th>Sample</th>
<th>$\sigma_{300}$ [$\mu$S/cm]</th>
<th>$N(E_F)$ [nm$^{-3}$meV$^{-1}$]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Kf 221</td>
<td>0.12</td>
<td>71</td>
</tr>
<tr>
<td>Kf 230</td>
<td>0.51</td>
<td>81</td>
</tr>
<tr>
<td>Kf 217</td>
<td>1.26</td>
<td>131</td>
</tr>
</tbody>
</table>

The comparison of the structural parameters of the layers summarized in Tables 5 and 6 with the values of specific conductivity and density of electron states at the Fermi level (Table 7) made it possible to conclude that as the size of diamond grains decreases, the content of amorphous carbon increases. As the content of the amorphous phase increases, the slope of the luminescence background in the Raman scattering spectra increases, which indicates an increase in the amount of adsorbed hydrogen in the amorphous phase (Table 5). At the same time, the conductivity and density of states at the Fermi level are increasing (Table 7). This confirms the hypothesis about the significant influence of shallow acceptor states associated with the hydrogen located mainly on the surface of the diamond layer. Because hydrogen is also present at the grain boundaries and in the discontinuities of the crystallite structure, its contribution to the conductivity of the diamond layer is crucial. An interesting result is also the observed decrease in the coefficient of texture $T_{C(220)}$ (Table 6) with decreasing microcrystalline size.

In order to separate the different mechanisms of conduction and to examine the temperature change in conductivity of diamond layers, compared impedance response two undoped layers of characterized by different structural parameters (Table 8), mainly different in the content of amorphous carbon [A.2.8.]. The measurements were performed in a co-planar electrodes configuration (Fig. 16a).

*Fig. 16. (a) Electrode system used during measurements. (b) Proposed replacement circuit [A.2.8.]*
The impedance spectra in the form of Coole-Colle configuration are presented in Fig. 17. A
equivalent circuit shown in Fig. 16b, was used to simulate the impedance properties of the
layers. It consists of two elements connected in series, Voigt, in which resistances $R_{gi}$ and $R_{gb}$
and capacitances $C_{gi}$ and $C_{gb}$ represent the impedance of grains of diamond (grain interior -
$R_{gi}$, $C_{gi}$) and grain boundaries ($R_{gb}$, $C_{gb}$).

Table 8. Structural parameters estimated by Raman spectroscopy and XRD diffraction techniques [A.2.8.].

<table>
<thead>
<tr>
<th></th>
<th>Pressure (mbar)</th>
<th>CH$_2$OH/H$_2$ (%)</th>
<th>Average grain sizes (µm)</th>
<th>The thickness of layers (µm)</th>
<th>sp$^3$/sp$^2$ ratio (%)</th>
<th>FWHM (cm$^{-1}$)</th>
<th>slope (cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>DPK25 (a)</td>
<td>80</td>
<td>3.00</td>
<td>0.58</td>
<td>11.50</td>
<td>24.22</td>
<td>9.4</td>
<td>9.98</td>
</tr>
<tr>
<td>DPK26 (b)</td>
<td>80</td>
<td>2.30</td>
<td>0.73</td>
<td>10.02</td>
<td>9.43</td>
<td>7.8</td>
<td>3.71</td>
</tr>
</tbody>
</table>

Fig. 17. Coole-Coole graphs obtained for diamond layers at different temperatures. (a) Layer with a sp$^2$ ~24%.
phase content. (b) Layer with sp$^2$ content ~9% [A.2.8.].

Numerical analysis taking into account, the temperature dependences of the impedance leads
to the conclusion that the capacities occurring in the system do not show temperature changes,
similarly the $R_{gb}$ resistor, the value of which is slightly dependent on the temperature. The only
element clearly sensitive to temperature changes is the resistance $R_{gi}$ (Figure 18).

Fig. 18. Temperature dependence of the resistance $R_{gi}$ of the examined layers [A.2.8.].

The conductivity across the grain boundaries should not depend on the temperature, because
with the temperature the structure of the crystallites does not change. The second process
associated with the interior of crystallites, and therefore also their defects and absorbed
hydrogen, may exhibit temperature variability due to the semiconducting nature and ability of
hydrogen to create shallow trap levels. This process, revealed for low temperatures, is clearly
visible for the sample Dpk26 (Fig. 17b), which probably results from the comparable quality of the crystallites of the examined layers, while definitely different amounts of amorphous carbon in the layers (Table 8).

For further studies the different diamond layers were used: non-doped and doped with varying degrees of boron doping [A.2.9.]. Structurally, the samples were studied by SEM, Raman and XRD spectroscopy. The electrical properties were studied using temperature-dependent DC characteristics and the QDLTS (Charge-based Deep Level Transient Spectroscopy) method. The use of the QDLTS method was oriented on detection of all active trap levels in the certain temperature range [33].

Structural differences between the layers are presented in Table 9.

Table 9. Structural parameters of the examined layers [A.2.9.].

<table>
<thead>
<tr>
<th></th>
<th>Dpk18</th>
<th>Ax768-3</th>
<th>Ax767-3</th>
</tr>
</thead>
<tbody>
<tr>
<td>B₂H₆</td>
<td>%</td>
<td>-</td>
<td>0.05</td>
</tr>
<tr>
<td>Average grain sizes (SEM)</td>
<td>μm</td>
<td>0.88</td>
<td>0.47</td>
</tr>
<tr>
<td>The thickness of layers</td>
<td>μm</td>
<td>7.5</td>
<td>2.5</td>
</tr>
<tr>
<td>sp²/sp³ ratio (f)</td>
<td>%</td>
<td>1.5</td>
<td>2.45</td>
</tr>
<tr>
<td>FWHM</td>
<td>cm⁻¹</td>
<td>7.9</td>
<td>11.2</td>
</tr>
<tr>
<td>Slope (m)</td>
<td>cm</td>
<td>5.4</td>
<td>23</td>
</tr>
<tr>
<td>The hydrogen content (H)</td>
<td>%</td>
<td>2.6</td>
<td>13.7</td>
</tr>
<tr>
<td>Texture coefficient (111)</td>
<td>%</td>
<td>5.1</td>
<td>6.0</td>
</tr>
<tr>
<td>(220)</td>
<td>%</td>
<td>74.6</td>
<td>29.5</td>
</tr>
<tr>
<td>(331)</td>
<td>%</td>
<td>20.3</td>
<td>64.5</td>
</tr>
</tbody>
</table>

For the sample Dpk18 a series of measurements of the current response to voltage changes in the diamond/n-Si system was made at temperatures from nitrogen to RT (Fig. 19a). For low voltage values, the current density can be described by the dependency [34]:

\[
J = N_V q \mu_p \frac{V}{d} \exp \left( -\frac{E_a}{kT} \right)
\]  

(7)

where: \( N_V \) - density of states in the valence band (\( 10^{19} \) cm\(^{-3} \) for diamond), \( q \) - elementary charge, \( \mu_p \) - mobility of majority carriers (holes), \( V \) - polarization voltage, \( d \) - layer thickness, \( E_a \) - activation energy.

Using the relationship (7) from the Arrhenius graph (Fig. 19b), the value of the activation energy was estimated: \( E_a = 0.064 \) eV.
Activation energy measurements were repeated using the QDLTS method (Figure 20a). The obtained result \( E_a = 0.055 \, \text{eV} \) is consistent (within the error limits) with the designated I-V-T techniques. The obtained activation energy values indicate the occurrence of shallow acceptor states.

QDLTS tests were carried out for boron doped layers, yielding activation energy values: \( \text{Ax768-3: } E_a = 0.046 \, \text{eV}, \text{Ax767-3: } E_a = 0.038 \, \text{eV} \) and cross sectional values for capture \( \sigma_{n,p} \) in the range \( 1 \times 10^{-21} – 1 \times 10^{-23} \, \text{cm}^2 \), for all layers.

The boron doping due to the mismatch of ionic radiuses affects the structural properties of the diamond layers (Table 9); i.e., the average crystallite size decreases, the amount of amorphous phase and the hydrogen contained in it decreases, which affects the electrical properties of the layers. Probably the higher hydrogen content for the doped layers, increasing with the doping level, will increase the concentration and energies of acceptor level associated with hydrogen and the decrease in the activation energy value is observed. The values of active cross-sections to the uptake are characteristic of point defects and dangling bonds. In the analyzed temperature range, the energy levels characteristic of the boron acceptor, were not identified [35]. It follows that doping with boron does not change the nature of the conductivity of the diamond layers in the studied temperature range and may be important for higher
temperatures.

In the publication [A.2.10.], the results of the studies of undoped diamond layers synthesized at different hydrocarbon concentrations in the reaction working gas (MCD-2.3 2.3%, MCD-2.5 2.5%, MCD-2.7 2.7%) on n-type silicon (111). The X-ray diffraction method (XRD) was used to determine structural parameters of layers (Table 10) and I-V-T characteristics in the voltage range of (-5V to +5V DC) in the temperature range of 90 K - 300 K, allowed to analyze the mechanisms charge transport.

<table>
<thead>
<tr>
<th>Sample</th>
<th>L(1 1 1) [nm]</th>
<th>L(2 2 0) [nm]</th>
<th>T_{C(111)} [%]</th>
<th>T_{C(220)} [%]</th>
<th>T_{C(311)} [%]</th>
<th>T_{C(331)} [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>a) MCD-2.3</td>
<td>36</td>
<td>67</td>
<td>1.4</td>
<td>84.3</td>
<td>3.0</td>
<td>11.3</td>
</tr>
<tr>
<td>b) MCD-2.5</td>
<td>34</td>
<td>56</td>
<td>2.5</td>
<td>81.1</td>
<td>2.4</td>
<td>14.1</td>
</tr>
<tr>
<td>c) MCD-2.7</td>
<td>25</td>
<td>36</td>
<td>4.9</td>
<td>73.2</td>
<td>6.4</td>
<td>15.4</td>
</tr>
</tbody>
</table>

In summary, as the average crystallite size decreases, the number of grains directed (220) decreases and the number of targeted crystals (111), (311), (331) increases. The analysis of DC diagrams (Fig. 21a and b) allows for the separation of parts with an ohmic character of conductivity and a part controlled by a space charge, from which on the basis of [36] the conductance values described by the formula were calculated:

$$\sigma = q\mu_p N_v \exp \left(-\frac{E_F}{kT}\right),$$  \hspace{1cm} (8)

where: $E_F$ - Fermi level.

![Fig. 21. a) Characteristic IV for sample MCD-2.3, b) logarithmic graph of changes in current density as a function of voltage for the conductive direction of the structure under studies (Au-diamond-Si-Au electrode system) [A.2.10.].](image)

Taking into account the linear changes in the conductivity as a function of $T^{1/4}$ function (Fig. 22), it seems reasonable to use the Mott model [37] of variable-range hopping conductivity (VRH - Variable Range Hopping).
In the VRH model for low temperatures, the charge is transferred via energy states nearby Fermi levels, the density states \( N(E_F) \) described by the relationship:

\[
N(E_F) = 2.12 \times 10^9 \times \sigma_{oo}^3 \times T_0^{\frac{1}{2}} \left[ eV^{-1} \times cm^{-3} \right], \tag{9}
\]

where: \( \sigma_{oo} \) and \( T_0 \) are experimental constants.

At the set temperature, the distance (R) and energy (W) of hopping are described as:

\[
R = \frac{9}{8\pi\kappa TN(E_F)}, \tag{10}
\]

\[
W = \frac{3}{4\pi R^3 N(E_F)}, \tag{11}
\]

where: \( \alpha \) - the measure of the extent of the localized function, expressed by the formula:

\[
\alpha = 22.52 \times \sigma_{oo} \times T_0^{\frac{1}{2}} \left[ cm^{-1} \right]. \tag{12}
\]

The determined values of R and W (Table 11) of the examined diamond layers indicate their dependence on structural parameters, especially preferential orientation, which may be related to the observed different susceptibility to structure defects for different crystallographic planes. Diamonds in polycrystalline layers increase initially in the X, Y and Z directions, and after the coalescence step they grow only in the Z direction, forming columnar structures. The nucleation density and the synthesis conditions (especially the temperature of the substrate) determines the growth rate of crystallites and their crystalline perfection.

\[
Table 11. Parameters of the Mott model of the examined layers [A.2.10.].
\]

<table>
<thead>
<tr>
<th>Sample</th>
<th>( \alpha ) [cm(^{-1})]</th>
<th>( N(E_F) ) [eV(^{-1}) cm(^{-3})]</th>
<th>R [cm]</th>
<th>W [meV]</th>
</tr>
</thead>
<tbody>
<tr>
<td>a) MCD-2.3</td>
<td>1.68 \times 10^5</td>
<td>1.66 \times 10^{15}</td>
<td>1.49 \times 10^{-5}</td>
<td>43.5</td>
</tr>
<tr>
<td>b) MCD-2.5</td>
<td>2.01 \times 10^5</td>
<td>7.14 \times 10^{14}</td>
<td>1.76 \times 10^{-5}</td>
<td>60.7</td>
</tr>
<tr>
<td>c) MCD-2.7</td>
<td>1.47 \times 10^5</td>
<td>2.21 \times 10^{14}</td>
<td>2.56 \times 10^{-5}</td>
<td>142.3</td>
</tr>
</tbody>
</table>
Analyzing the data presented in Table 11, I found that in the studied temperature range, the estimated values of $W$ and $\alpha$ meet the conditions of $W > kT$ and $aR > 1$, which is a necessary condition for the applicability of the Mott model [37]. It can therefore be assumed that at temperatures slightly lower than RT, the electrical conductivity of the diamond layers is dominated by the variable-range hopping conductivity through states localized near the Fermi level. The density of states changes with the change of crystallite size and the preferential orientation of the crystallites in the layer. This means indirectly that defects (point) and imperfections (dislocations) of the crystalline structure, which results from technological parameters in the HF CVD process, play a dominant role here.

My original achievements in this area include:

- confirmation of the key significance of the amorphous carbon content in the electric conductivity in polycrystalline diamond layers [A.2.8.],
- demonstrating that heat treatment in an inert atmosphere does not change the degree of hydrogen termination of the diamond surface - temperature stability [A.2.6],
- showing the significance of the degree of hydrogen termination on the electrical conductivity of the un-doped diamond layers [A.2.7.],
- confirmation of the occurrence of shallow acceptor states related to the absorbed hydrogen on diamond surface and its role in transport mechanism in un-doped diamond layers [A.2.8.],
- confirmation that the activation energy values obtained for both the un-doped and boron doped layers are characteristic for shallow acceptor trap levels [A.2.9],
- demonstration that in the RT-400K temperature range no holes associated with boron doping are involved in the charge transport mechanism [A.2.9],
- it was shown that the studied temperature ranges main transport mechanism is Variable Range Hopping (VHR) [A.2.10.],
- estimation that the $R$ range of the VHR conductivity and its activation energy $W$, well meet the criteria of the Mott model [A.2.10].

Problem IV

What are the possibilities of using diamond layers in dosimetry? Thermoluminescence (TL) and cathodoluminescence (CL)
After structural analysis (SEM, Raman spectroscopy), the TL curve of the diamond layer after exposure to $\alpha$ and $\beta$ radiation were recorded. The results of measurements of the glow curves were published in [A.2.11.]. The analysis of TL curves indicates the independence of the shape of TL curves from the type of irradiation. Deconvolution (using the Glow-Fit program, assumed first-order kinetics) indicated the existence of three maxima for temperatures of 620 K, 550 K and 430 K. Calculated values of activation energies in the case of $\alpha$ radiation have following values: 0.86 eV, 0.31 eV and 0.29 eV respectively, and for $\beta$ radiation: 0.83 eV, 0.43 eV, 0.25 eV.

![Glow curves](https://example.com/glow_curves.png)

*Fig. 23. The glow curves of the examined layer after exposure to radiation a) $\alpha = 27$ Gy, b) $\beta = 940$ Gy [A.2.11.]*

The observed difference in the intensity of the glow curves for different types of radiation results from different irradiation doses and different depths of penetration. The quality of the crystallites of the layer is also important. The diamond layers used for the research were characterized by good quality of the crystal structure (FWHM of the diamond line was 4.3 cm$^{-1}$) and a small concentration of the amorphous phase of about 2%. The dominant thermoluminescent trap band with activation energy $E_a = 0.8$ eV allows registration of even weak signals, and the temperature range of release of traps (from 500 K to 600 K) is high enough to prevent spontaneous emission under normal storage conditions (so-called *fading*).

The research was carried out in terms of the use of undoped diamond layers in oncological diagnostics as passive dosimeters. Particular attention is paid to the precision of measurement, the ability to detect small doses, linearity of the thermoluminescent response, independence from the type of radiation and the size of the dose, and the potential miniaturization of the potential dosimeter.

Based on measurements of catholuminescence spectra (CL) [A.2.12.], I obtained basic knowledge about possible types of defects in layers (Fig. 24a).
Visible (Fig. 24a) maximum at 430 nm is identified as the A-band, while the weaker line at 501 nm is the center of H3 (N-V-N), respectively associated with the occurrence of associated dislocation with two nitrogen atoms [38, 39]. The presence of nitrogen admixture in undoped layers is possible, due to the presence of this element in residual gases at many technological stages of the layer synthesis itself. For the second layer, the same results of cathodoluminescence were obtained.

The quality of the crystal structure, amorphous carbon content, defect concentration and associated concentration and distribution of trap levels have the biggest influence on the thermoluminescent properties of diamond layers. The obtained after preheating (450°C - emptying traps) and irradiation of β (940 Gy, source ⁹⁰Sr/⁹⁰Y) (Fig. 24b), the glow curves (heating speed 1 K/s) for the examined layers differ only in intensity, while maintaining a similar shapes, which is understandable because of different layer thicknesses. This confirms the thesis about the possibility of repeatable synthesis of diamond layers for applications in passive dosimetry (TL).

Despite the small thickness of the layer and the small dimensions of the samples (2x2 mm),
the obtained glow curves indicate a clear maximum at about 640 K (Fig. 25). The dependence of the intensity of the TL curve on the dose size (insert, Fig. 25) shows a linear relationship, which potentially fulfills the condition of applicability of this material in passive dosimetry. Attention should also be paid to the previously unpublished results indicating the relationship between the predominant orientation of crystallites in polycrystalline diamond layers with cathodoluminescence and, as a consequence, the shape of thermoluminescence curves (for UV and X radiation).

If in the layers predominate crystallites with orientation (400), generally the cathodoluminescence has the shape shown in Fig. 26a and the maximum of the thermoluminescence spectrum at a temperature of around 370 K (curve (a), Fig. 27, without a clear maximum at high temperatures).

![Fig. 26. a) Cathodoluminescence spectrum recorded for layers with predominantly crystallite orientation (400), b) cathodoluminescence of a layer with a comparable amount of crystallites (111), (220) and (400) [B.10.16].](image)

For layers with comparable percentage of crystallites of type (111) or (220) and (400), the catholuminescence spectrum has the most common shape as in Fig. 26b and the curve TL as in Fig. 27 (curve (a), has two maxima).

![Fig. 27. TL curves for layers with different preferential crystallite orientations.](image)

Summarizing the above and the results of the works [A.2.11] and [A.2.12], it should be noted
that it is possible to synthesize diamond layers with reproducible thermoluminescent properties.

My original achievements in this area include:

- prove that the shape of the glow curves undoped diamond layers is not dependent on the type of radiation [A.2.11.],
- show that the obtained glow curves can be broken down into two components described by 1st order kinetics [A.2.11.],
- an indication that the main maximum of the glow curves is observed at temperatures above 600 K [A.2.11.], [A.2.12.],
- show that the parameter values of the main TL spectral component (maximum 640 K) has the activation energy of approx. 0.9 eV and the so-called capture speed of $10^{-8}$ s [A.2.11.],
- show that the preferential direction of crystal structure growth of the diamond layer determines its thermoluminescence and catholuminescence properties [A.2.12.].

The research carried out in this part of the study, clearly indicates the potential applications of diamond layers in clinical dosimetry. This is particularly important due to the biocompatibility of diamond and human tissues, whose effective atomic numbers are respectively $Z_{\text{dia}}=6$ and $Z_{\text{tk}}=7.6$. In addition, the diamond is a non-toxic material and resistant to any type of radiation.

B.1.3. **Summary and perspectives**

The monothematic series of works, which I presented as the main scientific achievement, concerns the mechanisms of electrical conductivity and electrochemical and dosimetric properties of thin undoped diamond layers. In my opinion, the significant contribution of this work to the development of thin layer physics lies in the determination of the impact of the amorphous phase and defects on the physical properties of thin polycrystalline films. The results obtained by for thin layers of polycrystalline diamond, can be used as reference point for other polycrystalline materials.

I would like to emphasize that the experimental results presented in the publication cycle cover a wide range of research, ranging from the determination of parameters allowing the control of morphological properties of thin diamond layers through structural, electrical,
electrochemical and optical measurements.

In summary, in the scientific cycle of publications presented as a scientific achievement, I proved that:

- doping with boron is not a prerequisite for the use of diamond layers as an electrode material in electrochemistry,
- acceptor states related to the admixture of boron do not take part in electrical conductivity at temperatures below 120°C,
- amorphous carbon phase play a special, specific role in the polycrystalline layer,
- existence of shallow acceptor states is associated with the hydrogen termination of the diamond layer,
- the degree of hydrogenation of the surface of the diamond exhibits temperature stability,
- at RT and lower temperatures, the charge transport mechanism has hopping character and is in full agreement with the Mott (VHR) model,
- thermoluminescent properties indicate the applicability of the polycrystalline diamond layer in passive dosimetry.

The obtained results enabled a full description of the physical properties of the diamond layers obtained with the HF CVD method, which is the basis for the search and evaluation of potential application possibilities. These results can be treated as a sufficient basis for continuing work on selected applications. This is also important cognitive, because so far the vast majority of published works and available applications have been associated with doped layers, in particular with boron doped.

C. Discussion of other scientific and research achievements

C.1. Description of the scientific activity before obtaining the doctoral degree

After graduating from master's studies in 1984 and completing basic military service for graduates, I started work (in 1987) at the Research and Development Center of Electronic Specialized Systems Mera OBREUS in Toruń, as an assistant-technologist at the DC1 lab, headed by dr. Andrzej Sobkowiak. Work in Mera OBREUS and then, after ownership transformations in Vigo Sensor S.A. and VigoTor Sp. z o.o. she was very inspiring to me and from the perspective of years, I think, she shaped me for life. Initially, I was responsible for
controlling the purity of technological lines in the processes of diffusion and redifusion and metallization. As is known, obtaining a p-n coupling by diffusion into silicon is a complex process. One of the main challenges was to obtain a masking layer of silicon oxide, which at every stage of production would maintain high dielectric properties. This created the following problems (1) the oxide layer had to fulfill a satisfactory protective role and (2) the increase, due to the required thickness of the oxide, had to be, for practical reasons, fast enough. In practice, the "dry-wet-dry" oxidation method is used, i.e. initially oxidation is carried out at high temperature (about 1100°C) in the presence of oxygen to add water vapor to the atmosphere after a certain period of time, obtaining lower quality oxide, but growing faster after the oxidation process ends in the atmosphere of oxygen itself. The main contamination of silicon oxide are sodium ions, which due to the specificity of the oxide growth process, especially at the "wet oxidation" stage, can easily penetrate into the volume of the layer, causing a change in its dielectric properties. Methods of controlling the content of sodium ions in the oxide layers developed and implemented by me in Mera OBREUS are described in Appendix 3, point C.16.5.

Ownership changes of Mera OBREUS and transformation of the Center into a typical production enterprise resulted in personnel changes. The departure of many key employees resulted in consolidation of the duties of other team members. Future projects such as the gas sensor have been abandoned. The increase in market demand, especially on pressure sensors and reference diodes (temperature-stable Zener diodes), resulted in two projects that I co-authored. The first is a position for eutectic connection of silicon wafers (with ready-made structures) with glass, the second is the position-idea of filling the pressure sensor elements with silicone oil as the separating factor of the appropriate silicon diaphragm of the sensor from the stainless steel membrane. The projects were innovative, and their quality is evidenced by the fact that they became part of the production line and until 2000, in which the silicon technology department was liquidated, they worked without any problems.

The creator of the reference diode, Dr. Andrzej Sobkowiak, died several months after my employment at Mera OBREUS. Over the next years, the designs, both the reference diode and the pressure sensor, were subject to numerous modifications. I participated in these works, expanding the range of products offered. However, I was always mainly interested in experimental work, which is why I focused on optimizing technological processes. Most of the original solutions and significant technological changes were published in periodic reports and internal company studies. Unfortunately, even if these documents survived, I do not have access to them.
In 2005, I was employed at the Department of Physics at the Kazimierz Wielki University in Bydgoszcz. In the described period, the apparatus base of the Cathedral was very modest. Thanks to the sensible and well thought-out policy of the Chair of the Department in matters of acquiring technological and measuring equipment and my work, in a short time the Thin Layer Technology Laboratory was created and (with the substantive support of Professor Waclaw Balá) the first advanced positions of electrical measurements. Among other things, it was possible to transform the Department of Physics into the Institute of Physics and the planned opening of the second degree of study in the field of Physics.

In the period up to 2013, i.e. before obtaining the degree of doctor of physical sciences, I was the author and in most cases the main contractor of the following technological positions: HF large surface reactor CVD, prototype stand for vacuum deposition of organic layers (e.g. phthalocyanin), positions for applying organic layers spin-coating system. I modernized the stand for gold and aluminum metallization using the method of evaporation from resistively heated sources and a separate station for vapor deposition of refractory metals using an electron gun. The most important measuring stations designed and personally made can also include: IV(T) DC measurement station enabling testing in the range of nitrogen temperatures up to RT, AC test stand (frequency range 1 mHz to 5 MHz, in temperatures from nitrogen to 400°C), stand prototype for measurements using the QDLTS method (temperature range 0°C to 120°C), and prototype stand for low-temperature TSC (Thermally Stimulated Current) measurements.

The areas of my scientific interests in the discussed period mainly concerned polycrystalline diamond layers, their electrical and partly optical properties [B.1.25.-B.1.27.], [B.1.31.], [B.1.32.], [B.3.6.], [B.3.8.] and organic layers [B.1.28.-B.1.30.], [B.3.2.], [B.3.3.-B.3.5.], [B.3.7.] as well as their potential application possibilities. One of the previously unused application projects was a prototype of an organic transistor (master's thesis). Another issue that I am developing, is a sensor realized as a SGFET (Solution Gated Field Effect Transistor) transistor in which the active area is a polycrystalline diamond layer. So far, prototypes of the device have been made and the work on its development is being continued. At present, the doctoral dissertation of Lidia Mosińska, in this area of research (supervisor of the work of professor Kazimierz Fabisiak), which I am the auxiliary promoter, is being finalized.

C.2. Description of scientific activity after obtaining the doctoral degree

In the period after obtaining the doctoral degree, I focused my interests around undoped and doped polycrystalline diamond layers [B.1.20.], [B.1.21.], [B.1.23.], [B.3.1.] and research
in the area of selected issues related to oxide compounds, in particular complex A3B5O12 grenades (A = Lu, Y, Gd, B = Al, Sc, Ga) crystallized in the form of monocristalline layers, by rainbow epitaxy (LPE growth) [B.1.1. - B.1.13.], [B.1.15. - B.1.19.].

I deal with the subject of research on oxide compounds and related materials as a contractor of grants. I conduct research in the field of cathodoluminescence measurements of layers and precise estimation of the elemental composition of both studied substrates as well as layers synthesized on them. Their composition is controlled by the EDS (Energy-Dispersive X-ray Spectroscopy) method. In this method, the correct calibration of the measuring device, stability of measurements and correct interpretation of results are extremely important. This was achieved thanks to the creation of dedicated algorithms that allow for repeatability of initial settings and software written from scratch to analyze the results obtained and to some extent automate the process of this analysis. While the EDS measurements are for my research the correctness of the applied synthesis technology, the measurements of the cathodoluminescence of the layers are an actual examination of their optical properties. In addition to the registration of the classic spectrum of catholuminescence, I also examine the dependence of spectra on the energy of the electron beam and the time of exposure of electrons to the layer. This allows a more complete description of the layers and analysis, among others, of their homogeneity towards the substrate and the proper distribution of possible admixtures.

The subject matter concerning diamond layers was an extension of the theoretical and experimental work previously conducted at the Institute of Physics. In addition to the issues discussed in point A of the Annex 2, which constitute "an achievement resulting from art. 16 sec. 2 of the Act ", my research focused on determining the electrical and optical properties of diamond layers in combination with the possibilities of deliberate selection of technological parameters of synthesis. Such determination of priorities was caused by ongoing work on developing the application capabilities of the layers. In order to find a practical application of the prototype of the SGFET transistor based on the CVD diamond, it was necessary to conduct experimental work on matching the electrical properties of the gate, which is a diamond layer. These properties depend on a number of factors: the size and orientation of the crystallites, the content of the amorphous phase, and finally the quality of the layer, i.e. on the type and distribution of the defects. This is a difficult issue, requiring a complex theoretical analysis, as well as experience in the field of diamond film technology. The result of my work was to gain control over the desired ordering of diamond microcrystallites, the rate of layer growth, its quality and the content of amorphous carbon.
In a sense, the "accidental" effect of my research was to see the possibility of using catholuminescence measurements of undoped diamond layers to determine the suitability of these layers in the work on their use in the construction of active and passive detectors of ionizing radiation. The results of these works have so far been published in the form of two master's theses, which I was a promoter and one conference speech. The results of thermoluminescence (TL) of undoped diamond layers confirmed their application potential as ionizing radiation detectors. It turned out that the recorded glow curves of layers exposed to ionizing radiation have a similar shape with a maximum at a temperature of about 500 K, which does not depend on the type of radiation (UV, X, α, β). There were also promising tests of the dependence of changes in the maximum intensity of the TL signal on the radiation dose (linear relationship) and the time of relaxation to the basic state (detector memory).

C.3. Future plans and research directions

In the future, I would like to continue my further scientific development in terms of what constitutes my main research passion, i.e. experimental works in the field of technology for the production of new materials and the development of experimental and measurement techniques for testing their physical properties.

In the subject area of oxide compounds, described in item C.2., I would like to extend the scope of EDS control measurements to X-ray diffraction measurements and measurements of Raman scattering on layers. Raman measurements, especially in confocal technique, carry information about the distribution along the Z axis (along the depth of the layer), which should correlate with the measurements of cathodoluminescence at different excitation energies. X-ray diffraction can confirm the existence of a layer with the expected crystalline structure and indicate structural defects.

Obtained so far results of research on undoped diamond layers are very promising. I would like to continue to develop these studies, but to orient them towards the application side. This approach will require some modifications and hardware retrofits that will allow, for example, the application of ohmic contacts to the diamond layer in the form of titanium electrodes. At the moment I am taking part in advanced works on a passive dosimeter model based on an undoped diamond layer. Previous results of measurements made in cooperation with medical physicists are promising and open perspectives on the target use of this type of dosimeters in oncological radiotherapy. The growing number of cancer cases (global forecasts predict in 2050 about 18 million deaths from cancer and about 27 million new cases), forces the development of prophylaxis and new therapies including therapeutic radiology, which in the
initial stage of disease development, acts locally destroys cells pathological, and during surgical treatment, it is used as part of intraoperative procedures. New methods of treatment, such as three-dimensional radiotherapy, radiotherapy with intensity modulation or radiosurgery, force the use of more precise instrumentation, both in relation to the dose and field of action. Precise determination of radiation dose requires more often miniature dosimeters. constructed from biocompatible materials with the human body.

Continuing work on the use of diamond layers in the dosimetric applications described will be crucial. Diamond is an allotropic variety of carbon, it is chemically pure and ecological, it is also characterized by "tissue equivalence", i.e. the amount of radiation absorbed by the "diamond dosimeter" will be approximately compatible with the amount absorbed by the biological material due to similar values of the atomic number of diamond and tissue soft.


<table>
<thead>
<tr>
<th></th>
<th>Before obtaining the doctoral degree (January 2013)</th>
<th>Now (data from 23/04/2018)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Scopus database</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Indeks Hirscha</td>
<td>3</td>
<td>8</td>
</tr>
<tr>
<td>Number of publications (JCR database)</td>
<td>12</td>
<td>50</td>
</tr>
<tr>
<td>Number of citations **</td>
<td>15</td>
<td>160</td>
</tr>
<tr>
<td>The average number of citations for work **</td>
<td>1.25</td>
<td>3.2</td>
</tr>
<tr>
<td>Total Impact Factor *</td>
<td>15.551</td>
<td>80.996</td>
</tr>
<tr>
<td>The sum of MNiSW points ***</td>
<td>255</td>
<td>1240</td>
</tr>
<tr>
<td><strong>Web of Science database</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Indeks Hirscha</td>
<td>2</td>
<td>7</td>
</tr>
<tr>
<td>Number of publications (JCR database)</td>
<td>9</td>
<td>46</td>
</tr>
<tr>
<td>Number of citations **</td>
<td>16</td>
<td>167</td>
</tr>
<tr>
<td>The average number of citations for work **</td>
<td>1.7</td>
<td>3.63</td>
</tr>
<tr>
<td>Total Impact Factor *</td>
<td>15.551</td>
<td>78.34</td>
</tr>
<tr>
<td>The sum of MNiSW points ***</td>
<td>255</td>
<td>1205</td>
</tr>
</tbody>
</table>

* Data consistent with the year of publication. ** For the period before the doctorate, current values were given until 2013. *** According to the list of Ministry of Science and Higher Education (26.01.2017)
D. Bibliography