Příprava a vlastnosti THz vlnovodu založeného na sp\(^2\) a sp\(^3\) hybridizovaném uhlíku

Deposition and properties of sp\(^2\) and sp\(^3\) hybridized carbon layer for THz waveguide application

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Diploma Thesis Assignment

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Title: Příprava a vlastnosti THz vlnovodu založeného na sp2 a sp3 hybridizovaném uhliku
Deposition and properties of sp2 and sp3 hybridized carbon layer for THz waveguide application

Description:
Obsahem práce bude příprava uhlikových vrstev (aC, aC:H) na křemíkovém (Si) substrátu. Technologie přípravy bude založena na chemické depozici z plynné fáze. Vzláštní pozornost bude věnována závislosti kvality vrstev na teplotě substrátu. Motivací této práce je použití těchto vrstev pro THz vlnovody. Dále práce bude obsahovat strukturní a elektronové charakterizace těchto vrstev. Předpokládané charakterizační techniky jsou vodivost, Ramanovská spektroskopie, optické metody (elipsometrie).

The thesis focuses on preparation of carbon layer (aC and aC:H) on Si substrate using photoemission-assisted plasma-enhanced chemical vapor deposition. Special attention will be paid to quality of the films with substrate temperature. The motivation of this work is application of those layers for THz waveguides. Furthermore, the thesis will contain structural characterization of those layers as well as characterization of their electronic structure using various techniques. The envisaged characterization techniques to study those films are conductivity, Raman spectroscopy and optical methods (ellipsometry).

References:

Extent and terms of a thesis are specified in directions for its elaboration that are opened to the public on the web sites of the faculty.

Supervisor: Mgr. Jaroslav Hamrle, Ph.D.

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V Ostravě dne 15. května 2014

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I declare, that I have worked up this Diploma Thesis myself. I have presented all References that I used.

Ostrava May 15th 2014
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Also, I would like to express my gratitude to doc. Dr. Ing. Kamil Postava who helped me with optical measurements of prepared samples and finally to my supervisor Mgr. Jaroslav Hamrle, Ph.D. for his leadership and factual comments. Both previously named from Nanotechnology Center and Department of Physics, VŠB-Technical University of Ostrava.
Tato práce měla za úkol vyvinout vlnovod/opláštění z diamantu-podobné uhlíkové (DLC) vrstvy pro THz injekční laser s grafenovým kanálem. DLC vrstva, která sestává z $sp^2$ a $sp^3$ hybridizovaného uhlíku, je nanesena pomocí stejnosměrné fotoemisí-asistované plazmové depozice z plynné fáze (PA-PECVD) při různých teplotách a dosažitelných tloušťkách s cílem dosáhnout tloušťky nejméně $10 \mu m$ pro použití jako THz vlnovod/opláštění, na $n$-dopovaném, nebo nedopovaném Si substrátu. Vliv teploty nanášení na vlastnosti DLC vrstvy byl zkoumán pomocí stejnosměrného měření vodivosti, měření dielektrické konstanty pomocí střídavého proudu v oblasti MHz frekvencí, měřením za pomoci spektroskopie sekundárních iontů (SIMS), Ramanovy spektroskopie, spektroskopické elipsometrie, FTIR spektroskopie a THz spektroskopie. Z výsledků je zřejmé, že struktura DLC vrstev se mění s nárůstem teploty a s jejím nárůstem se chová více jako vodič a skládá se z více $sp^2$ vázaných atomů uhlíku namísto $sp^3$ vazeb. To má za následek možnou výrobu silnější dielektrické vrstvy se zvýšením teploty, ale rovněž snížení jeho schopnosti použití jako vlnovod. Nicméně, při asi $200 ^\circ C$ jsme byli schopní vytvořit dostatečně silné DLC vrstvy, které by měly mít stále vhodné vlastnosti pro použití jako vlnovod/opláštění grafenové vrstvy pro injekční laser v THz oblasti.

**Klíčová slova:** THz vlnovod, fotoemisí-asistovaná plazmovou-iniciovaná chemická depozice z plynné fáze (PA-PECVD), diamantu-podobný uhlík (DLC), vlnovod z hybridizovaného uhlíku.
Abstract


In this study we are developing Diamond-Like Carbon (DLC) waveguide/cladding layer for graphene-channel THz injection laser. DLC layer, consisting of \(sp^2\) and \(sp^3\) hybridized carbon, is deposited by DC Photoemission-Assisted Plasma-Enhanced Chemical Vapor Deposition (PA-PECVD) at different temperatures and achievable thicknesses, with goal to achieve at least 10 µm thickness for THz waveguide, on \(n\)-doped or \(n\)-non-doped Si wafer. The influence of deposition temperature on DLC properties has been investigated by means of DC conductivity measurement, AC dielectric constant measurement in MHz region in standard MIS configuration, SIMS measurement, Raman spectroscopy, spectroscopic ellipsometry, FTIR spectroscopy and THz spectroscopy. From the results it is clear, that the DLC structure changes with increase of deposition temperature to act more like conductor and consists of more \(sp^2\) bonded carbon atoms instead of \(sp^3\). This results in possible thicker dielectric layer deposited at higher temperature in used DC plasma device, but decrease of its ability to be used as a waveguide. However, at about 200 \(^\circ\)C we are able to deposit sufficiently thick DLC layers, which should still has suitable properties as a waveguide/cladding in THz region.

Keywords: THz waveguide, Photoemission-Assisted Plasma-Enhanced Chemical Vapor Deposition (PA-PECVD), Diamond-Like Carbon (DLC), hybridized carbon waveguide.
**List of Used Abbreviations and Symbols**

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<td>AC</td>
<td>Alternating Current</td>
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<tr>
<td>a-C</td>
<td>amorphous carbon</td>
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<td>a-C:H</td>
<td>hydrogenated amorphous carbon</td>
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<td>AFM</td>
<td>Atomic Force Microscopy</td>
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<tr>
<td>A/O</td>
<td>analog to digital (converter)</td>
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<td>CCP-RIE</td>
<td>Capacitively-Coupled Reactive Ion Etching</td>
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<td>CVD</td>
<td>Chemical Vapor Deposition</td>
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<td>D-peak</td>
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<td>DC</td>
<td>Direct Current</td>
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<td>DLC</td>
<td>Diamond-Like Carbon</td>
</tr>
<tr>
<td>EBPVD</td>
<td>Electron Beam Physical Vapor Deposition</td>
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<td>FarIR</td>
<td>far-infrared spectral region from 400 cm⁻¹ to 10 cm⁻¹</td>
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<tr>
<td>FET</td>
<td>Field Effect Transistor</td>
</tr>
<tr>
<td>FFT</td>
<td>Fast Fourier transformation (numerical)</td>
</tr>
<tr>
<td>FTIR</td>
<td>Fourier Transform Infrared (spectroscopy)</td>
</tr>
<tr>
<td>FWHM</td>
<td>Full Width at Half Maximum of measured peak</td>
</tr>
<tr>
<td>G-peak</td>
<td>graphite peak in Raman spectra of carbons</td>
</tr>
<tr>
<td>G-CFET</td>
<td>Graphene-Channel Field Effect Transistor</td>
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<tr>
<td>HOPG</td>
<td>High Oriented Pyrolytic Graphene</td>
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<tr>
<td>HPDPECVD</td>
<td>High-Plasma-Density Plasma Enhanced Chemical Vapor Deposition</td>
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<td>IR</td>
<td>Infrared spectral region of electromagnetic radiation</td>
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<td>K-point</td>
<td>point in the reciprocal space</td>
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<td>MEM</td>
<td>Micro Electromechanical System</td>
</tr>
<tr>
<td>MidIR</td>
<td>mid-infrared spectral region from 4,000 cm⁻¹ to 400 cm⁻¹</td>
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<td>MIS</td>
<td>Metal-Insulator-Semiconductor</td>
</tr>
<tr>
<td>MLG</td>
<td>Multi Layer Graphene</td>
</tr>
<tr>
<td>MOS</td>
<td>Metal-Oxide-Semiconductor</td>
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<tr>
<td>MOSFET</td>
<td>Metal-Oxide-Semiconductor Field Effect Transistor</td>
</tr>
<tr>
<td>nc-graphite</td>
<td>nanocrystallized-graphite</td>
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</table>
NIR – near-infrared spectral region from 13,000 cm$^{-1}$ to 4,000 cm$^{-1}$

$p_x, p_y, p_z$ orbital – type of atomic orbitals forming $\pi$ bonds e.g. in graphite

PA-PECVD – Photoemission-Assisted Plasma-Enhanced Chemical Vapor Deposition

PECVD – Plasma-Enhanced Chemical Vapor Deposition

RF – Radio Frequency

RIE – Reactive Ion Etching

SIMS – Secondary Ion Mass Spectroscopy

$sp^{1,2,3}$ – hybridization state of carbon

$ta$-C – tetrahedral amorphous carbon

$ta$-C:H – tetrahedral hydrogenated amorphous carbon

THz – electromagnetic radiation spectral region usually defined by frequency between 300 GHz to 3 THz. In this work the designation THz is for radiation with frequency between 60 GHz to 3 THz (2 cm$^{-1}$ to 100 cm$^{-1}$)

TMP – Turbo Molecular Pump

UV – Ultraviolet spectral region of electromagnetic radiation

VIS – Visible Spectrum of electromagnetic radiation

Roman Alphabet

$A$ – absorbance [-]

$A_{R_0}$ – electric field amplitude of measured reference [V·m$^{-1}$]

$A_{S_0}$ – electric field amplitude of measured sample [V·m$^{-1}$]

$C_{60}$ – fullerene with 60 carbon atoms composed of five-fold and six-fold carbon rings

$C_{Si}$ – electric capacity of the Si layer in the sample [F]

$C_{Is}$ – electric capacity of the insulator layer in the sample [F]

$C_T$ – electric capacity of whole stack of capacitors [F]

$E$ – Energy [eV]

$E_r$ – field before interaction with the sample [V·m$^{-1}$]

$E_s$ – field after interaction with the sample [V·m$^{-1}$]

$I_0$ – incident light intensity [W·m$^{-2}$]

$I$ – transmitted light intensity [W·m$^{-2}$], or electric current in $I$-$V$ curves [A]

$I_D$ – intensity of $D$ peak in Raman spectroscopy [W·m$^{-2}$]

$I_G$ – intensity of $G$ peak in Raman spectroscopy [W·m$^{-2}$]
$L_a$ – in-plane correlation length [m]
$L_{IS}$ – thickness of the insulator layer in capacity measurements [m]
$R_a$ – surface line roughness parameter [m]
$R_{Holder}$ – reflectivity of the holder alone in FTIR measurement [-]
$R_{Reference}$ – reflectivity of the holder with Au reference in FTIR measurement [-]
$R_{Sample}$ – reflectivity of the holder with a sample in FTIR measurement [-]
$T$ – transmittance [-]
$T(n)$ – Fresnel reflection losses [-]
$T_{Holder}$ – transmittance of the holder alone in FTIR measurement [-]
$T_{Sample}$ – transmittance of the holder with a sample in FTIR measurement [-]
$V$ – voltage [V]
$V_B$ – bias voltage of used PA-PECVD [V]
$c$ – unspecified constant
$c_0$ – the seed of light in vacuum $c_0=299,792,458 \text{ m} \cdot \text{s}^{-1}$
$d$ – thickness of the sample [m]
$n$ – index of refraction [-], or number of primary electrons in PA-PECVD
$k_z$ – the wave vector in $z$ direction of the $m$-th layer, $(\frac{2\pi}{\lambda}) n^{(m)} \cos \theta_m$ [m$^{-1}$]
$r_p$ – reflection coefficient for a $p$ polarized wave [-]
$r_s$ – reflection coefficient for a $s$ polarized wave [-]
$x$ – unit distance [m]

**Greek Alphabet**

$\Delta$ – ellipsometry parameter defining the phase difference of the waves [$^\circ$, rad]
$\Psi$ – ellipsometry parameter defining the azimuth [$^\circ$, rad]
$\alpha$ – number of secondary electrons produced by primary electrons [-]
$\alpha$-regime – type of discharge manner in PA-PECVD
$\gamma$-regime – type of discharge manner in PA-PECVD
$\delta_p$ – phase of the $p$ polarized wave [$^\circ$, rad]
$\delta_s$ – phase of the $s$ polarized wave [$^\circ$, rad]
$\epsilon_r$ – pseudo-dielectric function of whole measured system in spectroscopic ellipsometry
\( \epsilon_0 \) - electric permittivity of vacuum \( \epsilon_0 = 8.85 \times 10^{-12} \) Fm\(^{-1}\)

\( \epsilon_1 \) - real part of the material dielectric constant [-]

\( \epsilon_2 \) - imaginary part of the material dielectric constant [-]

\( \epsilon_r \) - relative dielectric constant [-]

\( \theta \) - angle of incidence beam on the sample \([^\circ, \text{rad}]\)

\( \lambda \) - wavelength of the electromagnetic radiation (vacuum) [m]

\( \pi \)-bond - covalent bond between two atoms where two lobes of one atomic orbital overlap the two lobes of the other atom forming double kidney-like orbital

\( \rho \) - ratio between \( p \) and \( s \) polarized wave reflection coefficients [-]

\( \sigma \)-bond - direct covalent bond between two atoms formed by head-on overlapping of atomic orbitals

\( \phi_{S_0} \) - electric field phase of measured sample \([^\circ, \text{rad}]\)

\( \phi_{R_0} \) - electric field phase of measured reference \([^\circ, \text{rad}]\)

\( \phi_{Si} \) - work function of Si [eV]

\( \omega \) - angular frequency of the electromagnetic radiation [rad·s\(^{-1}\)]
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1 Introduction

Since the invention of the transistor [1] in the middle of the twentieth century, the electronics including computer technology has been amazingly developed. The first transistor was made of germanium, but this material was soon replaced by silicon due to the contrast between poor interface passivation by germanium oxide (GeO$_2$) and excellent one by silicon dioxide (SiO$_2$) [2–5]. The scaling down limit of transistor has been exceeded year by year according to the Moore's law. Now, the state-of-the-art industrial technology has reached the 22 nm half-pitch (i.e., half distance between identical features), starting to exhibit the quantum size effects. Great effort to overcome the speed limit of transistors, which is dominated and restricted by carrier mobility of the material and its size (the scaling rule), has been made, and new transistor structure designs and materials for their production introduced. One of the most promising materials is graphene.

Graphene, which is an one-atom-thick honeycomb layer of bonded $sp^2$ hybridized carbon benzene rings, has attracted much attention in the last decade because of its superior properties such as large carrier mobility (200,000 cm$^2$·s$^{-1}$), high thermal conductance, saturation velocity, and saturation current density (see for instance [6–9]). Thus, graphene is one of the candidates to replace Si as a channel material of the field-effect transistor (FET). The mass-less Dirac fermions behavior of the graphene carriers causes its extraordinary carrier mobility. A large graphene sheet without defects is a zero band-gap semiconductor, but the gap can be opened by changes in its dimensions, impurities, doping, stacking, etc. Due to the linear energy-momentum dispersion property of graphene, both electrons and holes can travel coherently, recombine, and allows emission of the THz electromagnetic wave. That is an essential property for a graphene-channel current-injection-type THz laser discussed below. It should be also noted that oxide layers such as SiO$_2$ and HfO$_2$ employed so far as a gate dielectrics for Si MOSFET’s are no longer suitable for the graphene-channel FET’s, because of the chemical interaction between the graphene and the oxide, which causes not only changes of the electronic properties of graphene but also the lattice defects via CO and CO$_2$ desorption.

Diamond-like carbon (DLC), is an amorphous carbonaceous material composed of $sp^3$ carbon, $sp^2$ carbon, and hydrogen [10]. Its electrical properties can be widely tuned by changing the ratio of those three components from a conductor to an insulator; high and low dielectric constant [11]. As an dielectric for graphene-channel devices, instead of mentioned oxide layers (SiO$_2$, HfO$_2$), DLC is promising due to its carbonaceous affinity with graphene, and chemical inertness. In one of the previous reports [12], a top-gate graphene-channel FET with a 48-nm DLC gate dielectric, which was formed by photoemission-assisted plasma-enhanced CVD (PA-PECVD), exhibited successful ambipolar characteristics.

As a photonic application of graphene an electrically-controlled terahertz (THz) laser is expected [13–18]. The system consists of a THz photonic cavity structure and to maximize the THz gain, the THz electromagnetic field must be confined in the vicinity of the gra-
phene layer. Due to the ten µm-order wavelength of the THz photons, a micrometer-scale thick insulation layer should be introduced as a cladding layer. Precise tuning of the properties of the cavity material, such as the relative dielectric constant, resistivity, band gap, and thickness is then crucial. For this purpose, the author tried to grow thick DLC films by PA-PECVD, which differs from conventional PECVD’s, as will be explained further. In a previous report by Yang [19], the influence of the source gas on DLC properties was clarified. Following this work, DLC films have been prepared by PA-PECVD at different temperatures, with goal to increase its growth time and achieve the necessary thickness at least several µm. Also, the corresponding changes of its properties with the deposition temperature has been measured. Next the annealing experiments were conducted to estimate the thermal stability of DLC films.

This study will encourage further development of THz microelectronic and laser devices, for example THz scanners, graphene-channel transistors, ultrafast THz optical triggers, etc. The description of the components and fabrication way of the proposed THz laser device is described in the theoretical background section.
2 Theoretical background

2.1 Diamond-Like Carbon (DLC)

In the last two decades, lots of important advances in science of carbon has been reported. For instance the discovery of fullerenes (C$_{60}$), and carbon nanotubes [20], or development of the chemical vapor deposition (CVD) of diamond [21–23]. Those carbon technologies were developed in parallel with each other, and also with the technology of disordered carbons. One of such material is diamond-like carbon (DLC).

Diamond-like carbon is a metastable form of amorphous carbon containing a significant fraction of $sp^3$ bonds [10]. DLC exhibits very high mechanical hardness, chemical inertness, optical transparency, and low-mobility semiconductor behavior, with a band gap between 1-4 eV [10, 24]. Because of its properties, DLC has been already implemented as protective coating for optical windows, magnetic storage discs, car parts, biomedical coatings, and also as a material for micro electromechanical devices (MEMs).

The reason for such a variety of carbon crystalline and disordered structures is its ability to exist in three hybridizations, $sp^3$, $sp^2$, and $sp^1$ (Fig. 1). In the $sp^3$ configuration, as in diamond, four valence electrons of a carbon atom are each assigned to a tetrahedrally-directed $sp^3$ orbital, which makes a strong $\sigma$ bond to an adjacent atom. In the three-fold coordinated $sp^2$ configuration, as in graphite, three of four valence electrons enter trigonally directed $sp^2$ orbitals, which form $\sigma$ bonds in a plane. The fourth electron lies in an orbital, which lies normal to the plane of the $\sigma$ bonds. This $p_z$ orbital forms a weaker $\pi$ bond with those of other atoms. In $sp^1$ configuration, two of four valence electrons enter $\sigma$ orbitals, each forming a $\sigma$ bond directed along the $x$-axis, and other two electrons enter $p_y$ and $p_z$ orbitals to form $\pi$ bonds with other orbitals [10].

The extreme physical properties of diamond are due to its strong and directional $\sigma$ bonds [21]. Diamond has a wide 5.5 eV band gap, the highest atom density, largest thermal conductivity at room temperature, smallest thermal expansion coefficient, and largest electron and hole saturation velocities of any semiconductor [21]. Graphite is another form of carbonaceous allotrope with a layered structure, which has strong intra-layer $\sigma$ bonds in each layer and weak van der Walls bonds between layers. A single graphite plane is a zero band gap semiconductor (graphene), and in three dimensions graphite is an anisotropic half-metal [20, 25].

DLC has some properties similar to diamond, such as hardness, elastic modulus and chemical inertness. Those are however achieved in an isotropic disordered thin film with no grain boundaries [10]. Also, DLC is much cheaper to produce compared to diamond, leading to its wide spread application in coatings.

The $sp^3$ bonds in DLC leads to many beneficial properties similar to diamond mentioned above. However, DLC does not consist only of amorphous carbons ($a$-C), but also of hydrogenated amorphous carbon alloys ($a$-C:H). The various forms of amorphous C-H alloys are showed in a ternary phase diagram (Fig. 2), adapted from Robertson [10] and first used by
Figure 1: The $sp^3$, $sp^2$, and $sp^1$ hybridized bonding (adapted from Robertson [10]).

Jacob and Moller [26]. There is a great variety of $a$-C’s with disordered graphitic ordering, such as evaporated $a$-C, chars, soot, and glassy carbon. Those all lie in the left-hand corner of the diagram. Two hydrocarbon polymers, polyethylene $(CH_2)_n$, and polyacetylene $(CH)_n$, define the limits of a triangle in the right-hand corner, beyond which the interconnecting C-C networks cannot form, and only the molecules are stable. Various deposition methods, like sputtering, have been developed to prepare $a$-C’s with increasing degree of $sp^3$ bonding. With high degree of $sp^3$ bonding in the structure, McKenzie [27] suggested that this kind of structure should be called tetrahedral amorphous carbon ($ta$-C), to distinguish it from the $sp^2$ bonded $a$-C. Other range of deposition methods, such as plasma enhanced chemical vapor deposition (PECVD), are able to reach the inferior of the diagram and produce hydrogenated amorphous carbons ($a$-C:H). This material contains a lot of hydrogen and its $sp^3$ bonding concentration is not so large. High-plasma-density PECVD (HPDPECVD) is able to create a more $sp^3$-bonded material, and that structure is called hydrogenated tetrahedral amorphous carbon ($ta$-C:H), according to Weiler et al. [28].

Figure 2: Ternary phase diagram of bonding in amorphous carbon-hydrogen alloys (adapted from Robertson [10]).
In present work the designation diamond-like carbon (DLC) is used for previously specified a-C:H and DLC films were deposited by photoemission-assisted plasma-enhanced chemical vapor deposition (PA-PECVD).

2.2 Photoemission Assisted-Plasma Enhanced CVD

First it is appropriate to mention why the PA-PECVD was used instead of conventional, well established, CVD processes. In used method the plasma is generated at relatively low bias voltage, meaning the low power consumption, but more importantly the method is usable in the clean room conditions. This is because the produced plasma needed for ionization and decomposition of used CH$_4$ deposition source gas is situated only above the substrate of the sample and minimizes the formation of soot, its deposition at the inner walls of vacuum chamber, and subsequent contamination of the substrate and the clean room. Also, the high power plasma can cause a damage of graphene channel layer during the top dielectric fabrication over the THz laser structure graphene channel region.

In PA-PECVD system, the photo-current of 10$^{12}$ e$^-$·cm$^{-2}$·s$^{-1}$ order can be generated by UV irradiation, which makes it possible to generate the glow discharge at a relatively low DC bias voltage ($V_B$), compared to conventional PECVD systems. The glow discharge in PA-PECVD is caused simultaneously by two working regimes, the $\alpha$ and $\gamma$ regimes (Fig. 3). In the $\alpha$ regime, photoelectrons are emitted from the substrate (Si) by UV irradiation and accelerated by an electric field to sufficient kinetic energy, which causes ionization of gas molecules in the chamber. In $\gamma$ regime, the ions accelerated by electric field reach the Si substrate, resulting in electron transition from Si to Ar with an Auger energy which emits other electrons from Si as Auger electrons. Thus, when the bias voltage is high enough for a given gas atmosphere, the electron avalanche causes the glow discharge. With different source gases and at different discharge conditions PA-PECVD allows the deposition of various films on the Si substrate. Detailed description of the method and glow discharges in PA-PECVD follows in the corresponding experimental section below.

2.3 Proposed THz laser structure and its principle of operation

When graphene is installed into a proper THz cavity, THz lasing is expected. Because of the graphene $\pi$-electron transition, the vector of electric field must lie within the graphene plane. This permits the gain for THz photons propagating either perpendicular or parallel to the graphene plane [18]. Therefore, the structures with vertical [29, 30] and waveguide type [15] cavities can be used to construct a graphene THz laser. Waveguide cavity has been chosen, because it can have larger volume of the gain overlap, distributed along the length of the cavity in which the THz photons propagate, meaning higher quantum efficiency and consequent lower pumping threshold [18]. Also, this kind of waveguide structure is easier to prepare with DLC.
Proposed device structure of the THz laser with a DLC layer as a waveguide is shown in the figure below (Fig. 4). This structure is composed of a Si substrate, a DLC thick layer (>10 µm), which serves as a waveguide for the propagation of the THz electromagnetic wave, and on this layer CVD/HOPG graphene, or multilayer graphene (MLG), is deposited/transferred. Graphene has source and drain electrodes, and the channel region is covered by thin DLC film. Two top-gate electrodes on the DLC film encloses the structure. The direction of the photon propagation is shown by the red arrow.
3 Experimental Methods

In this section, the basic principles of used methods will be explained, including sample prior deposition treatment, deposition method itself and used characterization methods for declaring the properties of prepared samples. For greater detail, please see the corresponding references.

3.1 Sample Prior Deposition Treatment

DLC films were grown on heavily arsenic-doped n-Si(100) substrates, which were 525 µm thick with a resistivity of 0.001 to 0.003 Ω·m. The Si wafers with a 4-inch diameter were cut into 20×20 mm² pieces for individual samples. They were at first immersed in a 1:3 solution of 30 % H₂O₂ - 96 % H₂SO₄ (piranha solution) for 10 minutes, and then dipped in a 10% hydrofluoric acid (HF) solution for 2 minutes. The substrates were rinsed with pure water between each treatment. Finally, they were immersed again in piranha solution for 10 minutes to prepare a thin native oxide layer (approx. 1 nm thick) at the surface, followed by rinsing with pure water and drying by a pure nitrogen jet.

After the wet treatment, the substrate was transferred into the PA-PECVD apparatus, and annealed in a 10 kPa H₂ gas flow at 200 °C for 20 min., and then sputtered by the Ar plasma at 800 Pa, 200 °C, with 10 mA plasma current for 10 min. Those procedures were conducted to remove adsorbents like grease and moisture from the substrate surface and Ar plasma helps to partially remove the surface SiO₂ layer and helps to better DLC adhesion to substrate.

3.2 Generation of Glow discharge in PA-PECVD

The Photoemission-Assisted Plasma-Enhanced CVD (PA-PECVD) system is shown below (Fig. 5). The main parts are a reaction chamber, an UV light source, a stage with heater, two gas exhaust lines, and a plasma-control electrical circuit. The pressure in the reaction chamber can reach 10⁻⁶ Pa order, but in the present experiments it was usually maintained only up to 10⁻⁵ Pa order. The first gas exhaust line was equipped with a smaller turbo molecular pump (TMP) with an evacuation rate of 33 L/s (Oerlicon Leybold Vacuum TURBOVAC 50), and a rotary pump in series, which allows to achieve pressure in order of 10⁻³ Pa. The second line was equipped with a larger TMP with evacuation rate of 345 L/s (Oerlicon Leybold Vacuum TURBOVAC 361), connected to a rotary pump in series. Those lines can work together to achieve mentioned pressure in order of 10⁻⁶ Pa. During DLC deposition, the second line was closed, small TMP of the first line was stopped, and chamber pressure was controlled by the valve opening for the rotary pump of the first line.

The reaction gases were CH₄ (99.999 %) and Ar (99.9999 %). Also, hydrogen gas was used to remove surface adsorbents and contaminants at the substrate. The gas flow rates during DLC deposition were maintained by mass flow controllers (HORIBA STEC SEC-
Figure 5: Schematic of PA-PECVD apparatus.

7330R), and the total pressure was monitored by a capacitance manometer (MKS Baraton type 626). The UV light source was a Xe excimer lamp (USHIO UER20H-172A) with the emitting wavelength 172 nm ($E=7.2$ eV). The lamp was placed outside the chamber and the irradiation reached the substrate inside through a fused quartz window. The area between the light source and window was continuously filled with nitrogen gas to avoid toxic ozone gas creation. Both quartz window and nitrogen gas are transparent to the UV light.

Every sample was placed on the stage (Fig. 6) and its deposition area was restricted to a circle with 16 mm diameter (approx. 2 cm$^2$) by a quartz retainer with hole in the center. The stage is composed of a Mo support (pad) and a radiation shields. The stage was heated by AC current, whose circuit was separated from the plasma circuit by a transformer. The counter top electrode was made of copper and has a duckboard-like shape to allow the UV irradiation of the sample. The distance between the electrodes was 18 mm. The plasma circuit is composed of top and bottom electrodes, a resistor, an ammeter, and a constant DC voltage source. The resistor was used to restrict the plasma current during the discharge, because in the glow discharge, the impedance of plasma drastically decreases. The chamber wall and top copper counter electrode were grounded to avoid the photocurrent flowing from the wall to the electrode by any electric field applied between them.

The basic mechanism of the glow discharge generation is already explained above. Now, the discharge results during the samples preparation in this study will be discussed further.
For most of the prepared samples, the photoelectron current in vacuum is in an order of $10^{-6}$ A, as shown in Fig. 7. This with 2 cm$^2$ size of the irradiated Si wafer spot means approximate number of initial photoelectrons about $(n_0) \times 3.1 \cdot 10^{12}$ e$^-$·cm$^{-2}$·s$^{-1}$. The current remains constant at this value when the bias voltage $V_B$ is larger than 10 V. Below this, the electrons are not sufficiently collected at Cu electrode [11]. Also, the initial energy of photoelectrons, given by difference between Xe excimer lamp photon energy ($E_{Xe}$) and Si work function ($\varphi_{Si}$), ($E_{Xe}-\varphi_{Si}=7.2-4.8=2.4$ eV), plays the role in this initial behavior because of random photoelectrons radiation direction from substrate, and so the el. field has to have a sufficient energy to change their direction primarily to the counter electrode.

Figure 6: Picture of PA-PECVD sample stage. Top Cu electrode normally placed at the top of four covered screws is placed aside at the picture.

Figure 7: Discharge characteristic of PA-PECVD in vacuum and CH$_4$/Ar mixture at 500 Pa.
The total pressure for every deposition was maintained at 500 Pa and the discharge characteristic of Argon (Ar) diluted with methane (CH\textsubscript{4}) gas for this pressure is also shown in Fig. 7. Initial current for \( V_B \) under about 75 V in gas mixture is smaller due to so called ‘surface charge effect’ \[31\]. The electrons cannot be accelerated enough to obtain sufficient kinetic energy, and repeated elastic collisions with Ar atoms leads to energy loss. Finally, the electrons are bounded to the region close to the surface, which forms a space charge layer that suppresses subsequent photoemission. From Fig. 7 we can also see that plasma current increased exponentially up to applied voltage about 240 V. This is due to \( \alpha \) regime, when the photoelectrons emitted from Si substrate accelerate in electric field and collide with Ar atoms (with CH\textsubscript{4} also in every later case in this section). If they reach sufficient energy during its mean free path, they can ionize Ar atoms (above 15.8 eV for first ionization), which then emits secondary electrons. This relationship is expressed as

\begin{equation}
dn = \alpha nx,
\end{equation}

where \( n \) is the number of primary electrons, \( x \) is the unit distance, and \( \alpha \) is the number of secondary electrons generated by primary electrons. Because of the initial condition \((x, n) = (0, n)\), eq. (1) can be rewritten as

\begin{equation}
n = n_0 \exp(\alpha x).
\end{equation}

The secondary electrons sequentially collide with other Ar atoms in the same manner, causing an electron avalanche. Because the definition of current \( I \) as \( qn \), where \( q \) is an elementary electric charge, eq. (2) can be replaced by

\begin{equation}
I = I_0 \exp(\alpha x),
\end{equation}

where \( I_0 \) is the initial current \[11\]. The number of electrons in initial current was calculated from photocurrent in vacuum above \((n_0 = 3.1 \cdot 10^{12})\). Due to large number of initial photoelectrons, PA-PECVD doesn’t need high initial \( V_B \) like conventional PECVD’s, where accidental electrons from cosmic rays must be initially accelerated by high applied voltage. Without UV irradiation, plasma was not observed in any case of possible power source \( V_B \) from 0 to 500 V. Discharge in this exponentially increasing current region in Fig. 7 is called ‘photoemission-assisted Townsend discharge’ \[32\].

The plasma current in gas mixture of CH\textsubscript{4}/Ar jumped about 30 times at \( V_B \approx 240 \text{V} \), and then remains sequentially increasing with increase of bias voltage. This discharge is called ‘photoemission-assisted glow discharge’ and is attributed to \( \gamma \) regime \[33\]. In this regime, Ar (CH\textsubscript{4}) atoms are forced by electric field to reach Si substrate and then may undergo electron transition from Si valence band to the Ar 3p orbital via quantum tunneling. This transition can be observed as luminescence or Auger effect. In the later case, when another electron in the Si valence band obtain the Auger electron energy, and if the energy is larger than the difference between the vacuum level of substrate and energy level of the electron, Auger
electron can be emitted. The critical condition of $\gamma$ regime is expressed as

$$E_i - 2\phi > 0,$$

(4)

where $E_i$ is the ionization energy of gas molecule/atom and $\phi$ is the work function of the substrate. The Si work function is between 4.7 and 4.9 eV and the ionization energy of Ar is 15.8 eV. Thus with mean $E_i - 2\phi = 15.8 - 9.6 = 6.2$ condition for glow discharge holds. With the change of deposition temperature, also the initial conditions of glow discharge has changed. This is probably due to change of substrate energy levels and thermal energy of gas molecules. The resulting difference in deposition current is from 12.1 to 3.6 mA corresponding to deposition temperature range from 50 to 700 °C (Fig. 8).

Figure 8: Initial and final (after 5 minutes) glow discharge current for different deposition temperatures of DLC samples.

We can see that for deposition under 200 °C the final deposition current decreases with time. This however will be discussed in one of the next sections. The deposition current also greatly depends on CH$_4$/Ar ratio and pressure. Those results on PA-PECVD glow discharges and its explanation can be found in [11].

So far omitted exact energies and rules for ionization of CH$_4$ in gas mixture are similar to those of Ar with key difference of CH$_4$ more basic ionization states with different energies and loosing hydrogen atoms possibility during ionization process, when the bonding between C and H is broken. This means that with higher ionization it is possible to deposit layers with smaller H content.

### 3.3 Raman measurements of DLC’s

Raman spectroscopy is very useful non-destructive method to estimate the kind of carbon bonding in DLC films and its corresponding properties. Fig. 9 shows typical Raman spectra of carbons. The first one is of a diamond, which has a single peak at 1332 cm$^{-1}$, which is a zone-center mode of $T_{2g}$ symmetry. The second is of a single crystal graphite with a peak at
1580 cm\(^{-1}\), labeled ‘G’ peak as for ‘graphite’ and corresponding to a zone-center mode of \(E_{2g}\) symmetry \([10]\). In the rest of those carbon materials there are two dominant distinguishable peaks, even when the carbons do not have any particular graphitic ordering. Already mentioned G peak, and another disordered graphite second peak at 1350 cm\(^{-1}\) labeled ‘D’ as for ‘disorder’ of \(A_{1g}\) symmetry. The \(D\) peak corresponds to the breathing vibrations of the graphite six-fold rings at the K zone boundary \([35]\). Raman is light scattering by the change in polarizability due to lattice vibration \([36]\), and Raman spectra of a-C’s are dominated by scattering of the \(sp^2\) sites, because \(\pi\) states are lower energy states than \(\sigma\) ones, and so they are much more polarizable \([37]\). This gives the \(sp^2\) sites 50-230 times larger Raman cross-section than \(sp^3\) sites \([38-40]\). Also, the matrix element of \(sp^2\) sites has much stronger effect and so Raman spectrum becomes controlled by the order of \(sp^2\) sites, not by the \(sp^2\) fraction \([41]\).

Figure 9: Comparison of typical Raman spectra of carbons (adapted from Robertson \([10]\)).

The \(G\) mode of Raman spectra represents the stretching vibration of any pair of \(sp^2\) sites irrespective of C=C chains and aromatic rings \([41]\). Thus, the \(G\) mode does not only mean ‘graphite’, but also C=C chains. The \(D\) mode represents the breathing mode of \(sp^2\) sites only in rings, not in chains \([10]\).

The variations of the \(D\) peak intensity with atomic order is interesting. Tuinstra and Koenig \([35]\) noted few years ago that the intensity ratio of the \(D\) mode to the \(G\) mode (\(I_D/I_G\)) varies inversely with the in-plane correlation length (\(L_a\)), or in other words the grain size of graphite. This relation is shown on the right side of Fig. 10, and is expressed by

\[
\frac{I_D}{I_G} = \frac{c}{L_a},
\]

\((5)\)
where \( c \) is a constant. This equation demonstrates that the \( I_D/I_G \) is proportional to the number of rings at the edge of the grain. Also, relation cannot be extended to zero. Other data obtained from the high temperature deposition of \( ta-C \)'s suggests that for \( L_a \) smaller than 2 nm, the ratio decreases according to left side of Fig. 10 as \([10][41][42]\):

\[
\frac{I_D}{I_G} = cL_a^2. 
\]  

(6)

Figure 10: Variation of Raman \( I_D/I_G \) ratio with in-plane correlation length \( L_a \). The Tuinstra-Koenig relationship only applies for \( L_a \) over 2 nm (adapted from Robertson [10]).

The \( G \) peak is due to all \( sp^2 \) sites, but \( D \) peak is only due to six-fold rings, so the \( I_D/I_G \) ratio falls as the number of rings per cluster falls and the fraction of chain groups rises [41]. Important factor for DLC’s is that \( L_a \) is always smaller than 1 nm, so that Tuinstra-Koenig relationship is never valid and eq. 6 should be used instead [10].

Fig. 11 shows the overall behaviour and features of the Raman spectra of disordered carbons. One feature of visible Raman spectra is that it cannot analyse C-H bonds, so we do not consider them in the present Raman analysis. The \( D \) peak intensity increases and decreases with in-plane correlation length \( L_a \) as shown in Fig. 10. For \( ta-C \)'s there is almost no \( D \) peak so that the cluster size is very small and the structure is mostly amorphous. With increasing size of graphitic clusters, the \( D \) peak rises up to \( L_a \approx 2 \) nm and then starts to decrease again, when for ideal graphitic structure \( D \) peak disappears again. With \( sp^2 \) sites clustering also \( G \) peak shifts to higher wavenumber values, but this behavior is only valid for the transition from \( a-C \) to nanocrystallized graphite (nc-graphite), and this shift is from about 1520 cm\(^{-1}\) to 1600 cm\(^{-1}\). There is another shift of the \( G \) peak to higher wavenumber from mentioned 1520 cm\(^{-1}\) to around 1570 cm\(^{-1}\) when the \( sp^2 \) sites fraction in \( a-C \) decreases and became \( ta-C \) including almost no aromatic rings. This correspond to mostly \( sp^3 \)-bonded carbons in \( ta-C \)'s.
Figure 11: Schematic of the factors affecting the position and height of the Raman G and D peaks of non-crystalline carbons (adapted from Robertson [10]).

Also, the $I_D/I_G$ peak ratio of Raman spectra increase from 0 to $\approx 2$ with graphite changes to nc-graphite, and decreases with nc-graphite transition to $a$-C, with peak ratio value of about 0.2-0.3, and to 0 for further transition to $ta$-C. This three stage model of increasing disorder has been found by Ferrari [41] and is applicable for Raman spectra of all disordered carbons. The problem of Raman spectra behavior of $a$-C’s is very complicated and so it will not be discussed any further in this part. More detailed description of this problem is nicely summarized and explained by Robertson [10], from which the most of the previous results were taken.

Raman spectra of our DLC films were observed with Raman spectrometer (SPEX 500M, HORIBA Jobin Yvon), with the $\lambda=488$ nm Ar$^+$ ion laser at an output power of 0.3 W. The spectra were fitted by two Gaussians, which represents the D and G bands. They were analyzed by their central position, full width half maximum (FWHM), and areas rather than intensities.

### 3.4 Thickness and Roughness

The thickness of the DLC films was measured by a stylus profilometer (DEKTAK XT, Bruker). The thickness was estimated from the holes opened by capacitively-coupled reactive ion etching (CCP-RIE) (SAMCO RIE-10NR) in an oxygen atmosphere with a RF plasma power of 200 W. In the etching, the films were covered with a Pyrex hard mask having holes with an approximate diameter of 0.6 mm in the interval between each other of about 2 mm. The DLC films in the uncovered areas were removed by oxygen RIE, but the Si substrate could not be etched. Thus, the precise thickness and uniformity was estimated. Roughness of the DLC films was measured in the tapping mode of an atomic force microscope (AFM) (Dimension FastScan, Bruker).
3.5 Dielectric Constant and Resistivity

The dielectric constant of DLC samples was measured by the standard metal-oxide-semiconductor (MOS) measurement, sometimes also called MIS (the metal-insulator-semiconductor) measurement, in the case that the dielectric is not an oxide material. This method is usually working with semiconductor substrate, an insulator (oxide) layer, and a top metal contact. The sample is set in a high frequency AC circuit with a small constant amplitude. The capacitance is measured as a function of DC bias voltage. The total capacitance of the stack ($C_T$) is given as:

$$\frac{1}{C_T} = \frac{1}{C_{Si}} + \frac{1}{C_{is}}, \quad (7)$$

where $C_{Si}$ is the capacitance of semiconductor substrate, and $C_{is}$ is the capacitance of the insulator (oxide) layer. Consequently, the dielectric constant (relative permittivity) of the insulator layer is calculated from the parallel plate capacitor equation with a known (in some cases excluded) series capacitance of $C_{Si}$:

$$C_{is} = \frac{\epsilon_r \epsilon_0 A}{L_{is}}, \quad (8)$$

where $\epsilon_r$ is the insulator dielectric constant, $\epsilon_0 = 8.854 \cdot 10^{-12} \text{F} \cdot \text{m}^{-1}$ is the permittivity of vacuum, $A$ is the area of the metal contact (capacitor), and $L_{is}$ is the thickness of the insulator layer [43].

In the present case, there is a thin SiO$_2$ layer between the deposited DLC film and $n$-Si(100) substrate. This layer works as another capacitor in the series as expressed by equation (7) and the final capacitance of the DLC film and the corresponding dielectric constant has to be corrected with the SiO$_2$ thickness determined by SIMS measurements discussed below.

For the dielectric constant and resistivity measurements, top contacts on the DLC films were deposited by electron-beam physical vapor deposition (EBPVD) through an original hard mask of a 0.1 mm thick Mo plate. This mask has a square holes with the sizes of 4, 1 and 0.25 mm$^2$, and Fig. 12 below shows the design of the holes and sample picture after evaporation. The areas of the holes are quite large due to the large thickness of the prepared DLC films (in $\mu$m order) compared to generally-measured thickness of a dielectric (an insulator) in a MOS (MIS) electronic measurement. The measurements were conducted with a LCR meter (Agilent E4980A).

The samples resistance was measured by a semiconductor parameter analyzer (Agilent 4156C) on the same 4, 1, and 0.25 mm$^2$ electrodes. The resistivity of the samples was estimated from the linear fitting of the measured current-voltage ($I - V$) curves in the DC bias voltage range from -1 V to +1 V.
3.6 Composition and Depth Profile by Secondary Ion Mass Spectroscopy (SIMS)

Secondary ion mass spectroscopy (SIMS) uses internally generated beam of both positive (e.g., Cs) and negative (e.g., O) ions (primary beam) focused onto a sample surface to generate other ions that are then transferred into a mass spectrometer across a high electrostatic potential, and are referred to as secondary ions. The interaction of the primary ion beam with the sample (in a vacuum) provides sufficient energy to ionize many elements. If the primary beam is composed of positively charged ions, the resultant ionization favors production of negative ions; primary beams of negative ions favors generation of positive ions. Although most atoms and molecules removed from the sample by the interaction of the primary beam and the sample surface (referred to as sputtering) are neutral, a percentage of these are ionized. These ions are then accelerated, focused, and analyzed by a mass spectrometer [44]. In addition, both elemental species and molecular fragments are detected in SIMS, which makes SIMS spectra difficult to interpret [43]. The primary ion beam gradually penetrates the surface and with the increasing time reaches deeper and deeper in the sample. Based on the power of primary beam and sensitivity of detector, one can achieve more than nm-resolution in the sample composition.

In present study, samples were measured by Secondary Ion Mass Spectrometer (HI-TACHI TOF.SIMS5) with the primary ion beam source composed of the positive Cs ions with the energy of 2000 eV (500 eV respectively) and the sputtered area was in range from 260×260 to 400×400 µm² for different samples. The analysis area was in every case restricted to 100×100 µm². Analyzed ion species were H⁻, C⁻, CH⁻, O⁻, OH⁻, and Si⁻.
3.7 Optical Methods

For determining the optical properties of DLC layers in visible region (VIS) spectroscopic ellipsometry was used, in infrared (IR) the Fourier Transform Infrared (FTIR) spectroscopy, and in THz the THz spectroscopy.

3.7.1 Spectroscopic Ellipsometry

Spectroscopic ellipsometry is an optical material characterization method based on a slant, respectively normal incidence on the sample and measuring the change of polarization of the reflected radiation. Experimental data are composed of two main ellipsometry parameters $\Psi$ and $\Delta$. These relationships are related to the Fresnel relations according to the equation:

$$\rho = \frac{r_p}{r_s} = \left| \frac{r_p}{r_s} \right| e^{i\Delta} = \tan \Psi e^{i(\delta_p - \delta_s)},$$

where $\Psi$ is an azimuth, $\tan \Psi$ is amplitude ratio of parallel and perpendicular reflection coefficients $r_p$ and $r_s$, and $\Delta$ is their phase difference.

After the measurement of ellipsometry parameters reverse analysis can determine, for example, the dielectric constant of the material, the thicknesses of thin films layered system, the anisotropy of the layers, their roughness, characterized so called buffer layers between the two environments and so on. For this, the fitting or in other words also reverse analysis is needed. It is essential to know at least some of the parameters of our structure, such as the substrate material and materials of the layers, their thickness, the type of layering, or other. With the increasing number of unknown parameters, fitting becomes difficult and the resulting data are difficult to interpret. Furthermore, to describe the function of the dielectric material itself the different types of models are used (e.g., Lorentz, Sellmeier and Cauchy, Tauc-Lorentz, Drude, etc.) with its own variety of adjustable parameters, and thus the complexity of determining the right model still increases. This may however also increase the results accuracy.

Measured ellipsometry values can also be converted into the pseudo-dielectric function ($\varepsilon_r$), which corresponds to the total dielectric function of measured system. The conversion is done according to:

$$\varepsilon_r = n_0^2 \sin^2 \theta \left[ 1 + \tan^2 \theta \frac{(\cos 2\Psi - i \sin 2\Psi \sin \Delta)^2}{(1 + \sin 2\Psi \cos \Delta)^2} \right] = \varepsilon_1 - i\varepsilon_2,$$

where $n_0$ is the refraction index of air (ambient medium), so $n_0 = 1$ and $\theta$ is the angle of incidence.

Next, for ellipsometry measurements of DLC thickness $d$ on Si substrate the model has to be proposed. It corresponds to model of air(0)/DLC(1)/Si(2), where complete reflection
coefficient is given by:

\[ r_{s,p}^{(012)} = \frac{r_{s,p}^{(01)} + r_{s,p}^{(12)} e^{-ik_z d}}{1 + r_{s,p}^{(01)} r_{s,p}^{(12)} e^{-ik_z d}} \]  

where \( r_{s,p}^{(01)} \) and \( r_{s,p}^{(12)} \) are reflection coefficients on the first and second interface respectively, \( r_{s,p}^{(012)} \) is complete reflection coefficient and \( k_z = (2\pi/\lambda)n^{(1)}\cos\theta_1 \). Reflection coefficients for individual interfaces are given by Fresnel relationships, which for example for interface (12), meaning interface DLC/Si, have form:

\[ r_{s}^{(12)} = \frac{n^{(1)} \cos \theta_1 - n^{(2)} \cos \theta_2}{n^{(1)} \cos \theta_1 + n^{(2)} \cos \theta_2} \]  

and

\[ r_{p}^{(12)} = \frac{n^{(2)} \cos \theta_1 - n^{(1)} \cos \theta_2}{n^{(2)} \cos \theta_1 + n^{(1)} \cos \theta_2} \]  

where \( n^{(1,2)} \) is an index of refraction of corresponding layer. Reflection coefficients for other interfaces are given analogically. Angles \( \theta_1 \) and \( \theta_2 \) are taken from Snell’s law:

\[ \theta_1 = \sin^{-1} \left( \frac{n^{(0)} \sin \theta_0}{n^{(1)}} \right) \]  

and

\[ \theta_2 = \sin^{-1} \left( \frac{n^{(0)} \sin \theta_0}{n^{(2)}} \right) \]  

Now, if we compare the resulting values of reflection coefficients for \( p \) and \( s \) polarizations, we will receive their relationship to ellipsometric parameters:

\[ \frac{r_{p}^{(012)}}{r_{s}^{(012)}} = \tan \Psi e^{i\Delta} \]  

where the measured values from ellipsometry and also the information about fitting model are already included. Closer theoretical introduction will not be covered. Further information on the relationships and general ellipsometry can be found in [45,46].

Used spectroscopic ellipsometer was from the J. A. Woollam Co., Inc. company, type RC2, with a range of used wavelengths from 193 nm to 1.7 \( \mu \)m. For the fitting was used a free software Complete EASE made by the Woollam company.

3.7.2 Fourier Transform Infrared Spectroscopy

Fourier transform infrared (FTIR) spectroscopy is based on the idea of the interference of radiation between two beams to yield an interferogram. The later is the signal produced as a function of the change of path length between the two beams. Two domains of distance and frequency are interconvertible by the mathematical method of Fourier transformation [47].
The basic component of FTIR spectrometer are the source, interferometer, sample, detector, amplifier, analog-to-digital converter (A/O converter) and the computer. The radiation emerging from the source passes through an interferometer to the sample before reaching a detector. Upon the amplification of the signal, in which high-frequency contributions have been eliminated by a filter, the data are converted to digital form by A/O converter and transformed to the computer for Fourier transformation. For more general information about FTIR spectroscopy, please see e.g. here used reference [47].

Used FTIR spectrometer was Bruker Vertex 70v. This equipment with the appropriate extensions allows the spectral range from Far-IR/THz through Mid-IR, NIR to Visible/UV corresponding to range from 10 cm\(^{-1}\) to 28,000 cm\(^{-1}\) [48]. In our case the range wasn’t so big due to absence of some extension modules so the allowed spectral range was from 50 cm\(^{-1}\) to approximately 8,000 cm\(^{-1}\) [49]. The optical bench can be maintained in vacuum or purged. The scan is acquired either in

- rapid scan with more than 70 spectra per second at 16 cm\(^{-1}\) spectral resolution, or in
- slow/step scan mode with 100 Hz (0.0063 cm/sec) speed with phase modulation and internal demodulation and final temporal resolution 6 \(\mu\)sec/2.5 nsec [48].

FTIR spectrometer also includes combined transmission and specular reflection module (Fig. 13) with the angle of incidence 11\(^\circ\) which enables obtaining of the reflectance and transmittance spectra in the same conditions without a requirement of handling with the sample or exposing the measurement chamber to the atmosphere [49].

Figure 13: Combined transmission and specular reflection unit (adapted from [49]).

The beam path in the other parts of the device (including the sample chamber input and output windows) is shown in Fig. 14. The radiation from source (globar) passes through an interferometer to the sample before reaching the detector. More information about the device can be found in [48][49].

The measurements of DLC samples were made in both transmission and reflection modes. The transmission spectroscopy is based on absorption of IR radiation at specific wavelengths. It is equal to the difference between the logarithm of the radiation intensity entering
the sample $I_0$ and the intensity of transmitted radiation $I$ [47]:

$$A = \log \left( \frac{I_0}{I} \right),$$  \hspace{1cm} (17)

The transmittance is defined as the ratio between the intensity of the transmitted $I$ and incident $I_0$:

$$T = \frac{I}{I_0},$$  \hspace{1cm} (18)

so the relationship is:

$$A = -\log \left( \frac{I}{I_0} \right) = -\log T.$$  \hspace{1cm} (19)

The reflection (reflectance) techniques can be used for samples that are difficult to analyze by conventional transmittance methods. Those methods can be divided into:

- internal reflectance measurements, which uses attenuated total reflection cell in contact with the sample and

- external reflection measurements, which involve an infrared beam reflected directly from the sample surface [47, 49].

In our case the external (specular) reflection is used where the radiation is focused onto the sample and can cause two kinds of reflection, specular and diffusive. Because of the measurement of reflected light the material has to be reflective or attached to reflective backing. Specular reflection occurs when the reflected angle of radiation equals to the angle of incidence and the amount of this specularly reflected light depend on the angle of incidence, the sample refractive index, its surface roughness and its absorption properties. For the dielectric materials the reflected energy is only from about 5 to 10\%, but for strongly absorbing materials the reflected intensity is higher [49]. The reflection coefficients are defined similarly as for the ellipsometry measurements mentioned above so they will not be discussed further.
3.7.3 THz Spectroscopy

This section is mostly based on the information provided in users manual of used THz spectrometer TPS Spectra 3000 from TeraView Limited company [50].

So called THz radiation is roughly the electromagnetic radiation with the frequency in the order from 300 GHz to 3 THz corresponding to the wavelengths under 1 mm to 100 µm, nevertheless with the respect to previous apportionment of the electromagnetic spectrum to microwaves and far infrared radiation is this ordering of THz corresponding region quite variable and varies a little bit in different publications. Recently the THz radiation was mostly used for characterization of pharmaceutic products. Also the techniques for THz pulse imaging and spectroscopy were developed, allowing the investigation of new information about materials in THz frequencies with better efficiency and smaller costs than previous types of those devices. In present measurement the labeled THz radiation is the one from 60 GHz to 3 THz, corresponding to wave numbers from 2 cm\(^{-1}\) to 100 cm\(^{-1}\), where this range is generated by pulse laser, as explained below.

The generation of THz pulse radiation is based on photo-conducting switching. Tera-hertz photo-conductive emitters rely on production of few-cycle THz pulses by ultrafast (femto-second) laser to the excitation of biased antenna from the gallium-arsenide. This technique is from its basis the broadband technique with the bandwidth of few THz, typically with already mentioned range from 60 GHz to 3 THz.

The detection of coherent radiation is achieved in a similar photo-conductive antenna circuit as the circuit source. By gating the photo-conductive gap with a femto-second pulse synchronized to the terahertz emission a current proportional to the THz electric field can be measured. By changing the optical path to the receiver the THz time domain can be sampled. Thus, we can determine both the amplitude and phase of the incident THz wave and for this method a dynamic range over 60 dB was demonstrated. The power of THz radiation used for measurement is below 1 µW, and thus the thermal stress formed in the sample with this level of radiation power does not exceed the background thermal radiation.

As mentioned above, THz radiation lies between microwave and IR region. In materials it can induce the rotational transitions, low frequency bonding vibrations, phonon vibrations of the crystal, stretching of the hydrogen bondings and torsion vibrations. Material response on THz radiation depends on both, radiation frequency and material properties. In gases dominates the rotational transitions, in liquids some hydrogen bondings and others low-energetic bonding vibrations, in solids the response is composed mainly of crystal phonon vibrations.

Crystal phonon vibrations, also known as lattice vibrations, deserves a special attention because they are important part in THz spectroscopy of solids. Those vibrations can be imagined like collective vibrations constructed from interaction of many intermolecular vibrations. Molecules in solids are close to each other and so the vibrations of one molecule influence the vibrations of neighboring ones. Interaction of intermolecular modes leads to
formation of collective mode, which propagates through the material. The existence and form of phonon vibrations depends on the bulk material structure. It has to have periodic structure to maintain phonon vibrations, corresponding to crystallized materials, which are able to maintain those modes. If the material is amorphous, the absence of regular ordering on the long distances blocks the propagation of phonon vibrations and energy connected with them is diffusively dispersed in the material.

Crystal phonon vibrations are quantized into discrete energy levels and can be characterized with the help of quantum mechanics. Phonon vibrations in a crystal, which can also lead to molecular crystal, are complex and consists of transversal and longitudinal waves depending on the molecules movements either perpendicular or parallel to the direction of wave propagation. Moreover they can be acoustic or optic depending on that if the neighboring molecules are moving in the same or opposite direction respectively.

The same selection rules as for absorption of IR radiation works also for THz, and so the crystal phonon vibrations which include big changes of dipole moment are strongly absorbed.

Above mentioned THz spectrometer TPS Spectra 3000 generates wide spectrum in the range from 60 GHz to 3 THz and spectroscopic measurements can be recorded in two modes

- fast scan mode where the optical delay is generated by thick movement of mirrors and
- step scan mode where the corner reflector is moved by step motor to receive a time delay.

In the fast scan mode 30 spectra are taken per second with spectral resolution of 32 GHz (1.2 cm$^{-1}$). In the step scan mode depends the time of measurement on required resolution and integration time to achieve desired signal vs. noise difference. The best spectral resolution is in this case 7.5 GHz (0.25 cm$^{-1}$). Irrespective of required resolution the whole width of source radiation can be used. This is the advantage in comparison with classical FT spectrometers where for achieving higher resolution the width of source radiation has to be reduced by aperture.

Spectral data are with TPS spectrometer taken in one-beam configuration, so for acquisition of absorption spectra we have to measure the background first, or THz course of device response. THz signal contains negative values because THz electric field is measured, rather than its intensity. Use of fast Fourier transform (FFT) on this THz course of electric field creates its frequency response. When the sample is placed into the holder, two obvious differences appears in THz electric field. First, the signal intensity is decreased because of the radiation absorption and second, signal maximum shifts thanks to the sample index of refraction. From FFT the information about basic vibration and lattice modes is received and are important for both qualitative and quantitative analysis. The traditional absorption spectra is obtained by dividing the frequency response of the sample by frequency response of the system. Also the THz frequency dependent index of refraction can be calculated. This procedure is discussed below.
From electromagnetic theory the ratio between strengths of the electric fields before $E_r$ and after $E_s$ transition through the sample gives the information about the investigated material. This relationship is as

$$\frac{E_s}{E_r} = T(n) \exp \left(-\frac{\alpha d}{2} + \frac{i\omega d}{c_0}\right),$$  \hspace{1cm} (20)

where $d$ is the thickness of the sample, $\omega$ is the angular frequency of THz radiation, $c_0$ is the speed of light in vacuum and $T(n)$ is Fresnel reflection loss on the surface of the sample. Thereby, if we measure the ratio of the electric fields we can estimate the frequency dependent index of refraction, same as absorption coefficient $\alpha$ of the sample material. In measurement the electric field is given by equation:

$$E_s = A_{S0} e^{i\phi_{S0}},$$  \hspace{1cm} (21)

and electric field of the background:

$$E_r = A_{R0} e^{i\phi_{R0}},$$  \hspace{1cm} (22)

where $A_{S0}$ and $A_{R0}$ are electric field amplitudes of sample and reference and $\phi_{S0}$ and $\phi_{R0}$ are the phases of THz pulses. The absorption coefficient can be estimated from

$$\alpha d = -20 \log \left(\frac{A_{S0}}{A_{R0}}\right) / T(n),$$  \hspace{1cm} (23)

Coefficients $A_{S0}$ and $A_{R0}$ are received from real part of fast Fourier transform (FFT). Index of refraction is given by relationship

$$nd = \frac{c}{\omega} (\phi_{S0} - \phi_{R0}),$$  \hspace{1cm} (24)

where $\phi_{S0}$ and $\phi_{R0}$ are phases of THz pulses of sample and reference respectively, which are obtained from imaginary part of FFT.

Absorption coefficient $\alpha$, which returns the spectrometer program at the output doesn’t count with Fresnel’s reflexion losses $T(n)$. 
4 Results and Discussion

4.1 DLC Film Thickness

In the first stage of this research, the author tried to create a thick DLC film (>10 µm). However, when the deposited films increased in thickness, the discharge current decreased with the plasma extinction from the center of the sample to the sides, and suddenly showed a steep drop in the deposition current from a few mA in the glow discharge to a few tens of µA in the Townsend discharge at room temperature. The DLC thickness for the endurance duration of the glow discharge at room temperature changes from 100-600 nm depending on the CH\textsubscript{4} concentration [19]. It is reasonable to ascribe the observed drop of the glow discharge current to the charge-up effect whereas DLC is an excellent insulator below 50 °C. Two possible solutions to overcome this effect were proposed. One is to restart the glow discharge by a few tens of V increase in $V_B$. Repeating this procedure step by step, the DLC films becomes thicker than few µm. Unfortunately, those films were not stable due to the internal stress caused by its non-uniformity and deformed in the scale of hours or days, depending on the used bias voltages and number of steps. Another solution is to decrease the resistivity of DLC films by increasing the deposition temperature. By this, the growth time has been rapidly elongated. After two hours deposition at $V_B$=270 V and 200 °C, an 11.4 µm-thick DLC film was deposited. The source gas total pressure was 500 Pa and it consisted of the CH\textsubscript{4}/Ar mixture with the flow rates of 5/55 sccm according to ref. [19] to maximize the DLC thickness. Fig. 15 shows the final sample.

Next figure (Fig. 16) shows the current vs. time characteristics during the DLC deposition at different temperatures with, or without, the step increase in bias voltage. The initial deposition currents in this case are different due to the different apparatus used for deposition. This is the case of deposition current at the top of Fig. 16, compared with bottom ones, where first mentioned has a bigger top electrode cross section and in general a little different dimensions of sample stage. It is also worth mentioning, that in PA-PECVD it is possible to control the thickness of DLC films proportionally to total charge that passes through the electrodes, if the deposition temperature is constant. The small alternation of deposition current, which can be clearly seen for deposition at 200 °C at the bottom of the figure, is due to maintaining the temperature, where heating has only ON/OFF mode and so the temperature varies between two values and consequently the deposition current slightly alternates with the time of deposition.

What are then the reasons for the above-mentioned deposition time extension? It has been estimated from the static measurements of the $I − V$ characteristics, that the resistivity of samples prepared at lower temperature (150 °C) is at the order of tens of GΩ·m, while that for samples prepared at 200 °C at the order of hundreds of MΩ·m. In this sample case it was hard to obtain the dielectric constant of the DLC films with sufficiently small error in the standard MOS configuration, because the films were too thick. The capacitance values measured were too small and beyond the measurement limit of the instrument. Furthermore,
Figure 15: Picture of sample with 11.4 thick DLC layer on Si.

Figure 16: Time vs current graph with noted temperatures of deposition. For 50 °C the $V_B$ was 280 V, for 150 °C 250, 265, and 290 V, and for 200 °C 270 V.
it is clear that from the measurements obtained with a step profilometer, those samples prepared at low temperatures are not uniform in thickness and a little bit thicker at the sides, which is what we have expected, because of the slowly side disappearing glow discharge with DLC thickness increase and sudden deposition current drop.

4.2 DLC Deposition at Different Temperatures

It is necessary to analyze the deposition time elongation and the changes of the characteristics depending on the deposition temperature. For this purpose, the preparation of DLC samples in series from 50 to 700 °C and their measurements has been conducted. All the samples in this series were prepared at source gas pressure 500 Pa consist of CH₄/Ar mixture with ratio 5/55 sccm, at bias voltage \( V_B = 280 \) V for 5 minutes.

Now, the dependence of DLC properties on the deposition temperature are analyzed further. Fig. 17 shows the Raman spectra of deposited DLC films. Fig. 18 and Tab. 1 shows the curve-fitting results from the spectra with two Gaussians. The \( G \) peak shifted to higher positions, which according to Robertson [10] leads to connection of carbon atoms into the chains and graphitic planes result in graphitic clusters growth and nano-crystalline graphite. This nano-crystallization process hypothesis is also supported by the decrease in the FWHM of the \( G \) peak. The vibration states of the graphitic clusters are more and more discrete compared to the broad amorphous mode energy range.

Figure 17: Raman spectra of the samples prepared from 50 to 700 °C.

Next, the \( I_D/I_G \) peak ratio, actually computed as an area ratio, is considered. When the in-plane correlation length \( (L_a) \) increases from zero, as for absolutely amorphous structure,
Figure 18: Fitted values of Raman spectra by two Gaussians for samples deposited from 50 to 700 °C; (a) D peak and G peak position, (b) $I_D/I_G$ ratio of the peaks.

Table 1: Measured Raman spectra characteristic of 50-700 °C series DLC samples

<table>
<thead>
<tr>
<th>Deposition temperature [°C]</th>
<th>D peak [cm$^{-1}$]</th>
<th>FWHM D peak [cm$^{-1}$]</th>
<th>G peak [cm$^{-1}$]</th>
<th>FWHM G peak [cm$^{-1}$]</th>
<th>$I_D/I_G$ [-]</th>
</tr>
</thead>
<tbody>
<tr>
<td>50</td>
<td>1266</td>
<td>269</td>
<td>1512</td>
<td>176</td>
<td>0.3</td>
</tr>
<tr>
<td>100</td>
<td>1282</td>
<td>319</td>
<td>1517</td>
<td>181</td>
<td>0.4</td>
</tr>
<tr>
<td>200</td>
<td>1330</td>
<td>368</td>
<td>1530</td>
<td>174</td>
<td>0.6</td>
</tr>
<tr>
<td>300</td>
<td>1350</td>
<td>358</td>
<td>1544</td>
<td>158</td>
<td>1.0</td>
</tr>
<tr>
<td>400</td>
<td>1354</td>
<td>343</td>
<td>1558</td>
<td>144</td>
<td>1.4</td>
</tr>
<tr>
<td>500</td>
<td>1360</td>
<td>313</td>
<td>1573</td>
<td>119</td>
<td>1.9</td>
</tr>
<tr>
<td>600</td>
<td>1344</td>
<td>312</td>
<td>1579</td>
<td>89</td>
<td>2.7</td>
</tr>
<tr>
<td>700</td>
<td>1346</td>
<td>269</td>
<td>1580</td>
<td>84</td>
<td>2.6</td>
</tr>
</tbody>
</table>
the $I_D/I_G$ ratio increase exponentially up to $L_a$ around 2 nm. After that, $I_D/I_G$ decreases inversely with $L_a$ to zero for ideal graphitic structure as shown in Fig. 10 above. Fig. 18b clearly demonstrates that the tendency of the $I_D/I_G$ peak ratio for the samples prepared at different temperatures shows a similar shape as that in Fig. 10. First the value of $I_D/I_G$ rises for samples deposited up to 600 °C and decrease again above this value. That corresponds to increase of the $L_a$ with deposition temperature. This result supports the previous one, that the DLC nano-crystallizes and connects the chains into the aromatic rings. Next, the long range polarizability enhances the peak intensity and particularly the increase of the $D$ peak intensity which correspond to the breathing mode of six-fold aromatic rings and possible graphite layer constructive interference of the eigenvectors of each ring [10].

As a result, those spectra shows that the DLC films prepared at higher temperatures include more $sp^2$-bonded carbons, but allows elongation of the possible deposition time due to the decrease of the resistivity caused by graphitization. The theoretical range of the $sp^3$-bonded carbon goes from 0.65, for the sample deposited at 50 °C, to 0.2 or 0, for the ones deposited at high temperatures.

When the deposition temperature increases, the growth rate and the resulting sample thickness also changes. Table 2 shows the results. The highest growth rate was observed at 100 °C and the thickness after 5 min. deposition was 1.02 µm. Roughness of the prepared samples ($R_a$) was measured by AFM and was in every case smaller than 1 nm. That demonstrates flat surface, which is suitable as a substrate for a graphene transfer. However, the AFM measurement should not be taken as a final results of sample roughness, because of the discovered systematic error in the measurement (measuring too small area), which has not been corrected yet and further analysis of roughness is needed.

The samples of the 16 mm circular diameter are relatively uniform in its thickness in the central area ($d=10$ mm), but are little bit higher at the edges. The height difference is about 4 % for the samples prepared at highest growth rates, as has been estimated by step profilometer.

Table 2: Measured thickness, growth rate and roughness ($R_a$) of 50 - 700 °C series DLC samples

<table>
<thead>
<tr>
<th>Temperature [°C]</th>
<th>Growth Rate [nm·min⁻¹]</th>
<th>Thickness [µm]</th>
<th>$R_a$ [pm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>50</td>
<td>190</td>
<td>0.93</td>
<td>366</td>
</tr>
<tr>
<td>100</td>
<td>200</td>
<td>1.02</td>
<td>315</td>
</tr>
<tr>
<td>200</td>
<td>190</td>
<td>0.94</td>
<td>500</td>
</tr>
<tr>
<td>300</td>
<td>155</td>
<td>0.79</td>
<td>380</td>
</tr>
<tr>
<td>400</td>
<td>105</td>
<td>0.52</td>
<td>478</td>
</tr>
<tr>
<td>500</td>
<td>75</td>
<td>0.37</td>
<td>333</td>
</tr>
<tr>
<td>600</td>
<td>40</td>
<td>0.19</td>
<td>354</td>
</tr>
<tr>
<td>700</td>
<td>40</td>
<td>0.21</td>
<td>581</td>
</tr>
</tbody>
</table>

The measurement techniques for the dielectric constant and resistivity of thick DLC films are described in the corresponding section above. Table 3 shows the results. They are con-
sistent with the proposed behavior of DLC films deduced from Raman measurements. The samples deposited at low temperature exhibits the resistivity in order of ten GΩ·m. The resistivity decreases to the order of kΩ·m for the samples prepared at high temperature (700 °C). This is also why it is possible to deposit thick DLC films at higher temperatures, because the samples do not undergo so severe charging up effect in the DC plasma discharge. The measurements of the dielectric constant in the standard metal-insulator-semiconductor (MIS) configuration in MHz measuring domain demonstrate the increase from around 3.8 for the sample prepared at 50 °C to 6.7 for those deposited at 300 °C. Further increase in the deposition temperature causes a DLC film transition from dielectric to conductor and the obtained values become unreasonable. As a result, the DLC films prepared at 200 °C, which can achieve sufficient thickness, shows the resistivity in the order of tens of MΩ·m and the dielectric constant around 5. These results suggests DLC films promising use as a cladding (waveguide) layer of a THz laser.

Table 3: Measured dielectric constant (relative permittivity) of DLC samples prepared from 50 - 700 °C

<table>
<thead>
<tr>
<th>Temperature [°C]</th>
<th>Dielectric constant [-]</th>
<th>Resistivity [Ω·m]</th>
</tr>
</thead>
<tbody>
<tr>
<td>50</td>
<td>3.79</td>
<td>1.126·10^{11}</td>
</tr>
<tr>
<td>100</td>
<td>4.36</td>
<td>1.416·10^{10}</td>
</tr>
<tr>
<td>200</td>
<td>5.09</td>
<td>4.682·10^{7}</td>
</tr>
<tr>
<td>300</td>
<td>6.70</td>
<td>1.580·10^{9}</td>
</tr>
<tr>
<td>400</td>
<td>-</td>
<td>4.764·10^{9}</td>
</tr>
<tr>
<td>500</td>
<td>-</td>
<td>1.530·10^{9}</td>
</tr>
<tr>
<td>600</td>
<td>-</td>
<td>7.798·10^{9}</td>
</tr>
<tr>
<td>700</td>
<td>-</td>
<td>3.139·10^{9}</td>
</tr>
</tbody>
</table>

4.3 Effect of Annealing

Because of the proposed CVD graphene deposition on the thick DLC films, further research has been made in measuring their thermal stability. All samples in this series were prepared at source gas pressure 500 Pa consist of CH₄/Ar mixture with ratio 5/55 sccm, at bias voltage V_B=280 V for 5 minutes at 150 °C. Their post deposition annealing up to maximum of 800 °C in the 1 kPa Ar atmosphere for 1000 s has been performed. Heating of the samples to high temperature wasn’t quick and so there actually was additional annealing time for the samples temperature rising and cooling. The reason for annealing study is that for direct growth of good quality CVD graphene on a substrate, so far, it is necessary to significantly increase its temperature during the deposition.

The annealed samples shows a similar tendency to change its properties with increase in annealing temperature. However, the Raman spectra shown in Fig. 19, and fitted results in Fig. 20 and Tab. 4 below, demonstrates that the annealed samples were more stable and compared to deposited ones reached the same values of I_D/I_G ratio at around 150 °C higher temperature.
Figure 19: Raman spectra of the samples prepared at 150 °C and annealed up to 800 °C.

Figure 20: Fitted values of Raman spectra by two Gaussians for samples deposited at 150 °C and annealed up to 800 °C; (a) D and G peak position, b) $I_D/I_G$ ratio of the peaks.
Table 4: Measured Raman spectra characteristic of samples prepared at 150 °C and annealed up to 800 °C

<table>
<thead>
<tr>
<th>Deposition temperature/Annealing temperature [°C]</th>
<th>D peak [cm⁻¹]</th>
<th>FWHM D peak [cm⁻¹]</th>
<th>G peak [cm⁻¹]</th>
<th>FWHM G peak [cm⁻¹]</th>
<th>I_D/I_G</th>
</tr>
</thead>
<tbody>
<tr>
<td>150/-</td>
<td>1300</td>
<td>356</td>
<td>1521</td>
<td>179</td>
<td>0.5</td>
</tr>
<tr>
<td>150/200</td>
<td>1303</td>
<td>349</td>
<td>1523</td>
<td>177</td>
<td>0.5</td>
</tr>
<tr>
<td>150/300</td>
<td>1311</td>
<td>350</td>
<td>1528</td>
<td>167</td>
<td>0.6</td>
</tr>
<tr>
<td>150/400</td>
<td>1329</td>
<td>346</td>
<td>1537</td>
<td>152</td>
<td>0.8</td>
</tr>
<tr>
<td>150/500</td>
<td>1343</td>
<td>332</td>
<td>1549</td>
<td>134</td>
<td>1.1</td>
</tr>
<tr>
<td>150/600</td>
<td>1346</td>
<td>307</td>
<td>1565</td>
<td>105</td>
<td>1.6</td>
</tr>
<tr>
<td>150/700</td>
<td>1336</td>
<td>289</td>
<td>1574</td>
<td>83</td>
<td>2.1</td>
</tr>
<tr>
<td>150/800</td>
<td>1333</td>
<td>294</td>
<td>1575</td>
<td>81</td>
<td>2.5</td>
</tr>
</tbody>
</table>

Narrowing of the samples G peak with the increasing annealing temperature and its shift to higher wave-numbers demonstrate the formation of larger sp²-bonded clusters at higher temperatures. If the annealing temperature is sufficiently high, the sp² clusters interconnects. They may not be separated any more by the sp³-bonded carbons and hydrocarbons. Clear temperature dependence of this behavior can be observed in the dielectric constant and resistivity measurements summarized below.

The dielectric constant and resistivity are stable to relatively high temperatures. The first significant changes were observed after annealing above and at 600 °C for dielectric constant and resistivity respectively. The results are shown in Tab. 5. Changes in dielectric constant and resistivity suggest the thermal threshold when the sp² clusters interconnects each other and DLC film loses its dielectric property and starts to behave as a poor conductor.

Table 5: Measured dielectric constant (relative permittivity) of DLC samples prepared at 150 °C and annealed from 200 - 800 °C

<table>
<thead>
<tr>
<th>Deposition temperature/Annealing temperature [°C]</th>
<th>Dielectric constant [-]</th>
<th>Resistivity [Ω-m]</th>
</tr>
</thead>
<tbody>
<tr>
<td>150/-</td>
<td>4.45</td>
<td>6.499·10⁸</td>
</tr>
<tr>
<td>150/200</td>
<td>4.59</td>
<td>7.564·10⁸</td>
</tr>
<tr>
<td>150/300</td>
<td>4.57</td>
<td>1.384·10⁹</td>
</tr>
<tr>
<td>150/400</td>
<td>4.77</td>
<td>1.018·10⁹</td>
</tr>
<tr>
<td>150/500</td>
<td>5.15</td>
<td>1.034·10⁹</td>
</tr>
<tr>
<td>150/600</td>
<td>5.27</td>
<td>5.350·10⁹</td>
</tr>
<tr>
<td>150/700</td>
<td>-</td>
<td>1.04·10⁷</td>
</tr>
<tr>
<td>150/800</td>
<td>-</td>
<td>8.988·10⁷</td>
</tr>
</tbody>
</table>

This suggest that after deposition at around 200 °C, it is possible to deposit CVD graphene by PA-PECVD at higher temperature without severe changes in the dielectric constant and resistivity.
4.4 Depth Profile

The results of the SIMS measurements gives the depth profile for DLC samples and are shown below. Four samples from previous series were measured and also four new thin samples for greater sensitivity in Si/SiO$_2$/DLC interface region were deposited and measured.

First two measured samples were the ones deposited at 300 and 400 °C and the measurements were made to estimate, if there is any difference in composition of DLC films at the transition between dielectric and conductive behavior, as explained above in the previous results. Example SIMS measurement depth profile of the first mentioned sample is shown in Fig. 21. Approximately estimated thickness of SiO$_2$ layer was 14.7 nm and 10 nm for the case of 300 and 400 °C sample respectively. This thickness is much higher than thickness expected after wet cleaning, and so this intermediate layer have a great influence to a dielectric properties of DLC films. In the case of samples composition, no change was observed for two mentioned samples and so the difference in electronic behavior should be caused by internal structure changes. Also, no hydrogen decrease for higher deposition temperature was observed. In addition, -OH groups has been observed at the DLC/Si interface together with the SiO$_2$. This can be due to the hydrogen treatment at elevated temperature before the deposition and reaction with SiO$_2$, or reaction of hydrogen in plasma with SiO$_2$, but most probably from the initial cleaning process, where thin SiO$_2$ layer is created by piranha solution ($\text{H}_2\text{O}_2 + \text{H}_2\text{SO}_4$). This is due to the center of the OH$^-$ peak, which is at the same position as the center of the O$^-$ peak. The SIMS depth profile of sample prepared at 400 °C showed no significant differences compared to the one taken for 300 °C deposited sample. Only small difference is the time of a sputtering, due to different thickness of the films, and already mentioned slightly different thickness of SiO$_2$ film.

Second two measured samples were the ones deposited at 150 °C and post annealed at 600 and 700 °C respectively. The measurements were also made, as in the previous case, to determine the differences in composition of DLC films at the transition temperature between dielectric and conductive behavior for annealed samples. SIMS measurement depth profile of a first sample annealed to 600 °C has the same concentrations of species, as previously presented DLC films, however in the case of the sample annealed to 700 °C, which is shown in Fig. 22., the great change in oxygen concentration has been observed. Due to the same intensity of the oxygen peak at the interface, the oxygen species were not desorbed from the interface, but they have been introduced from the outside. However, because the Ar atmosphere in the chamber ($p = 1\text{kPa}$) the only possible sources of oxygen are inner walls and quartz retainer. The desorption of an oxygen from the walls and decomposition from quartz retainer at high temperature caused the changes in DLC film composition. From Fig. 22 and known 1 µm film thickness, the composition change depth of about 0.68 µm has been estimated.

Needless to say that SIMS doesn’t have sufficient sensitivity for thin interfaces of thick
Figure 21: SIMS depth profile of DLC film prepared at 300 °C and with thickness of 0.79 µm. Estimated thickness of SiO₂ interface layer is 14.7 nm.

Figure 22: SIMS depth profile of DLC film prepared at 150 °C, annealed at 700 °C, and with thickness of 1.08 µm. Estimated approximate thickness of SiO₂ interface layer is 18.9 nm.
samples so the actual thickness could be different. For that, 4 thinner samples to investigate the SiO$_2$ thickness and interface composition in greater detail has been deposited. All of the samples were made at the same pressure 500 Pa of CH$_4$/Ar (5/55 sccm) mixture deposition atmosphere and with bias voltage of 280 V. First one was deposited at 150 °C for 30 seconds and corresponding thickness determined from the growth rate results of the previous samples was 100 nm. Second sample was deposited at 800 °C for 30 seconds, and its thickness is about 15 nm. Third one was deposited at the same conditions as second one, but for 3 minutes. Corresponding thickness should be about 60 nm. Fourth sample was deposited at 150 °C for 30 seconds and post deposition annealed at 800 °C. Its thickness is the same as the first sample one.

All of the measured samples shows the same behavior as the previously discussed ones, but the intensity of O$^-$ peaks and also OH$^-$ peaks are little higher at the interface. Furthermore, the thickness of the SiO$_2$ interface films was estimated smaller in every case, than for previously discussed samples, and varied from 4.8 to 10.1 nm. All three samples which were deposited or annealed at high temperature shows higher concentration of O$^-$ and OH$^-$ species in its structure, as can be seen from Fig. 23.

Figure 23: SIMS depth profile of DLC film prepared at 800 °C, and with thickness of 58.6 nm. Estimated approximate thickness of SiO$_2$ interface layer is 10.1 nm.

From discussed results of SIMS measurements it is clear that if we deposit the sample at higher temperature, more oxygen is contained in the structure. However, the oxygen is not the reason of behavior change of DLC from dielectric to conductor, as we could see from the measurement results of the samples deposited at 300 and 400 °C. Also, the DLC composition is not changed for the different temperatures of annealing up to high values (600 °C) and
the only reason for the behavior change must be due to the structural changes.

Now, with the results of SIMS measurement it is possible to correct the dielectric constant of prepared DLC films with use of e.q. (7), where one capacitor is DLC film and other is thin SiO$_2$ layer. For corrections the mean 10 nm value of SiO$_2$ thickness has been chosen and fitted into the equation. The results are shown in Fig. 24 and Tab. 6 below. The values not filled in the table are for measurements where DLC film already acts as conductor, rather than dielectric. As it can be seen from the table, the actual value of the DLC film dielectric constant has been reduced by the one of the SiO$_2$.

![Figure 24: Corrected values of dielectric constant (relative permittivity) for samples deposited from 50 to 300 °C, and samples deposited at 150 °C and annealed up to 600 °C.](image)

Table 6: Corrected values of dielectric constant (relative permittivity) for samples deposited from 50 to 300 °C, and samples deposited at 150 °C and annealed up to 600 °C. Unreasonable high values for high temperature samples were omitted.

<table>
<thead>
<tr>
<th>Deposition temperature/Annealing temperature [°C]</th>
<th>Initial $\epsilon_r$</th>
<th>Corrected $\epsilon_r$</th>
</tr>
</thead>
<tbody>
<tr>
<td>50/-</td>
<td>4.45</td>
<td>3.83</td>
</tr>
<tr>
<td>100/-</td>
<td>4.59</td>
<td>4.41</td>
</tr>
<tr>
<td>200/-</td>
<td>4.57</td>
<td>5.16</td>
</tr>
<tr>
<td>300/-</td>
<td>4.77</td>
<td>6.87</td>
</tr>
<tr>
<td>150/-</td>
<td>4.45</td>
<td>4.49</td>
</tr>
<tr>
<td>150/200</td>
<td>4.59</td>
<td>4.64</td>
</tr>
<tr>
<td>150/300</td>
<td>4.57</td>
<td>4.62</td>
</tr>
<tr>
<td>150/400</td>
<td>4.77</td>
<td>4.83</td>
</tr>
<tr>
<td>150/500</td>
<td>5.15</td>
<td>5.21</td>
</tr>
<tr>
<td>150/600</td>
<td>5.27</td>
<td>5.34</td>
</tr>
</tbody>
</table>
4.5 Optical Properties

In this section, the results of optical measurements will be covered. The results are not yet analyzed to sufficient details, because of the long absence of suitable sample for FTIR and THz spectroscopy. This kind of sample was made just recently and the measurements are not completed so far, however some basic data were already obtained. Parameters of those new samples are different from those discussed above because they are made on non-doped Si substrate and were grown for immensely long time to receive very large thickness.

4.5.1 Spectroscopic Ellipsometry Results

First, we have measured the thickness of the SiO$_2$ on the n-Si (doped) substrate on DLC prepared at 150 °C by spectroscopic ellipsometry (SE). The spectral range of used device is from 0.73 eV to 6.42 eV and SiO$_2$ layer thickness was determined at 3.71 nm. Next the sample was moved to area with thin DLC sample (105 nm) on Si substrate. Measured pseudo-dielectric constant corresponding to whole structure according to the equation (10) for angles of incidence 55°, 60° and 65° is on figure below (Fig. 25).

![Figure 25: Pseudo-dielectric constant components ε$_1$ (blue) and ε$_2$ (green) as a function of used radiation energy for reflection from DLC(105 nm)/Si interface for angles of incidence 55°, 60° and 65°.](image)

Results of fitting and model deviations from the measured values in case of model DLC/Si and model DLC/SiO$_2$/Si were almost identical and so we used a simplified model description without SiO$_2$ interlayer. Our first fitting with this model used data from the ellipsometer for DLC and then used the B-Spline to refine the results. The resulting DLC thickness was d=120.9 nm, which is in good agreement with the estimated parameters from the deposition current and time 105.7 nm. Next, the above mentioned very thick DLC on non-doped Si substrate was measured. This sample was prepared at 300 °C for 2 hours. Its thickness is so large, that interference for larger wavelengths was observed. Its estimated
thickness reached 13.4 \( \mu \text{m} \). The components of dielectric constant of DLC layers deposited at lower temperatures (under conductor transition temperature) determined from model (e.g., (11)) are very similar for both thin and thick sample and are shown in Fig. 26.

![Figure 26: Determined dielectric constant components \( \epsilon_1 \) (blue) and \( \epsilon_2 \) (green) as a function of used radiation energy for DLC(thin)/Si (solid line) and DLC(thick)/Si (dashed line) interfaces.](image)

For sample prepared at significantly higher temperature (800 °C), we have also measured the thickness of the SiO\(_2\) oxide layer on the \( n \)-Si (doped) substrate. It was estimated at 3.91 nm. Again, the DLC/Si layer itself was modeled. The both two models of this thin DLC sample used data from the ellipsometer database for general DLC layer with lower amount of \( sp^3 \) hybridized carbon atoms and then used the B-Spline for more accurate results. Determined layer thickness from the first model which did not count with a surface roughness was 60.3 nm, which is in a relatively good agreement with the estimated thickness from the parameters of deposition around 58.6 nm. The refractive index of DLC layer determined from the model is shown in Fig. 27.

![Figure 27: Determined dielectric constant components \( \epsilon_1 \) (blue) and \( \epsilon_2 \) (green) as a function of used radiation energy for DLC(800 °C)/Si interface. Model without surface roughness.](image)
In the second model with surface roughness, mentioned above, we have achieved a much better agreement of fitted data with measured values, but with high surface roughness. Specifically the layer thickness was estimated at 47.12 nm and roughness at 21.43 nm. Also, the model parameters have significantly correlated in some cases. The resulting graph is for completeness shown in Fig. 28 together with the estimated dielectric constant from another thick sample. This sample was again deposited for 2 hours, but because of the high deposition temperature (700 °C) and consequent small growth rate the thickness of the DLC was estimated from SE as 1.59 µm. The values varies more than in the previous comparison and the value of dielectric constant estimated from the thick sample should be more precise.

Figure 28: Determined dielectric constant components $\epsilon_1$ (blue) and $\epsilon_2$ (green) as a function of used radiation energy for surface roughness including model DLC(thin)/Si (solid line) and DLC(thick)/Si (dashed line) interfaces.

From discussed results of spectroscopic ellipsometry above it can be seen that two kinds of DLC layers act differently and thus the resulting structure must be different. We confirmed that the films prepared at different temperatures doesn’t have the same properties and that in case of high temperature sample the absorption of electromagnetic radiation is higher for discussed radiation energies.

4.5.2 FTIR Spectroscopy Results

In FTIR spectroscopy the new thick samples prepared on non-doped Si substrate were measured in vacuum and in spectral range from 7500 cm$^{-1}$ to 370 cm$^{-1}$. To remove the possible influence of the holder, the transmittance $T$ and reflectance $R$ were calculated accordingly to relations

$$ T = \frac{T_{Sample}}{T_{Holder}}, \quad R = \frac{R_{Sample} - R_{Holder}}{R_{Reference} - R_{Holder}}. $$

where $T_{Holder}$ is a transmittance of the holder alone, $T_{Sample}$ is holder transmittance with the sample, $R_{Holder}$ is a reflectance of the holder, $R_{Reference}$ is that of the holder and Au reference and $R_{Sample}$ corresponds to holder reflectance with the sample in place.
From the reflection measurements (Fig. 29) a difference between sample prepared at 300 °C (13.4 µm) and the one at 700 °C (1.59 µm) is clear. Due to the different thickness, samples are not easily comparable, but later one does not show any interference so it attenuates them and almost only reflection from the DLC/vacuum interface is measured. This is also the reason why the silicon peak around 610 cm\(^{-1}\) is almost not visible in the spectra. For the case of sample prepared at 300 °C the interference is strong, which means that the reflection from both DLC/vacuum and Si/DLC interfaces. This suggest smaller IR light absorption in lower temperature prepared DLC layers and because of the much greater thickness the actual absorption should be several times smaller than in high temperature prepared DLC’s. The Si peak in case of 300 °C disappeared in the mean value fit, but from the change of the interference pattern is clearly visible.

FTIR results of transmittance through the sample are in Fig. 30. The characteristics correspond with above mentioned character of DLC layers and the lower temperature prepared sample absorbs significantly smaller amount of IR radiation than high temperature one. Also in this case if we would plot the results to the same thickness of the DLC layer the difference would be even higher. One visible peak, except the silicon ones, is at around 2900 cm\(^{-1}\). This peak should correspond only to our DLC layer, but precise character of its absorption has to be investigated in the future. Also, the interference can be seen in low temperature DLC and finally the broad change of peaks in DLC between 500 and 1800 cm\(^{-1}\), which would need a further analysis to determine its character. Proposed reasons are either the broad DLC absorption band in this region, or enhancement of absorption corresponding with multiple interference reflections. Nevertheless, sample prepared at higher temperature shows much smaller transmittance, no interference and also no peak absorption enhancement.
4.5.3 THz Spectroscopy Results

With THz spectroscopy, so far only transmission through the thick samples has been measured (Fig 31) in spectral range approximately from $107 \text{ cm}^{-1}$ to $2 \text{ cm}^{-1}$. The measured signal shows high interference in all measurements, but in the case of high temperature sample interference intensity is damped due to high absorption. Measured data are fitted by polynomial showing their mean values from which the coarse is more clear. As can be seen from the results, DLC prepared at lower temperature has higher transmittance, even higher than used silicon wafer which can correspond to some DLC anti-reflection properties at this thickness.

Next, for comparison of transmittance measurements by FTIR and THz spectroscopies their spectra are plotted in one graph with logarithmic scale of wavenumbers (only mean value for Si substrate was kept, because of figure clarity). Figure proposes the consistency of measured data, but the far-IR region has to be measured for completeness. This measurements in far-IR region by our FTIR Bruker Vertex 70v takes a very long time because of the small signal and required long integration time for good results. However, this measurement will surely be conducted in the future for competition of spectral characteristics of our DLC’s.

At the end of this section the author would like to point out that for precise evaluation of measured FTIR and THz spectra, their modeling and subsequent confirmation a long time is needed, which was not available and so the data are presented at least in the first qualitative outline.
Figure 31: Mean transmittance of the DLC prepared at 300 °C (red line), DLC prepared at 700 °C (blue line) and non-doped silicon substrate alone (dark green line). The actually measured data for each corresponding sample are plotted by magenta, cyan and light green colors respectively.

Figure 32: FTIR and THz transmission spectra. Red is for DLC on Si prepared at lower temperature and blue is for DLC prepared at higher temperature. In case of THz spectra magenta and cyan lines corresponds to measurement and red and blue lines to mean values. Green line is for substrate Si signal alone, when the interference in the Si alone signal measurement has been omitted for better data clarity.
5 Summary

In this study, thick DLC films were deposited by PA-PECVD at different temperatures and their characteristics investigated. DLC films usage has been suggested as a waveguide or cladding layer for electrically-induced graphene-channel THz injection laser device and for this reason their possible highest deposition thickness, thermal stability, dielectric constant, resistivity, composition, and optical constants has been investigated.

In order to grow a thick DLC film (>10 µm thick), the deposition temperature needs to be raised at least up to 200 °C. The increase in temperature decreases resistivity of the film (to $4.682 \times 10^7 \ \Omega \cdot m$) and prevents from the charge-up effect during the deposition. The decrease in resistivity is due to nano-crystallization of the DLC film and increase in the concentration of the $sp^2$ bonded carbons. However, before the clusters connects each other and the DLC film becomes conductive, the dielectric constant (relative permittivity) only increase and its maximum value reaches 6.87 when prepared at 300 °C, suggesting that the thick samples deposited at higher temperature still exhibits sufficient electrical properties for waveguide fabrication.

Post deposition annealing of the DLC films shows a similar tendency to connect each $sp^2$-bonded clusters into larger ones so that its dielectric constant increases with temperature. However, the resistivity of those annealed samples stays almost constant up to 600 °C annealing and the sample acts as a dielectric up to this temperature, suggesting that it could be possible to deposit a CVD graphene sheet at higher temperature on the present thick DLC films.

The SIMS measurements demonstrate no change in composition of both samples prepared or annealed under 600 °C and increase in oxygen concentration in these films treated at higher temperatures. This is probably due to desorption of oxygen from the apparatus components and its reaction with DLC at high temperatures. The thickness of the $SiO_2$ inner layer between the DLC film and Si substrate is about 10 nm for most of the samples.

The growth rate of the DLC films changes with temperature of the deposition. It is about 200 nm-min$^{-1}$ at low temperature and decrease up to about 40 nm-min$^{-1}$ at high temperature (600≈700 °C). Also, the thickness of the DLC films can be controlled at constant temperature of deposition by electric charge flow in the plasma circuit.

Optical measurements clearly shows the difference between DLC layers grown at different temperatures. The dielectric constant in visible region has been determined from spectroscopic ellipsometry and shows its real part around 4 and imaginary around 1.5 for low temperature prepared DLC’s, which were proposed as waveguide layers for THz injection laser. Measurements made by Fourier transform IR and THz spectroscopy are not sufficiently evaluated yet, but the qualitative result is that also in IR and THz region the layers prepared at higher temperatures have bigger absorption and acts more like conductors.

The results received from mentioned measurements are promising, but more investigation of DLC properties has to be executed. Most importantly to determine the optical
band gap more precisely, dielectric constant in the THz frequency region and corresponding refractive index of prepared DLC films. Also, the creation of precise model for the photoemission-assisted Townsend and glow discharges on DLC surfaces, manufacturing of the top graphene layer with sufficient quality, and the final structure completion are still goals to achieve in following stages of research. Although it is necessary to make more measurements and clarify the properties of our DLC’s in greater detail, it is appropriate to say that our methods of DLC dielectric film fabrication are very promising for further research in the field of graphene based THz devices.

Bc. Radek Ješko
6 Reference


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