Carbon-based functional Materials for Application in Photonics, Optoelectronics and Sensorics

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Author: Helge Lux, M.Eng.

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1. Thesis advisor: Prof. Dr. Mauro Casalboni (University of Rome - Tor Vergata)

2. Thesis advisor: Prof. Dr. rer. nat. habil. Sigurd Schrader
(Technical University of Applied Sciences Wildau)

Abstract

Author: Helge Lux, M.eng.

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Content:

In this work, two different processes to deposit Graphene-based transparent conductive films on arbitrary insulating substrates have been developed and examined. The first process is a PE-CVD, based on a gas mixture containing hydrocarbons (e.g. methane) inside a vacuum chamber where the insulating substrates are placed on a temperature controlled heating plate.

The second process uses a pulsed filtered vacuum arc system (Φ -HCA) to homogeneously deposit a small, well defined amount of carbon on heated substrates. The substrates are tilted with respect to the particle beam and placed on a heating plate. A gas atmosphere consisting of Argon or Argon/Hydrogen decreases the particle energy and influences the morphology of the growing film.

For both processes, Scanning Tunneling Microscopy (STM), Transmission Electron Microscopy (TEM) and Raman spectra have been used for a thorough characterization of the samples in order to optimize the growth parameters. Subsequently, the results (sheet resistance, Hall mobility, transmittance) have been compared with respect to the state of the art, reported in literature. The best carbon layers have a surface resistance of $5 \cdot 10^3 \Omega_{\square}$ while the optical transparency of the coatings is 88% with an excellent homogeneity over areas of several cm^2 . Both for the PE-CVD and the Φ -HCA, the area of deposition is only limited by the respective area of the heated surface. The obtained results and the fact, that the process can be compatible with most semiconductor fabrication processes, makes them promising for various industrial applications.

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Table of used Unit Symbols

Unit Symbol	Name	Unit
ν_F	Fermi velocity	m/s
μ_H	Hall mobility	cm^2/Vs
$R_{\square}$	Sheet resistance	$\Omega_{\square}$
ρ	Specific Resistivity	Ωm
T_O	Optical transmission	%
λ	Wavelength	nm
Δf	Frequency shift	1/s
ΔE	Energy shift	eV
k_L	Wave vector of incident photon	1/m
k_{Sc}	Wave vector of scattered photon	1/m
q_P	Phonon Wave vector	1/m
$\omega_{Sc} = \frac{2\pi}{\lambda}$	Pulsatance of scattered photon	1/s
$\omega_L = \frac{2\pi}{\lambda}$	Pulsatance of incident photon	1/s
E_F	Fermi Energy	eV
J_T	Tunneling current	A
d_s	Gap between dip and surface	m
V_T	Bias voltage	V
Φ	Average barrier height	eV
V_z	Voltage in z-direction	V
σ	Electrical conductivity	S
$\vec{B}$	Magnetic field	kG
$\vec{E}_H$	Electric field	V/m
$\vec{F}_L$	Lorentz force	N
$\vec{v}$	Propagation velocity	m/s
q	Electron charge	$\approx 1.602 \cdot 10^{-19}C$
j_x	Current density in x-direction	A/m^2
n	Number of charge carriers	dimensionless
R_H	Hall constant	m^3/C
U_H	Hall voltage	V
p	Pressure	Pa
P_{Plasma}	Plasma power	W
$\dot{V}_{CH_4}$	Methane flow	sccm (standard cubic centimeters)
$\dot{V}_{Ar}$	Argon flow	sccm (standard cubic centimeters)

p_w	Working pressure	Pa
p_{Ar}	Argon pressure	Pa
p_{H_2}	Hydrogen pressure	Pa
T_s	Substrate temperature	°C
t_p	Process time	min
τ_p	Plasma arc time	ms
I_{arc}	Plasma current	A
I_F	Filter current	A
k	Extinction coefficient	dimensionless
α	Absorption coefficient	1/nm
N_p	Pulse count	dimensionless
V_b	Break down voltage	V
V_p	Plasma voltage	V
V_h	Heating voltage	V
λ_i	Mean free path for ionization	1/m
α	First Townsend coefficient	1/m
γ	Second Townsend coefficient	dimensionless
d_{Ar}	Diameter of an argon atom	0.376 nm
N_{Ar}	Number of argon atoms	dimensionless
N_{C^+}	Number of carbon ions	dimensionless
V_f	Volume of the filter arch	m^3
k_b	Boltzmann's constant	$1.38 \cdot 10^{-23} J/K$
e	Elementary charge	$1.602 \cdot 10^{-19} C$
R_t	Overall reflection	dimensionless
T_t	Overall transmission	dimensionless

Table of Abbreviations

USD	US-Dollar
TCO	Transparent Conductive Oxide
TFT	Thin Film Transistor
ITO	Indium Tin Oxide
Zn:O	Zinc Oxide
ZnO:Al	Aluminum Doped Zinc Oxide
ITO:Sn	Tin Doped ITO
CdO:In	Indium Doped Cadmium Oxide
GBT	Graphene Base Transistor
FET	Field Effect Transistor
IHP	Institute for High Performance Microelectronics
CNT	Carbon Nano Tube
SWCNT	Single Wall Carbon Nano Tube
MWCNT	Multi Wall Carbon Nano Tube
HOPG	Highly Ordered Pyrolytic Graphite
VHS	Van-Hove Singularity
FLG	Few-Layer Graphene
OLED	Organic Light Emitting Diode
PV	Photo voltaics
FPD	Flat Panel Display
EMI	Electromagnetic Induction
CVD	Chemical Vapor Deposition
DNA	Desoxyribonucleic acid
Φ -HCA	Filtered High Current Arc
PE-CVD	Plasma Enhanced Chemical Vapor Deposition
AFM	Atomic Force Microscopy
STM	Scanning Tunneling Microscopy
CCD	Charge Coupled Device
CU	Control Unit
DC	Direct Current
PVD	Physical Vapor Deposition
SEM	Scanning Electron Microscopy
BK7	Boron Crown Glass
TEM	Transmission Electron Microscopy

ToF-Sims	Time of Flight Secondary Ion Mass Spectrometry
RMS	Root Mean Square
RGO	Reduced Graphene Oxide
ta:C	tetrahedral amorphous carbon
UHV	Ultra High Vacuum
LMIG	Liquid Metal Ion Gun

1 Introduction

Carbon is regarded as one of the most interesting elements in the periodic system since it can appear in many different modifications. In 2004, Andre Geim and Konstantin Novoselov discovered that even one mono layer of carbon, consisting of a grid with sp^2 -hybridized carbon-carbon-bonds, is stable. For this discovery they got the Nobel prize for physics in 2010. Because of its extraordinary physical behavior, Graphene could be used in many different ways. The thermal and electrical conductivity are extremely high. The optical transparency is about 97.7 % and is nearly independent of the wavelength of light except for a dip at 270 nm, the van-Hove-singularity. In addition, the charge carriers inside the conduction band have high mobility and density. Because of its high optical transparency and good electrical conductivity, Graphene is possibly suitable as a substitute for TCO (Transparent Conductive Oxide). Currently, TCO is used as a transparent electrode for touch screens, TFT displays, and solar cells. The currently used materials are ITO (Indium Tin Oxide), ZnO (Zinc Oxide), ZnO:Al (with aluminum doped Zinc Oxide) or ITO:Sn (with Tin doped Indium Tin oxide)[1]. Since all these materials are semiconductors, the problems lie in either the high resistance at room temperature, the low charge carrier density and mobility inside the conduction band or in the complicated production with very narrow process windows. Additionally, any used materials are toxic ((CdO:In, with indium doped Cadmium oxide), have a low optical transparency (CuAlO_x, Copper Aluminum Oxide) or have a high reactivity (ZnO:Al). Furthermore, the high price and low availability of indium is one main problem of all indium based materials. Its price has risen from 97 USD per kg in 2003 up to 670 USD per kg in the last 10 years [2].

Another possible field of application for Graphene is the fabrication of transistors and other active devices in the semiconductor industry. The collaboration partner of the Technical University of Applied Sciences Wildau [FH], the Leibnitz institute of innovative high performance microelectronics (IHP) in Frankfurt (Oder) is interested in the production of transistors made of Graphene. For this purpose, a new architecture of transistors has been developed and patented [3], in which the Graphene is used as the transistor base. This GBT (Graphene Base Transistor) should not have the disadvantages of a Graphene-FET (Field Effect Transistor) such as a missing saturation current and a high leakage current, which is a result of the missing band gap in mono layer Graphene.

However, in order to introduce Graphene in a broad field of application such as TCO substitute, it would be desirable to produce large area Graphene targeted on arbitrary substrates. Until now, different processes have been published which work on catalytic metals such as copper and nickel. However, there is not yet a reliable fabrication process of Graphene which works directly on insulating substrates, neither for high-quality mono layer Graphene nor for any Graphene containing film with sufficient transmission and conductivity. Hence, for the current work, two different processes have been developed and optimized in order to deposit Graphene-containing, transparent and conductive carbon films on insulating substrates. Before describing the different approaches, the basics of Graphene will be described in the following section.

2 Basics of Graphene

2.1 Carbon modifications

With regard to the chemical bonds, carbon has three different modifications, which are known as sp^1 -, sp^2 - and sp^3 -hybridization. The sp -hybridization means, that the electrons of the p - and s -orbital form together one hybrid orbital. The sp^1 -hybridization is characterized by a hybrid orbital consisting of one s - and one p -electron. This bonding can be found in carbon containing gases like ethine or in compounds like diacetylenes.

To form Graphene or Graphene-like coatings, the carbon has to be predominantly sp^2 -hybridized. To build such a sp^2 -hybridization (Figure 2.1), one s -electron is lifted into the empty $2p$ -orbital with energy addition. Subsequently, three sp^2 -hybrid orbitals arise from two $2p$ -electrons and one $2s$ -electron [4].

Figure 2.1: Energy scheme of sp^2 -hybridization [4].

The sp^2 -hybridized carbon forms layers, consisting of strong lateral σ -bonds and π -bonds between the carbon atoms. In addition, the π -electrons undergo an additional π - π -interaction between these carbon layers. This is illustrated on the one hand by the short in-plane bond length of 1.4 Å between the carbon atoms, and on the other hand by the rather large inter-layer distance of about 3.3 Å in graphite.

Beyond graphite, the sp^2 -bonds can be found in Graphene as well as in Carbon Nano Tubes (CNT) and Fullerenes (Figure 2.2). Graphene is a mono layer of sp^2 -hybridized carbon atoms forming a two-dimensional hexagonal crystal lattice [5]. The name "Graphene" is derived from "graphite", the three-dimensional allotrope of sp^2 -bound carbon. Graphene was investigated first in 2004 by K. S. Novoselov and A. K. Geim et al. [6]. For groundbreaking experiments on the two-dimensional material Graphene, the Nobel prize in Physics 2010 was awarded jointly to Andre Geim and Konstantin Novoselov [7].

Carbon Nano Tubes as further allotrope of Carbon categorized as single-walled (SWCNT) and multi-walled (MWCNT). CNT's can be described as coiled Graphene sheets. Similar to Graphene, CNT's have also very interesting physical and electrical properties and the first fully functional micro-processor based on CNT's was already shown by Max M. Shulaker et al. [8] in 2013. Another special Fullerene is the so-called Buckyball (Buckminsterfullerene), which was investigated first in 1985 by H. W. Kroto et al. [9]. This C_{60} molecule has a truncated icosahedral structure formed by replacing each vertex on

the seams of a ball by a carbon atom [9]. For the discovery of Fullerenes, the Nobel Prize in Chemistry 1996 was awarded jointly to Robert F. Curl Jr., Sir Harold W. Kroto and Richard E. Smalley [10].

Figure 2.2: Different allotropes of sp^2 -hybridized carbon.

Another important carbon-carbon-bond is the sp^3 -hybridization which is formed by one s-electron and three 2p-electrons using the same hybridization mechanism as mentioned above [4].

Figure 2.3: Energy scheme of sp^3 -hybridization [4].

The sp^3 -hybridization allows the formation of very strong σ -bonds between carbon atoms which leads to materials such as diamonds and tetrahedral amorphous carbon (ta:C). The strength of σ -bonds are responsible for the high hardness of these materials and furthermore they can be found in gaseous hydrocarbons like methane.

2.2 Physical properties and applications

Due to their extraordinary optical and electrical properties, Graphene and Graphene-based materials are potentially useful in a broad field of application. Especially, the combination of high optical transmission and high thermal and electrical conductivity makes this sp^2 -modification of carbon a promising high tech material. Graphene has a honeycomb lattice both in the real crystal lattice and in the reciprocal space (Figure 2.4).

At the edges of the Brillouin zone, there are intersections of the Dirac cones and their bands hybridize, resulting in two saddle points in both the electron and the hole side [11]. The Fermi energy is located exactly between the Dirac cones and consequently, Graphene behaves like a semiconductor with a band gap of 0 eV. The electrons are massless Dirac fermions with a very high Fermi velocity $\nu_F \approx c/300$ if c is the speed of light ($\nu_F = (\sqrt{3}ta)/2\hbar \approx 10^6 m/s$) [12]. This high Fermi velocity is responsible for the high electron mobility and the very good electrical and thermal conductivity is provided by the missing band gap, resulting in a high charge carrier density inside the conduction band. The

Figure 2.4: Band structure of Graphene.

Table 2.1 shows a comparison of charge carrier mobility and thermal conductivity of Graphene and other established materials at room temperature [11].

Material	charge carrier mobility (cm^2/Vs)	thermal conductivity ($Wm^{-1}K^{-1}$)
Graphene	$2 \cdot 10^5$ [13]*	>3000
Copper	32	450
HOPG	$1.2 \cdot 10^4$	≈ 2000
Silicon (bulk)	1450	149

Table 2.1: Charge carrier mobility and thermal conductivity of Graphene and other established materials at room temperature. *For free-standing Graphene.

As can be seen from Table 2.1, free-standing Graphene reaches the highest electron mobility and the highest thermal conductivity as well. However, if Graphene is in contact with any substrate material (e.g. silicon oxide), its mobility significantly decreases by about one order of magnitude ($\approx 1.2 \cdot 10^4$ [11]). Nevertheless, this measured value is much higher than that for silicon and copper. Additionally, the optical transmission of about 97,7% is nearly independent on the wavelength of light except a local minimum at 270 nm. This peak in the ultraviolet region is caused by exciton-shifted van Hove singularity (VHS) in the Graphene density of states [14]. Figure 2.5 [7] shows the calculated band structure of Graphene with the conduction band (electron side), the valence band (hole side) and the Fermi energy, located at the intersection of the two bands. The key feature of the band structure is the presence of two saddle points. It leads to a diverging density of states, the VHS (Figure 2.5, red arrows).

Furthermore, in few-layer Graphene (FLG), other absorption bands can be seen at lower energies [14]. In case of rotated Graphene layers, the interlayer coupling results in another VHS near the intersection of the Dirac cones [11]. This absorption depends on the twist angle of one Graphene layer with respect to the layer underneath, and its energy gap is in the range of 0.1 eV to 0.5 eV. However, this very low absorption is located in the far infrared ($\lambda \approx 4 \mu m$) and it is not preserved at room temperature. Overall, the very high transmission and the flat absorption spectrum from 300 nm to 2500 nm makes

Figure 2.5: 3D-band structure of Graphene with the van Hove singularity (red arrows) [7].

Graphene a promising candidate for transparent conductive films. However, to use Graphene in this broad field of application, it has to fulfill the requirements regarding its transmission and sheet resistance. Figure 2.6 [15] illustrates the transmission vs. sheet resistance requirements for the application of Graphene in Organic Light Emitting Diodes (OLED), Photo voltaics (PV), Flat Panel Displays (FPD), Touch screens, and Electromagnetic Interference Shielding (EMI Shield).

First applications of Graphene in solar cells are already realized (Figure 2.6, inset) and the efficiency of the cells increases continuously.

Figure 2.6: Transmission vs. sheet resistance for different applications of Graphene, inset: Efficiency of Graphene solar cells.

Furthermore, full functional touch screens have been already presented e.g. by J. Kim et al. [16] and

OLEDs have been produced e.g. by T.-H. Han et al. [17]. Moreover, investigations have begun to use the small band gap of FLG, resulting from the VHS of a quantum dot structure of single layer Graphene, for fast broadband photo detectors [18, 19].

In addition, Graphene is not only useful as a substitute for transparent conductive coatings. Graphene layers deposited on different metals are also suitable for anti-corrosive coatings. This application was investigated by U. Mogeraa et al. for nickel [20], by V. Miskovic-Stankovic et al. [21] for copper and aluminum, and by N. T. Kirkland et al. [22]. However, the production of large-scale and high-quality Graphene on arbitrary substrates is very difficult but it plays a key role for all applications described above. Hence, different methods for the deposition of Graphene and the required technical equipment will be described in the following section.

3 Methods of deposition

3.1 Introduction

The deposition of high-quality Graphene is one of the biggest challenges in the broad field of carbon research. The first process developed by Geim and Novoselov is based on repeated pulling of graphite with the help of sticky-tape, until only one mono layer is left[1]. Using this procedure, high-quality Graphene can be produced with only little afford. However, this sticky tape method to produce ultra-thin single crystals has been known since 1965, as R. F. Frindt reported the production of molybdenum-disulfide with a thickness of only a few mono layers [23]. Nevertheless, only small Graphene flakes with a diameter in the μm -range can be produced using this approach. To introduce Graphene in a broad field of applications (such as semiconductor industry, transparent conductive layers, sensors, electrodes) it would be desirable to develop a reliable process which deposits Graphene on selected sites and/or covering large areas.

Currently, many other processes for deposition of large-area Graphene have been developed using different substrate materials such as catalytic metals and insulators. The following section describes different approaches with their advantages and disadvantages.

3.2 CVD on catalytic metal substrates

So far, the chemical vapor deposition (CVD) is one of the most established methods to fabricate large area Graphene films. It is based on cracking a carbon containing precursor gas on a heated metallic surface by using its catalytic properties. Under optimal conditions, the free carbon converts into Graphene and deposits on top of the substrate. A standard CVD process starts in a vacuum chamber by heating the substrates up to the required temperature of about 1000 °C. This temperature is kept constant during the Graphene growth. When the precursor gas is let into the chamber, the deposition process starts. Additionally, buffer gases (e.g. Argon) as well as functional gases (e.g. Hydrogen) can be added to the precursor gas in order to improve the deposition process. At the end, the substrates have to be cooled down to room temperature. It must be noted, that in case of nickel as substrate material, the cooling rate is an important parameter for optimization of the process. Figure 3.1 shows a scheme of a standard CVD process on catalytic substrates using a defined cooling rate for the Graphene production on a nickel surface.

Using different metals as substrate material, the CVD-process flows are nearly similar. However, the mechanism of building Graphene on copper and nickel is completely different. During the Graphene process on heated nickel substrates, the carbon diffuses into the surface. The required temperature depends on the used precursor gas (e.g. for methane: 950 °C). During the cooling procedure following the diffusion, the carbon leaves the surface and deposits as a mono- or multilayer on top of the substrate. Both the quality of the Graphene and the thickness strongly depend on the cooling rate after the diffusion process has finished. Hence, for that process a defined cooling rate is necessary as

Figure 3.1: CVD-process flow diagram for the deposition of Graphene on a catalytic metal[24].

well as a defined process time for the diffusion of carbon atoms.

In contrast to the nickel process, nearly no carbon diffuses into the surface by using a copper substrate. Furthermore, the copper process is self-limiting after deposition of one or two Graphene layers, because the thickness of the Graphene does not depend on any carbon diffused into the substrate material. Consequently, the cooling rate is not an important parameter.

The CVD of Graphene on such catalytic substrates is currently state of the art and frequently published. A CVD-process on copper foils is described e.g. by Zheng Han et al. [25], and by Xuesong Li et al. [26]. The application of evaporated copper films on silicon as substrate material is described by Li Tao et al. [27]. Also, the process on nickel films has been well understood and examined e.g. by Qingkai Yu et al. [28]. The Graphene layers deposited using CVD-processes exhibit good quality and cover large areas. However, for most applications the Graphene films have to be lifted-off from the metal surface by a suitable carrier foil and subsequently transferred to the area of operation in the respective device or sample to be fabricated based on this so-called "exfoliation process". Usually, this process damages the Graphene and leaves contaminations on the Graphene (substrate material, polymers from the carrier of the transfer process or organic solvents). Therefore, to introduce Graphene into a broad field of applications such as the semiconductor industry it would be necessary to develop a reliable coating process without exfoliation. With the aim of substituting TCO, Graphene has already been produced using deposition on catalytic metals and subsequent exfoliation with all the difficulties mentioned above [17]. To avoid these problems, thin metal films have been coated on dielectric substrates to support the deposition of Graphene. This process was developed and studied by Zheng Yan et al. for nickel [29] and Ching-Yuan Su et al. for copper films [30]. Unfortunately, even this process does not ensure a metal free Graphene after removing the supporting metal film.

Overall, the use of intermediate metal films as well as metal foils is not favorable to substitute TCO in mass production because all processes require an exfoliation process that entails all the problems

mentioned above. Therefore, the next section describes different approaches to form Graphene, Few Layer Graphene (FLG), or related carbon coatings directly on insulating substrates.

3.3 Deposition on dielectric substrates

To avoid the exfoliation process it would be desirable to deposit the Graphene directly on the surface of a functional substrate (e. g. Silicon oxide or other insulating material). The biggest challenge in accomplishing this alternative to the exfoliation process is that no catalytic effect of the material can be used. Consequently, all established CVD processes hardly work on insulating substrates.

One possible process for Graphene fabrication directly on dielectrics without any catalytic metal is the epitaxial growth on silicon carbide [31]. This method produces high quality Graphene covering large areas. However, this process requires substrate temperatures near 1600°C and it is limited to silicon carbide as substrate material. For that reason the process is hardly applicable in semiconductor technology. Other investigations were carried out on CVD-processes on very special insulating substrates e. g. by Mark H. Rummeli et al. on magnesium oxide [32], by Jie Sun et al. on sapphire and silicon oxide [33], and by Fanton et al. on sapphire [34]. In addition U. Wurstbauer et al. [35], and J. Hackley et al. [36] have demonstrated that there are regions of few layer Graphene growth on dielectrics (silicon oxide) using molecular beam epitaxy. However, this approach produces only small Graphene flakes instead of a fully closed film. Furthermore, a reduction method of reduced Graphene oxide (RGO) is used to prepare few-layer Graphene in large quantities on arbitrary substrates [36]. These coatings can reach a broad field of application such as bio-sensors, gas sensors and DNA sensors [36]. However, due to the unfavorable conditions during the chemical reduction process, the lattice of the Graphene is damaged [36]. Consequently, until now these coatings do not have reliable electrical and optical properties.

To sum up, there is still no reliable fabrication process of Graphene as TCO-substitute, which works directly on insulating substrates, neither for high-quality mono layer Graphene nor for any Graphene containing film with sufficient transmission and conductivity.

Hence, the present work is devoted to investigate two different and new approaches for Graphene synthesis on functional substrates. The first one is the filtered arc evaporation, which is also known as filtered high current arc (Φ -HCA). This technology was originally developed for the production of ultra-hard and dense tetrahedral amorphous carbon (ta:C) [37, 38, 39]. However, this technology has been already used to deposit a carbon layer with the aim to thermally convert it into conductive sp^2 -hybridized carbon [40]. Even the fundamental growth process of such carbon films has been theoretically described in detail by N. A. Marks et al. [41]. These descriptions show a predominantly perpendicular growth of graphitic carbon layers with respect to the surface. This theoretical work has been verified by Y. Yin et al. [42] using this technology to deposit graphitic carbon coatings on heated substrates under different gas conditions. However, still no publication could be found which deals with optimization of optical and electrical properties as well as the crystallographic structure

and orientation of Graphene-containing carbon coatings deposited by use of the Φ -HCA technology. The second approach consists of a PE-CVD process under low pressure and by heating the substrate. Standard CVD-processes on insulating substrates have already been carried out e.g. by M. A. Fanton et al. [34], M. Rmmeli et al. [32] and G. Hong et al. [43]. However, to improve the quality of the Graphene, the deposition can be supported by igniting a plasma during the carbon growth process. This possibility will also be described and investigated in the current work.

4 Methods for Analysis

4.1 General

To characterize the quality of the produced carbon coatings, several measuring methods for optical, electrical, and structural analysis have been used. The frequently used measuring methods will be described in the current section.

One important property of the carbon films is the ratio between sheet resistance (R_s in $\Omega/\square$) and optical transmission T_O . With regard to possible applications of Graphene, high optical transmission and good electrical conductivity are desirable. In this work the optical transmission was determined by use of Spectral Photometry and Reflectometry (Perkin Elmer UV-Vis-NIR Spectral Photometer Lambda 1050). The electrical properties (Sheet Resistance, Charge Carrier Mobility) have been measured using two different Hall-devices: Lakeshore LS 4005 and Lakeshore LS 7600.

To reduce the effects of scattered light and to optimize the transmission, the topography of the films has to be flat and the roughness should be as low as possible. In this work, the topography and the roughness of the samples has been determined using AFM measurements (Atomic Force Microscopy) and STM (Scanning Tunnel Microscopy). The AFM measurements were performed using an AFM CP II (Veeco) in contact mode. The STM measurements have been performed using a WA-Technology microscope with a tungsten tip in constant-current mode and the tunneling conditions were optimized from time to time in order to attain the highest resolution. The STM images have been analyzed using the freeware scanning probe microscopysoftware WSXM [44].

In addition, one important technology to analyze Graphene is the Raman Spectroscopy. This method will be described in more detail in the following section 4.2. The used Confocal Micro Raman Microscope (WiTec Alpha 300) is combined with a x-y scanning table and an optical microscope. Using this arrangement, the crystallinity and chemical quality of the Graphene can be determined as well as the homogeneity (high resolution mapping).

Furthermore, the purity of the coatings has been determined using a Time-of-flight mass spectrometer (ToF SIMS) with a Liquid Metal Ion Gun (LMIG). The detection limit of the used device (ION-TOF 5) is about 10^9 - 10^{10} *at/cm²* (according to single mono layer).

The structural analysis has been carried out using TEM measurements with a Tecnai Osiris from FEI operated at 200 kV. The samples have been prepared conventionally by grinding, polishing and argon ion milling and subsequently analyzed in cross-section.

4.2 Micro Raman Spectroscopy and Microscopy

4.2.1 General

The Raman Spectroscopy is one of the most popular methods to analyze Graphene. The Raman signal contains information about the crystallographic structure, quality, chemical purity as well as the thickness of the Graphene. In this work, a Confocal Micro Raman Microscope (WiTec alpha 300) with an excitation wavelength of $\lambda = 488\text{ nm}$ has been used to record single spectra and high resolution mappings of the carbon films. For all investigations, the laser power was set to a value of 30 mW in order to generate a proper signal-to-noise ratio without degrading the layer.

The main effect, known as Raman effect, was theoretically predicted in 1923 by Adolf Smekal and experimentally verified in 1928 by Chandrasekhara Venkata Raman. First devices used a mercury vapor lamp as monochromatic light source. The record of spectra was very difficult because of the lack of sensitive detectors. Today, mercury vapor lamps are substituted for lasers and the Raman signals can be recorded using Charge Coupled Devices (CCDs). The measurement method of Raman Spectroscopy will be explained in more detail by the following.

If matter is illuminated using a monochromatic light source (e.g. a laser), it interacts with photons in different ways (e.g. absorption, reflection, inelastic and elastic scattering).

In contrast to Rayleigh scattering (elastic scattering), the Stokes and Anti-Stokes interactions are inelastic. However, in all of these scattering processes, the photons of incident light excite the atoms of the sample and lift one or more electrons from the ground state N_0 to a virtual (unstable) energy level N_2 (Figure 4.1 a). In case of elastic scattering, the scattered photon has the same energy as the incoming one. Consequently, the scattered spectrum contains no information of the illuminated matter.

In case of inelastic scattering, the incoming photon either loses energy (Stokes Scattering) or wins energy (Anti-Stokes Scattering). The frequency of the light is now shifted to higher or lower energy. This effect is called Raman shift. The frequency shift Δf of the Stokes or Anti-Stokes lines is proportional to the energy difference ΔE between the incoming and scattered photon ($\Delta f \propto \Delta E$). ΔE depends on the polarizability of the material and provides informations about elements and chemical bonds as well as about crystallographic structure. The principle of the Raman scattering process is illustrated by Figure 4.1 b and will be described by the following.

The incident photon ω_L interacts with a phonon Ω (photon-phonon-scattering). Subsequently, the scattered photon ω_{Sc} is emitted. For Raman scattering, the fundamental Raman rule, known as the "energy and momentum conservation", has to be fulfilled. If k_L is the wave vector of the incident photon and k_{Sc} is the wave vector of the scattered photon, the resulting phonon vector q has to be zero:

Figure 4.1: a) Scattering processes of light and matter, b) principle of the Raman scattering process.

$$k_L = k_{Sc} + q$$

(1)

$$\text{for } k_L \approx k_{Sc} \rightarrow q \cong 0$$

If more than one phonon is involved in the scattering process, this fundamental Raman rule is always satisfied: $\sum_i q_i \cong 0$ because $q + (-q)$ and consequently the overtone of such a scattering process is always Raman-active. Overall, the Raman light can be regarded as a fingerprint of the sample and the Stokes scattering as well as the Anti-Stokes scattering can be used for Raman Spectrometry. In most cases, the Stokes Scattering (lower energy, higher wavelength) on the right side of the spectrum is used because of its higher intensity. Figure 4.2 shows a schematic of the used Confocal Imaging Raman Microscope "WiTec alpha 300" [45].

Figure 4.2: Schematic of the Confocal Imaging Raman Microscope "WiTec alpha 300" [45].

This modern Confocal Micro Raman Microscope is a combination of an optical microscope and a Raman spectrometer. The required laser light is coupled into the microscope via waveguides and

focused on the surface of the sample. The scattered light is filtered by an optical edge filter to eliminate the original laser wavelength (Rayleigh Scattering) and analyzed using a spectrometer. The detection was made using a sensitive CCD. In this work, a semiconductor laser with a wavelength of 488 nm with a laser power of 35 mW (cw, continuous wave) was used to analyze the Graphene coatings.

4.2.2 Raman Microscopy on Graphene

The Raman spectrum of different carbon layers provides valuable informations about the sample, e. g. about quality, crystal size, sp^3 -content, and thickness. If carbon is predominantly sp^2 -hybridized, the Raman spectrum shows a strong G-Peak (Graphite peak) at 1580 cm^{-1} . This peak is caused by the breathing mode of sp^2 -rings and chains (Figure 4.3 a)). Moreover, Figure 4.3 b) shows the energy scheme of this process which is a one phonon process with at least one virtual energy state.

Figure 4.3: a) Breathing vibration mode in a sp^2 -ring, b) energy scheme of the G-peak Raman process [46].

It illustrates the linear dispersion relation with the Fermi-energy E_F , separating the valence and conduction band. An electron, excited by a photon ω_L with circular frequency moves the electron into an higher virtual level (green arrow) and is subsequently deactivated by generating a phonon Ω and a secondary (scattered) photon with a frequency ω_{Sc} . The sole involved phonon Ω (black arrow) fulfills the Raman selection rule ($q = 0$). This peak is visible both in graphite and Graphene spectra and its intensity changes by different carbon thicknesses. If the number of Graphene layers increases, the intensity of the G-Peak increases as well and reaches its maximum by analyzing bulk material.

Another important Raman-active vibration mode in Graphene and highly ordered graphite causes the 2D-peak which is centered at about 2700 cm^{-1} . The precise position depends on the number of Graphene layers [47] and on the substrate material [48] because of the interaction between the excitation laser and the substrate. Figure 4.4 shows the energy scheme of this double resonant scattering process. This process starts by moving an electron from the ground state to a higher virtual level by an incident photon ω_L .

Subsequently, the scattered photons ω_{Sc} and ω'_{Sc} were emitted. All involved phonons fulfill the Raman selection rule ($\sum_i q_i = 0$). As a result, the 2D-peak is always visible in Graphene, Graphene-

Figure 4.4: Energy scheme of the 2D-peak Raman process [46].

like coatings and graphite without any defect scattering. It reaches the maximum intensity on mono layer Graphene and the intensity decreases if the number of layers increases. Additionally, the center of the peak shifts to a higher wavenumber with higher thickness. In highly amorphous carbon (e.g. ta:C), the 2D-peak is not visible. Thus, the intensity of the 2D-peak provides information about the Graphene-like character of the analyzed carbon material. However, the 2D-peak is only an overtone of the D-peak (Defect peak) which is important to determine the defect density as well as the grain size of the Graphene domains. In contrast to the 2D-peak, the D-intensity is zero by analyzing pure defect-free Graphene because the Raman selection rule can only be fulfilled by defect scattering. Figure 4.5 shows the energy scheme of the defect peak Raman process. The scattering starts similar to the 2D-process by moving an electron from the ground state to a higher virtual level by an incident photon ω_L and by a subsequent emission of a K' -phonon.

Figure 4.5: Energy scheme of the D-peak Raman process [46].

The scattered photon ω_{Sc} is emitted but the electron cannot reach a stable level without multiple defect scattering. The reason for that phenomenon is still disputed in literature [46]. From the intensity of the D-peak and G-peak, the distance between two defects can be calculated. This gives information about the density of the grain boundaries and the size of the Graphene crystals [49], and it can indicate the presence of amorphous carbon as well.

Beyond the most often used and previously described Graphene peaks (D, G, 2D) a new Raman

intensity, called C-mode, was discovered recently. Although it has been already measured in 1975, this layer-breathing mode has attracting new interest in analyzing Graphene. The C-mode is caused by relative motions of the planes themselves, either perpendicular or parallel to their normal [50] and is centered at 42 cm^{-1} . However, this mode is located very close to the excitation wavelength and below the cut-off wavelength of the used spectrometer. Thus, in this work, the C-mode cannot be used for the characterization of the Graphene-containing coatings.

Overall, the Raman spectroscopy is a very versatile tool for studying the properties of Graphene and other Graphene-containing carbon coatings. However, the spectrum has to be carefully interpreted especially by analyzing Graphene-like coatings with small grains and a high density of grain boundaries.

4.3 Scanning Probe Microscopy

4.3.1 Atomic Force Microscopy AFM

The AFM (Atomic Force Microscopy) and STM (Scanning Tunnel Microscopy) are methods for imaging the topography of a surface in sub-nanometer scale. In both cases, a sharp tip scans the surface of the sample. Using the Atomic Force Microscopy, a laser beam is focused on the cantilever and reflected to a CCD (Charge Coupled Device). Deflecting the cantilever moves the laser beam on the CCD and the deflection can be detected (Figure 4.6). Since the deflection of the tip correlates with the real topography of the surface, the structure of sample can be reconstructed. A typical AFM-picture is a false color picture and the different colors represent the intensity of the tip deflection.

Figure 4.6: Schematic of AFM (Atomic Force Microscopy [51]).

The scan of the surface can be conducted using different scanning modes. In case of the tapping mode, the AFM-tip is oscillating with a frequency near to the resonance frequency at (200...400) kHz. The

amplitude of this oscillation changes as a function of the gap between the tip and the surface. By recording the changes of the amplitude during the scan process, the topography can be reconstructed. Another method of scanning the surface is the contact mode. However, the tip does not touch the sample but scans the surface by keeping a small distance of a few nanometers between it and the surface. In this case, the strength of van-der-Waals forces can be used as the measuring signal. The contact mode is used for scanning rough surfaces with a high scanning speed, whereas the tapping mode is able to scan flat samples with a higher lateral resolution.

4.3.2 Scanning Tunneling Microscopy STM

The Scanning Tunneling Microscope allows high resolution scans of the surface topography. The microscope works either under vacuum conditions (UHV-STM) or under normal air pressure. Lateral scans provide resolutions of about 1 nm (lateral) and 0,1 nm vertical, sufficient to define single atoms [51].

The measuring principle consists of a close conductive metal tip (first electrode), which is brought close to the conductive surface (second electrode, distance $d=(0.3...1)$ nm). By applying an operating voltage (10 mV...1 V), a measurable current flows between these two electrodes. The tunneling current varies typically from 0.2 nA to 10 nA. The STM can be operated in either the constant current mode or the constant height mode [51]. Using the scanning mode "constant height", the tip scans the surface while the tunneling current is measured. This method is practical especially for very rough surfaces. Alternatively, in the constant current mode, a feedback network keeps the tunneling current constant by varying the distance d of the tip. The height of the tip is controlled using piezoelectric drives. The measuring signal of the constant current mode consists of the voltage applied to the piezoelectric drive, which is necessary to keep the tunneling current constant. Figure 4.7 shows a schematic of the STM designed by Binnig and Rohrer.

The piezo drives P_x , P_y and P_z are moving the tip into the desired direction. The tunneling current J_T is a function of the gap d_s between tip and surface. It can be described by:

$$J_T \propto V_T \cdot e^{(-A \cdot \sqrt{\Phi} \cdot d_s)} [51]. \quad (2)$$

V_T is the bias voltage, Φ is the average barrier height and A is a constant: $A = (\sqrt{1.025 \text{ eV}} \cdot \text{\AA})^{-1}$ [51]. This arrangement is very sensitive for small changes in d_s . The tunneling current J_T changes by one order of magnitude for an angstrom change in d [51]. The control unit (CU) applies the voltage V_z to the piezo drive P_z to change the gap d_s and hold the tunneling current J_T constant (in constant current mode).

Figure 4.7: Scheme presentation of STM by Binnig and Rohrer [51].

4.4 Electrical measurements

In the current work, the electrical properties (conductivity, Hall mobility) of the carbon films have been determined using a Hall measurement arrangement. The sheet resistance $R_{\square}$ can be measured using the van-der-Pauw method. To determine $R_{\square}$ of the sample, the surface has to be connected with four contacts A, B, C, D (cf. Figure 4.8).

Figure 4.8: Schematic of a van-der-Pauw arrangement.

The region of the contacts must be small in relation to the area of the sample. First, a precise power source provides a defined current between the contacts CD . Measuring the voltage between the contacts AB provides the first resistance $R_{CD,AB} = U_{AB} \cdot (I_{CD})^{-1}$. Subsequently, the arrangement is changed and the current flows between the contacts AC . Now, the voltage between the contacts DB is measured and provides the second resistance $R_{AC,DB} = U_{DB} \cdot (I_{AC})^{-1}$. The sheet resistance can be derived easily from the following equation, known as van-der-Pauw equation:

$$e^{-\frac{\pi}{R_{\square}} \cdot R_{CD,AB}} + e^{-\frac{\pi}{R_{\square}} \cdot R_{AC,DB}} = 1 \quad [52] \quad (3)$$

If the sample is symmetric (all distances between the contacts and the edge of the sample are equal, $R_{AC,DB} \approx R_{CD,AB}$), the equation simplifies to:

$$\begin{aligned} 2 \cdot e^{-\frac{\pi}{R_{\square}} \cdot R_{CD,AB}} &= 1 \\ \ln(2) + \ln(e^{-\frac{\pi}{R_{\square}} \cdot R_{CD,AB}}) &= 0 \\ \ln(2) - \frac{\pi}{R_{\square}} \cdot R_{CD,AB} &= 0 \\ \frac{\pi}{R_{\square}} \cdot R_{CD,AB} &= \ln(2) \\ \frac{\pi}{\ln(2)} \cdot R_{CD,AB} &= R_{\square} \end{aligned} \quad (4)$$

However, most of the real samples are not symmetrical. Hence, the equation has to be corrected for asymmetric samples using the arithmetic average of the two resistances ($R_{AC,DB}$ and $R_{CD,AB}$) as well as an error term f :

$$\frac{\pi}{\ln(2)} \cdot \frac{R_{CD,AB} + R_{AC,DB}}{2} \cdot f = R_{\square} \quad (5)$$

For f there is no analytical solution, but it can be solved numerically using an asymmetric factor $a = \frac{R_{AC,DB} - R_{CD,AB}}{R_{AC,DB} + R_{CD,AB}}$ and numeric constants:

$$f = 0,9999967 - \sqrt{a} \cdot (0,346108 + 0,102327 \cdot \sqrt{a}) \quad [53] \quad (6)$$

Another important electrical property is the mobility of the charge carriers ($[\mu_H] = \frac{cm^2}{Vs}$). This parameter can be determined by measuring the electrical conductivity ($\sigma = \frac{1}{\rho}$) and the Hall voltage U_H . The principle of the Hall measurement is derived by the following and schematically illustrated in Figure 4.9.

First, the sample is placed in a magnetic field. A voltage is applied and the electrons are moving into negative x-direction (against the electric field $\vec{E}$). The magnetic field $\vec{B}$ is applied orthogonal to the $\vec{E}$ -field in z-direction. Consequently, the moving charge carriers experience a force, which is known as Lorentz force $\vec{F}_L$.

$$\vec{F}_L = q \cdot (\vec{v} \times \vec{B}) \quad (7)$$

In this equation, $\vec{v}$ represents the propagation velocity, and q the charge (for electrons: $-1.602 \cdot 10^{-19}$ C). Due to this force, the path of the charge is curved and they accumulate on one side of the sample.

Figure 4.9: Schematic of the Hall effect measurements.

Hence, this asymmetric distribution of charge carriers causes an electric field $\vec{E}_H$ along the y-direction, which can be measured as the Hall voltage U_H . The electric field $\vec{E}_H$ creates an opposite force to the Lorentz force. The resulting equilibration gives:

$$q \cdot (\vec{E}_H + \vec{v} \times \vec{B}) = 0 \quad (8)$$

This effect is called Hall effect. In the present case, the electrons move with velocity $\vec{v}$ only in x-direction ($\vec{v} = (v_x, 0, 0)$) and the magnetic field acts only in z-direction ($\vec{B} = (0, 0, B_z)$). This results in:

$$\vec{E}_H = v_x \cdot B_z \quad (9)$$

Additionally, the current density $\vec{j}_x$ is given by:

$$\begin{aligned} \vec{j}_x &= n \cdot q \cdot v_x \\ v_x &= \frac{\vec{j}_x}{n \cdot q} \end{aligned} \quad (10)$$

Here, n represents the density of charge carriers, which are involved in the electronic transport. Replacing v_x in $\vec{E}_H$ provides:

$$\begin{aligned} \vec{E}_H &= \frac{1}{n \cdot q} \cdot j_x \cdot B_z \\ \vec{E}_H &= R_H \cdot j_x \cdot B_z \end{aligned} \quad (11)$$

R_H is called Hall constant and it is given by $\frac{1}{n \cdot q}$. Now, the sample with an applied electric field can be mathematically handled as a capacitor where $\vec{E}_H$ and j_x are given by:

$$\begin{aligned} \vec{E}_H &= \frac{U_H}{b} \\ j_x &= \frac{I}{b \cdot d} \end{aligned} \quad (12)$$

The Hall current is given by I , and the dimension of the sample is represented by thickness b and width d . Consequently, the formula simplifies to:

$$\begin{aligned} U_H &= R_H \cdot \frac{I \cdot B_z}{d} \\ \vec{E}_H &= R_H \cdot j_x \cdot B_z \end{aligned} \quad (13)$$

To determine the Hall mobility μ_H , the Hall constant R_H has to be substituted by $\mu_H = \sigma \cdot R_H$ [54]. This provides:

$$\mu_H = \frac{U_H \cdot \sigma \cdot d}{I \cdot B_z} \quad (14)$$

The conductivity σ can be substituted by the sheet conductance $\sigma = \frac{G_{\square}}{d}$ and $R_{\square} = \frac{1}{G_{\square}}$. The resulting equation for calculating the Hall mobility from the measured values U_H and $R_{\square}$ is:

$$\mu_H = \frac{U_H}{R_{\square} \cdot I \cdot B_z}, \quad (15)$$

at given current I and induction B_z . Using this equation, the mobility of the charge carriers can be calculated only by measuring the Hall voltage (U_H) and by determining the sheet resistance ($R_{\square}$). The sample thickness need not be known, since both former values are independent of that value.

5 Deposition Tool for PECVD

5.1 Introduction

5.2 Vacuum chamber

The vacuum chamber which has been used in the current work, is schematically shown in Figure 5.1. This vacuum chamber was originally designed to deposit Graphene on different catalytic substrates (metal foils and films) by means of standard CVD processes [55].

Figure 5.1: Vacuum chamber for the PE-CVD process [56].

The apparatus is pumped by a rotary vane pump and a turbo pump (Pfeiffer Balzers TPU050). The achievable base pressure is about 10^{-3} Pa at room temperature and the residual gas pressure at working temperature ($500^{\circ}\text{C} \dots 1050^{\circ}\text{C}$) is about 10^{-3} Pa without any buffer- or precursor gas. The chamber contains a heating plate made of boron nitride (tectra, Boralectric heating element HTR1003), which is able to heat the substrates up to 1800°C . To determine the usable heating area with an homogeneous temperature, the temperature profile of the heating plate was created by measuring the temperature on different points. The temperature of the center was kept constant and set to 970°C . The resulting heating profile is plotted in Figure 5.2.

With regard to this result, the usable area of the heating plate is in the center of the plate with a dimension of about $(3 \times 3) \text{ cm}^2$. Beyond this area, there is a strong temperature gradient in the direction of the edges. Hence, the substrates have to be carefully placed in the center of the heating element to avoid any influence of variation in temperature. The walls of the chamber are protected from overheating by a water-cooled heat shield above the heater and by a water-cooled copper serpentine around the whole chamber.

In addition, a gas supply has been realized with four mass flow controllers (controlled by the MKS Multi Gas Controller 647C, MKS instruments). Using this flexible arrangement, different precursor

Figure 5.2: Temperature profile of the heating plate Boralectric HTR1003 with a central temperature of 970 °C.

gases (e. g. methane, ethene) as well as buffer gases (e. g. argon) and functional gases (e. g. hydrogen) can be led into the chamber. Monitoring of the substrate temperature is provided contactless by a pyrometer (DIAS infrared systems, Pyrospot DGE 10N).

However, to use this chamber for a PE-CVD process, a plasma has to be ignited inside the chamber. For that purpose, different types of plasma could be used [57]:

- glow discharge,
- arc evaporation,
- corona discharge (Ionization in a strong electric field),
- high frequency plasma (with inductive or capacitive coupling),
- barrier discharge (Isolation of at least one electrode).

In order not to damage the growing film during the process, it would be desirable to have a low thermal energy of the electrons [58]. Therefore, the glow discharge as plasma source was chosen to keep the plasma power and the energy of the electrons as low as possible and to ignite a plasma discharge with only little afford. To ignite a glow discharge, two electrodes have to be placed inside a low pressure gas. Referring to the Paschen curve, every kind of gas has its ignition minimum at different values for $p \cdot d$ (Figure 5.3b). This Figure contains the Paschen curves for methane (red line) [59] and argon (black line) [60]. The unit of the abscissa is the product of the pressure p and the distance between the two electrodes d , measured in $[Pa \cdot m]$ and the ordinate is the breakdown voltage, measured in volts. In most cases, the ignition minimum is between 100 V and 500 V at $p \cdot d = 0,1 Pa \cdot m \dots 1,0 Pa \cdot m$ [57]. A glow discharge is characterized by two different processes which contain two parameters, known as the Townsend parameters α and γ . The process for igniting such a plasma (Figure 5.3a) starts by

applying a DC voltage between the two electrodes which is higher than the breakdown voltage of the referring product $p \cdot d$.

Figure 5.3: a) I-V-curve of a glow discharge [57], b) Paschen curves of methane (red line) [59] and argon (black line) [60].

Due to the electric field, free electrons -e.g. from the natural radioactive radiation- which can ionize the gas atoms by multiple collisions were accelerated. Hence, the density of the free electrons and positive ions increases. This process is invisible and also known as Townsend discharge, used for example in a radiation-counter tube. It is characterized by the first Townsend coefficient α , with $\alpha = \lambda_i^{-1}$. In this equation, λ_i is the mean free path for ionization of the atoms and it is inversely proportional to the pressure p .

Subsequently, the ions propagate to the cathode and they can emit secondary ions by hitting the cathode material (secondary ion emission). This emission is described by the second Townsend coefficient γ . This secondary electron emission coefficient depends on the electrode material and the kind of gas. If the amplification of this two Townsend processes is high enough (the voltage is higher than the breakdown voltage), the current increases and ignites a stable discharge which is known as glow discharge. According to the following equation, this breakdown voltage V_b can be calculated, using the second Townsend coefficient γ and the gas properties A and B :

$$V_b = \frac{B \cdot p \cdot d}{\ln(A \cdot p \cdot d) - \ln[\ln(1 + \gamma^{-1})]} \quad [61] \quad (16)$$

At some critical minimum value of $p \cdot d$, V_b goes infinite due to the vacuum insulation [61]. If the plasma power rises above a critical value, the glow discharge changes to an abnormal behavior and the possibility of arc discharges increases [57]. Thus, the glow discharge works stably only in a narrow process window.

To realize such kind of plasma inside the chamber, an electrode made of copper has been installed inside the chamber. The electrode has been insulated using ceramic jackets. The second electrode is provided by the heating shield above and beside the heater. The minimum distance between the plasma electrode and the heating shield (second electrode) is about 5 cm. The full experimental

arrangement including the plasma electrode is shown in Figure 5.4. To reach a high amplification (high second Townsend coefficient), the plasma electrode is connected to the minus pole and the heating shield is grounded. Consequently, the electrons propagate to the heating shield with its large surface, and can emit a great number of secondary ions. Hence, the second Townsend coefficient γ is as high as possible for the current experimental setup.

Figure 5.4: Experimental arrangement inside the vacuum chamber.

After igniting the plasma, the discharge can be noticed by the emission of light. The Figures 5.5 a,b,c show the photographed light emission resulting from a glow discharge of different gases (hydrogen, argon, methane).

Figure 5.5: Light emission of different glow discharges: a) Hydrogen, b) Argon, c) Methane. [62]

Furthermore, to realize a PE-CVD process, the substrates have to be heated up to a defined temperature. Subsequently, the glow discharge starts after switching on the gas supply and the plasma voltage. It has to be ensured that no arc discharge ignites both a) between the plasma electrode and the electrical supply of the heater, and b) between the plasma electrode and the walls of the vacuum chamber. For that reason, a buffer resistor with $100\text{ k}\Omega$ has been installed. All components of the equipment have been grounded at one point to avoid any possible errors such as inductances and ground loops. A circuit diagram of the electrical arrangement with the buffer resistor, the plasma

Figure 5.7: a) Photograph of the chamber inside during a PE-CVD process [62]. b) Spectrum, emitted by a methane glow discharge.

pristine methane atmosphere. Additionally, no other high intensities which could indicate a high level of impureness of the plasma can be identified. Consequently, it has been shown, that the experimental arrangement can fully comply with the requirements for realizing a PE-CVD process. However, this technology depends on several free parameters such as plasma power, substrate temperature, and gas mixture, and the required optimization process of these different parameters will be explained in section 7.2. The following section is devoted to describe the second deposition process used in the current work, the filtered high current arc (Φ -HCA).

6 Deposition Tool for Φ -HCA

6.1 Introduction

During the last years, arc evaporation became one of the standard technologies for producing hard and dense amorphous carbon coatings as well as wear-protective coatings (e.g. Titan Nitride). For that purpose, the conventional unfiltered Arc-PVD uses a direct current (DC) discharge, which burns continuously with about 100 A and produces both plasma and macroscopic droplets. These droplets reach the surface of the substrate and increase the roughness of the coating dramatically. Figure 6.1 shows a SEM picture of such an Arc-PVD coating. The film is about $2\text{ }\mu\text{m}$ thick and has a high roughness due to the high content of macroscopic droplets.

Figure 6.1: SEM picture of a carbon coating deposited using a DC-Arc evaporation process.

To avoid such a high roughness, the plasma can be filtered by means of a strong magnetic field inside a filter arch. This type of filter has been designed and described by Aksenov et. al. [64]. Additionally, Petereit et. al combined this technology with a pulsed high current arc instead of the conventionally used DC-evaporation [37]. Here, the arc reaches several thousands of ampere and provides a high deposition rate, whereas the magnetic filter is able to nearly completely eliminate the uncharged droplets. The current apparatus (Figure 6.2) uses a round graphitic plate, which is used as the solid carbon source. The evaporator is connected to the deposition chamber by a magnetic macro particle filter. The carbon cathode (inside the evaporator) is surrounded by a cylindrical, water-cooled anode. The evaporator works in a pulsed mode using 1.0 ms pulses with an arc current of up to 3000 A. Figure 6.3 shows an oscillogram of the voltage characteristic (blue line) and the arc current (red line) of the discharge. Before igniting the arc, a voltage of several hundred volts is applied between both electrodes. Subsequently, the discharge starts by an ignition spark on the target surface. Due to the arising plasma, the arc discharge burns continuously and the voltage decreases to a characteristic burning voltage of about 50 V, whereas the current rises up to 3000 A.

After igniting the arc discharge, the plasma reaches the magnetic macro particle filter. This filter arrangement consists of a filter arch, which is surrounded by a water-cooled copper coil. The magnetic field is built up by applying voltage on the copper coil. The strength of the magnetic field can be regulated by varying the filter current. Inside the magnetic filter, only the charged particles (ions,

Figure 6.2: Filter arc arrangement for carbon depositions.

electrons) can be influenced by the magnetic field. However, only the electrons are able to follow the lines of magnetic flux, because the mass of the carbon ions is too high. Hence, the electrons distance from the ions and a zone of negative charge (electrons) and positive charge (ions) is formed. The ions propagate in the direction of the gradient of different potentials and pass the filter. All neutral atoms, particles and droplets can not be influenced by the magnetic field. They are adsorbed by the walls of the vacuum chamber. Thus, at the exit of the filter, nearly 100 % ionized plasma reaches the substrate. By increasing the filter current, the strength of the magnetic field also increases and more ions can be guided through the filter arch. Hence, the deposition rate increases.

After about one millisecond, the voltage is switched off and the discharge stops. On top of the carbon cathode, the cathodic arc spots of the discharge leaves characteristical erosion tracks. To illustrate this, Figure 6.4a) shows an unused carbon target with its ignition pin in the middle, whereas Figure 6.4b) shows an used target with its typical erosion and the carbon aggregation around the ignition pin.

In contrast to conventional DC-Arc coatings, the resulting layers are hard, dense, and have a very low roughness. Figure 6.5 shows a SEM picture of a ta:C-layer with a thickness of about $1.5 \mu\text{m}$. The coatings provide a high percentage of sp^3 hybridized carbon-carbon bonds (up to 80 %) and the roughness of the ta:C is extremely low.

Consequently, using this Φ -HCA technology makes it possible to precisely deposit ultra-thin carbon coatings with a very low roughness homogeneously on large areas. These properties are requested not only for the production of hard ta:C carbon but also for the deposition of Graphene and Graphene-like coatings on arbitrary substrates. Hence, the Φ -HCA can provide an excellent starting point for the formation of that kind of coating. However, to form such carbon films from predominantly sp^3 hybridized ta:C, the Φ -HCA technology has to be modified in order to deposit flat sp^2 -hybridized carbon. The basic ideas for that modification will be described in the following section.

Figure 6.3: Arc Voltage characteristic (blue line), and arc current (red line).

Figure 6.4: (a) Unused carbon target, (b) used carbon target.

Figure 6.5: SEM picture of a carbon coating deposited using a pulsed filtered Arc Evaporation Process (Φ -HCA).

6.2 Basic assumptions for Graphene deposition using the Φ -HCA technology

With the aim to produce carbon coatings with a high content of sp^3 -hybridized carbon using the Φ -HCA technology, two very different approaches can be applied. The first one consists of the thermal transformation (annealing) of a thin carbon layer. This thermal annealing process has already been published in literature e.g. by Illie et. al [40] and by Ferrari et. al [65]. In this experiment, a strong decreasing resistivity of the amorphous carbon has been shown following the annealing. However, the Raman measurements of the treated coatings provide a quite constant sp^3 -content of the films, if the temperature is lower than 1500°C (cf. also [66]). Consequently, it seems to be not possible to convert amorphous carbon into a predominantly sp^2 bond carbon modification at proper conditions (lower temperature) only by heating. This can be caused by several processes such as the subplantation. Subplantation means that the carbon ions are pushed with high energy up to some atomic layers under the surface and subsequently into the growing film, resulting in a dense amorphous structure [67, 68]. After the deposition process, the thermal treatment is not able to transform the amorphous structure into an ordered graphitic one. Hence, the first approach of the current work attempts to reduce the impinging energy of the ions during the deposition process in order to avoid a deep implantation into the substrate material. This promotes a gentle deposition of carbon within in the first atomic layers. This can be done either by changing the impinging angle (tilt the substrate with respect to the particle beam) or by using a buffer gas (noble gas atmosphere). After depositing the carbon on a cold (room temperature) substrate, the subsequent heating should give the atoms a limited mobility and allow them to form a Graphene-like layer.

The second approach uses the possibility of parallel heating. In this case, the substrate is heated before the deposition process starts. A higher buffer gas pressure should give the carbon ions the possibility to form C_x -agglomerates before they reach the tilted substrate. Furthermore, the effect of the magnetic field is switched off and the carbon is guided through the filter arch only by multiple scattering on the buffer gas atoms. Subsequently, due to the scattering process, the carbon reaches the surface not directional but mostly diffuse. Thus, the tilt of the surface has possibly no effect on the impinging energy of the carbon particles. Moreover, the high substrate temperature can give the pre-formed agglomerations the possibility to form a high ordered graphitic structure without forming amorphous carbon. In this case, no transformation process of the carbon films is necessary, because the growing film should already be predominantly sp^2 -hybridized. The greatest challenge of this approach is, however, to control the orientation of the graphitic sheets. Previous investigations of Yin et. al show a predominantly perpendicular growth instead of flat lying Graphene sheets [42]. Furthermore, this work was verified by theoretical calculations of Marks et. al [41]. A perpendicular graphitic growth should be avoided, due to the fact that it has a negative effect on the sheet resistance because Graphene has good electrical conductivity only in lateral direction.

Nevertheless, to realize the two described approaches, the Φ -HCA apparatus has to be modified in

different ways. The modifications include the heating element, the possibility of tilted substrates, and a proper gas supply for the buffer gas. To realize this, a new design of the apparatus has been developed and it will be described in the following section.

6.3 Design of the Φ -HCA apparatus

As mentioned above, the most important modifications of the apparatus are the installation of a heating element and the realization of a proper gas supply for at least one gas (e.g. buffer gas). This process does not need any carbon containing precursor gas, because the carbon is only provided by the plasma beam coming from the arc evaporator. With regard to the small installation space inside the vacuum chamber, the heating plate (Boraletric HTR1001, teratec) with a dimension of $(2.5 \times 3.52) \text{ cm}^2$ was chosen. This heating plate is made of boron nitride and it is able to heat the substrates up to 2000 K in high vacuum. The device has a low power consumption of max. 220 W. Consequently, the vacuum chamber does not need any active cooling (e.g. water or gas cooling). However, to protect the walls from overheating, the heater is encapsulated into molybdenum plates. Because of constructional limitations (position of the turbo pump, the heating shield and the filter arch) a contactless temperature measurement is not possible. The reason for this is the missing direct intervisibility of the heating plate during the process to realize such an optical measurement. With regard to the results of previous investigations, conventional thermo couples do not provide sufficient precise measurement results [55], because one of the main challenges is to establish a proper thermal contact between the heating plate and the thermo couple. Hence, another method to determine the temperature of the heating element should be chosen. Since the electrical resistance of the heating plate changes with the temperature, a calibration of the power consumption and the resulting temperature is possible. This calibration procedure was conducted in a separate vacuum chamber, and the temperature of the heating plate was measured at different power ratings by means of an optical pyrometer (DGE 10N, Dias infrared). Figure 6.6a) shows the installed and encapsulated heating element with two samples on top. In this arrangement, the plasma beam comes from the right. In Figure 6.6b), the temperature of the heating plate is plotted vs. the heating current. All measuring points are labeled with the resulting voltage. Using this calibration curve, the temperature of the heating plate can be precisely determined by measuring the heating current.

The heating plate is tilted in the direction of the plasma beam. However, due to multiple scattering in the buffer gas, the effect of the tilt angle will be low at higher gas pressure and it will be important only for the experiments in high vacuum or low pressure below 1 Pa.

As mentioned above, a gas supply has to be realized to moderate the kinetic energy of the carbon particles and to influence the carbon growth by different process gases. The necessary gas supply has been realized using needle valves. To introduce buffer gas (argon) as well as functional gas (hydrogen), two different needle valves have been used. If the pressure before the needle valve is constant, the resulting gas pressure inside the chamber will be proportional to the valve position because the pressure

Figure 6.6: a) Photograph of the heating plate and the heating shield [69], b) Temperature vs. heating current of the Boralectric HTR1001.

is given by the equilibrium between the gas flow and the throughput of the vacuum pump. However, it has to be noticed that at high gas pressure (above 10 Pa), the turbo pumps have to be switched off and consequently the overall throughput decreases. Hence, the two valve positions have to be carefully adjusted by hand for each process with different gas pressure.

Finally, after all modifications, the apparatus is able to deposit carbon coatings from a solid source on a heated substrate. The substrate temperature can be determined and set to different values. Additionally, the chamber can be filled with two different gases during the deposition process. Figure 6.7 shows a photograph of the whole experimental arrangement.

The evaporator is connected to the filter arch, which is surrounded by a water-cooled magnetic coil (blue isolated copper hose). Furthermore, the chamber is connected to a flow box to handle the substrate under clean-room conditions (if necessary). The experiments and the full optimization process will be explained in detail in section 7.3.3.

Figure 6.7: Photograph of the modified Φ -HCA plasma source with integrated heating plate [69].

7 Experiments

7.1 General

This section deals with the the main experiments, conducted with the aim to optimize the two previous described processes for deposition of Graphene and related sp^2 -carbon coatings directly on insulating substrates. First, the optimization process of the PE-CVD will be described. The main free parameters of this process are the gas atmosphere (gas mixture), the plasma conditions (plasma power), the substrate temperature, and the substrate material.

Second, the experimental part of the Φ -HCA process will be described, including the investigation of the main parameters of the Φ -HCA technology (plasma pulse duration, plasma pulse current, filter current). Subsequently, the general process parameters (gas atmosphere, substrate temperature, substrate material) will be analyzed.

Both investigations include a part of structural analysis, where the properties of the referring coating (roughness, topography, purity, composition) will be explained. The experimental part starts with the optimization of the PE-CVD in the following section.

7.2 Optimization of the PE-CVD process

7.2.1 Gas atmosphere

This section is devoted to analyzing the effect of different gases and gas mixtures on the results of the deposition. At the beginning, methane (CH_4) was used with a gas flow of 70 sccm as a precursor (carbon containing gas). This parameter is a result of previous work using a copper substrate as catalytic material [55] and represents the starting point of this investigation. Subsequently, argon was added to the atmosphere to improve the stability and uniformity of the plasma, as described for example by F. Bonaccorso et al. [14]. Using the flexible gas supply with multiple mass flow controllers (cf. section 5.2), the methane flow and the argon flow can be varied independently. To examine the influence of the methane flow on the deposition process, the overall gas flow was kept constant by varying both gas flows simultaneously. It has to be noticed that for igniting a glow discharge, the working gas pressure must be carefully adjusted. The process window is provided by the minimum and maximum working pressure. As described above in section 5, the breakdown voltage for igniting a glow discharge is given by the Paschen law. The important value is the product of the working pressure p_w and the distance between the two electrodes d . The minimum working pressure is given by the point where the breakdown voltage begins to diverge, resulting in the vacuum insulation. As shown in Figure 7.1, the minimum product $p_w \cdot d$ is about 0.25 Pa m.

Thus, the minimum working pressure $p_{w,min}$ is given by: $p_{w,min} = 0.25 \text{ Pa m}/d$. The distance d is given by the space between the plasma electrode and the heating shield which is about 0.05 m. Hence, pressure inside the chamber has to be higher than 5 Pa to ignite a stable glow discharge. On the other

Figure 7.1: Paschen curves of methane (red line) [59] and argon (black line) [60].

hand, the maximum pressure is given by the maximum gas ballast for the rotary vane pump which is about 100 Pa. That means that the working pressure can only be varied in a range between 5 Pa and 100 Pa. Consequently, the following experiments were done using a working pressure of 70 Pa in the middle of the process window. The substrate temperature was set to 1050°C, which arises from previous investigations of CVD-processes on catalytic metals. However, detailed experiments with regard to the substrate temperature will be described in a separate section. The plasma power was set to 1 W, because at this value, the plasma seems to have the most stable behavior at the given pressure. All important parameters for that investigation are summarized in the following Table 7.1:

Parameter	value
Plasma power (P_{plasma})	1 W
Methane flow ($\dot{V}_{CH_4}$)	(5...70) sccm
Argon flow ($\dot{V}_{Ar}$)	(0...70) sccm
working pressure (p_W)	(60...90) Pa
Substrate temperature (T_s)	1050 °C

Table 7.1: Deposition parameters for the investigation in different gas mixtures using PE-CVD.

The gas pressure inside the chamber changes by varying the methane to argon ratio. The lowest pressure of 60 Pa represents a gas mixture of 5 sccm methane and 105 sccm argon (lowest amount of methane). The pressure increases, if the methane flow increases, and reaches 86 Pa at 40 sccm methane flow. The highest pressure of 90 Pa has been measured by using pure methane with 70 Pa. However,

all pressures fit into the narrow pressure range determined before.

As a result, Figure 7.2(a) shows the Raman spectra of a carbon coating deposited with a pure methane plasma (red line) and with a gas mixture of methane and argon (blue line). The red spectrum is dominated by broad D- and G-bands and a very low 2D-intensity. This spectrum indicates a low oriented graphitic structure with a grain size of about 1 nm which was already published e.g. by M. H. Rummeli et. al [26].

Figure 7.2: a) Raman spectra of a carbon coating deposited with a pure methane plasma (red line) and with a gas mixture of methane and argon (blue line) b) I_D/I_G ratio (black triangle) and I_{2D}/I_G ratio (black squares) vs. methane flow.

In contrast, the D- and G-peaks of the blue spectrum (argon and methane mixture) are much sharper. The I_D/I_G ratio indicates a grain size of about 5 nm. Furthermore, the 2D-band is higher as well, which is a result of higher oriented graphitic structures. Regarding that comparison, it can be supposed that the electrical conductivity of the sample, deposited under argon and hydrogen atmosphere, will be much better than without argon. Additionally, the process using an argon-methane-mixture seems to be very stable with regard to any variations of the methane flow. This is illustrated in Figure 7.2(b) which shows the I_D/I_G and I_{2D}/I_G ratio vs. methane flow. It can be seen that both the relative height of the defect peak (I_D) and the relative height of the 2D-peak is quite constant and hardly influenced by different methane flow rates. This finding is supported by Figure 7.3 where the sheet resistance is plotted vs. optical transmittance. It illustrates that the ratio of transmission and sheet resistance of the coatings hardly changes, if the methane flow is varied between 5 sccm and 40 sccm. Only the film, coated under a pristine methane atmosphere, provides a much higher resistance than that deposited under argon buffered atmosphere.

This supports the previous assumption derived from the analysis of Raman spectra. However, a variation of the methane flow using an argon background cannot change the electrical properties of the referring carbon coating, if the flow rate is changed in the narrow process window of working gas pressure.

Figure 7.3: Sheet resistance vs. optical transmittance with 20 sccm methane (black line) and with varied methane flow (red squares).

7.2.2 Plasma power

This section is devoted to analyze the effect of plasma power on the quality of the deposited carbon layers. As described above, the plasma for current the PE-CVD process is provided by a glow discharge, which produces the excited atoms, ions, and electrons. By measuring the current and the DC-voltage, the plasma power can easily be calculated, according to Ohm's law. Using the current experimental setup, the minimum plasma power depends on the avalanche voltage of the referring gas and the pressure inside the chamber. The process window of this investigation is given by a minimum plasma power, according to the lowest possible plasma voltage for igniting a stable discharge. For argon and methane, a minimum plasma power of about 0.25 W (at 300 V) has been observed to ignite a stable plasma at the given working pressure.

On the other hand, the highest reachable power is given by the point, where the glow discharge becomes unstable and the probability of arc discharges increases. At the current experimental arrangement, this point is reached at a plasma voltage of 600 V. which corresponds to a power of 2 W. It has to be noticed, that even at 600 V, the probability of arc discharges during the deposition process is enhanced. Thus, it is not desirable to work with a plasma power on the upper limit. To determine the effect of plasma power variation, the samples have been coated keeping all other deposition parameters constant. They are summarized in Table 7.2. The values for working pressure and gas mixture are a result of previous investigations and the substrate temperature has been kept constant at 1050°C. The process required 10 min in order to produce coatings with a measurable absorbance and conductance, which are significantly different from that of the substrate material.

To illustrate the experimental results, Figure 7.4(a) shows the I_D/I_G and I_{2D}/I_G ratio from the Raman spectrum vs. varied plasma power.

Parameter	value
Methane flow ($\dot{V}_{CH_4}$)	20 sccm
Argon flow ($\dot{V}_{Ar}$)	90 sccm
working pressure (p_W)	70 Pa
Substrate temperature (T_s)	1050 °C
process time(t_p)	10 min

Table 7.2: Deposition parameters for the investigation in different plasma power using PE-CVD.

Figure 7.4: a) I_D/I_G ratio (black triangle) and I_{2D}/I_G ratio (black squares) vs. plasma power b) Deposition rate vs. plasma power using PE-CVD.

As well as determined before at varied methane flow, both the relative height of the defect peak (I_D) and the relative height of the 2D-peak are quite constant and hardly influenced by different plasma power. However, the deposition rate (Figure 7.4(b)) increases linearly with the plasma power. As expected from the comparison of the Raman spectra, no significant changes in electrical and optical quality of the Graphene-based carbon coatings can be identified, if the plasma power is varied between 0.25 W and 2.0 W (cf. Figure 7.5). All measured values are very close to the line which fits the data points for 1.0 W (blue line).

It can be concluded that the plasma power only changes the deposition rate if it is varied between 0.25 W and 2.0 W. A variation in a larger process window is not possible because of several physical preconditions and the experimental setup. Since a higher plasma power increases the probability of arc discharges, it was set to 1.0 W for all of the following experiments.

Figure 7.5: Sheet resistance vs. optical transmittance with 1.0 W plasma power (blue line) and with varied plasma power (red squares).

7.2.3 Substrate temperature

This section is devoted to analyze the effect of the substrate temperature on the quality of the Graphene-like coatings. For that purpose, the temperature of the substrate has been varied between 500°C and 1050°C. The substrates have been coated using the optimized parameters (Table 7.3), which arise from the previous optimization process.

Parameter	value
Plasma power (P_{plasma})	1 W
Process time (t_p)	10 min
Working pressure (p_w)	70 Pa
Gas mixture	Ar/ CH_4 = 90/20

Table 7.3: Deposition parameters for the investigation in different substrate temperatures during a PE-CVD process.

Subsequently, the carbon coatings have been analyzed using the measuring methods, described above. Figure 7.7(a) shows the peak ratios I_{2D}/I_G and I_D/I_G from the Raman spectra of carbon coatings with a varied temperature. It illustrates, that the 2D intensity increases, if the temperature rises from 700°C up to 1050°C with only small changes between 800°C and 1050°C. That indicates a better crystallographic structure of the Graphene flakes at higher temperatures.

Additionally, the I_D/I_G ratio gives information about the lateral size of the Graphene flakes, according to [49, 50]. The curve of the lateral size of the grains (L_a) and I_D/I_G separates the material into two stages: In those with only sp^2 -rings (described by Tuinstra and Koenig [70]), and in those containing sp^2 -chains, such as in amorphous and diamond-like carbons [50](cf. Figure 7.6).

Figure 7.6: Variation of the $I(D)/I(G)$ ratio with the grain size L_a and the broad transition between the two stages (dashed line).

It can easily be seen, that for both stages, the materials could have the same I_D/I_G ratio. However, the G-peaks do not have the same width (Full Width Half Maximum, FWHM) because the FWHM(G) increases with disorder. This allows a separation of the two material stages. The fit of the experimental data of stage 2 gives:

$$L_a(nm^2) = \frac{4.3 \cdot 10^3}{E_e^4(eV)^4} \cdot \left(\frac{I_D}{I_G}\right)^{-1} [71] \quad (17)$$

In this equation, E_e is the excitation energy (in eV) and (L_a) is the size of the grains. In case of amorphous carbon (stage 1) the fit to the data for small grain sizes provides:

$$L_a(nm^2) = 5.4 \cdot 10^{-2} \cdot E_e^4(eV)^4 \cdot \frac{I_D}{I_G}, [71] \quad (18)$$

According to that behavior, the measured peak ratios has been fitted to the resulting curves. Figure 7.7(b) illustrates, that the grain size of the Graphene flakes increases at higher temperatures and reaches its maximum at 950 °C. A higher temperature has no effect on the I_D/I_G ratio and the grain size, respectively.

Between 500 °C and 700 °C, all coatings have no measurable conductance and the transmission is equal to that measured on uncoated quartz. However, at 700 °C a carbon-like Raman spectrum can be measured, which indicates a carbon deposition (cf. Figure 7.7(a,b)). It can be concluded that only a little amount of carbon will be deposited at such low temperatures using this PE-CVD process without forming a closed film. Nevertheless, if the substrate temperature rises up to 800 °C, the deposition process starts and the samples provide a measurable conductance as well as a reduced transmission. However, the deposition rate shows a high dependence on the substrate temperature. To illustrate that, Figure 7.8(a) shows the transmission vs. sheet resistance for different substrate temperatures

Figure 7.7: a) Peak ratios I_{2D}/I_G and I_D/I_G from the Raman spectra of carbon coatings with a varied substrate temperature b) I_D/I_G vs. grain size at different substrate temperatures fit to data from literature [49].

(red squares), Figure 7.8(b) shows the charge carrier mobility at different substrate temperatures. For that experiment, all other parameters have been kept constant. It can easily be seen that the layer transmission increases by using a low substrate temperature, which corresponds to a lower thickness.

Figure 7.8: a) Sheet resistance vs. transmission for different substrate temperatures (red squares). b) Charge carrier mobility at different substrate temperatures.

However, the ratio of sheet resistance and transmission at 800 °C is nearly equal to that at 1050°C (Figure 7.8(a), blue line). Consequently, the substrate temperature in this PE-CVD process has an effect only on the deposition rate but hardly on the ratio of resistance and transmission. For that reason, the PE-CVD process is also suitable for normal glass (e.g. BK7) as substrate material because it withstands temperature treatments at 800°C without reaching the softening temperature. (Figure 7.8(a), purple star) represents one experiment on BK7 at 800°C. It can be seen that the resistance of this coating is slightly higher than that on quartz at equal transmission. However, it has been shown that a deposition of transparent conductive films on BK7 is possible using this PE-CVD process.

Additionally, the electron mobility was determined using a Hall measurement device. For that mea-

surements, the magnetic field was varied between 0 kG and 10 kG. The average charge carrier mobility of the analyzed samples was not influenced by the strength of the magnetic field ((Figure 7.8(b)), but it increases, if the samples have been coated at higher substrate temperatures (cf. Table 7.4).

Substrate temperature ($^{\circ}\text{C}$)	800	900	1050
Electron mobility (cm^2/Vs)	14	24	43

Table 7.4: Charge carrier mobility at different substrate temperatures.

Overall it can be summarized, that the substrate temperature has a high influence on the deposition rate. The lower the temperature, the lower is the rate of deposition. If the substrate temperature during the process is too low (below 800°C), only a small amount of carbon will be deposited and the respective coatings have no measurable conductance. A lower temperature causes a smaller grain size as well as a lower electron mobility. However, the transmission to resistivity ratio at 800°C is hardly worse than that at 1050°C . Thus, the PE-CVD process using glow discharge as a plasma source is also suitable for normal glass substrates (e.g. BK7) which withstands temperatures of up to 800°C .

7.2.4 Substrate material

The PE-CVD process can theoretically work on arbitrary substrates which withstand the required temperature treatment. The reason for this is that the plasma produces ions and excited atoms. In contrast to the conventional CVD process, no catalytic material is required. To prove this assumption, another transparent and insulating material has been tested. Sapphire (aluminum oxide Al_2O_3) withstands temperatures up to 2400°C and it has been already successfully used for the Graphene synthesis [29, 34]. For the current investigation, the sapphire and quartz substrates have been coated using optimized parameters (Table 7.5), which arise from the previous optimization process. To produce different thicknesses, the process time has been varied between 2 min and 20 min.

Parameter	Value
Plasma power (P_{plasma})	1 W
Working pressure (p_w)	70 Pa
Gas mixture	$\text{Ar}/\text{CH}_4 = 90/20$
Substrate temperature	1050°C

Table 7.5: Deposition parameters for the investigation of different substrate materials for the PE-CVD process.

Figure 7.9(a) shows a comparison between the Raman spectra of the referring carbon coatings on sapphire and quartz. It illustrates that no changes in Raman intensity or peak ratios can be identified. The whole Raman spectrum for carbon on sapphire has slightly shifted to a higher wavenumber with respect to the spectrum on quartz. This effect is described in literature and it is caused only by

the interaction between the excitation laser and the substrate material [48]. With regard to the comparison of the Raman spectra, no influence of the substrate material can be identified.

Figure 7.9: a) Comparison between the Raman spectra of carbon coatings on quartz (red line) and sapphire (blue line). b) Sheet resistance vs. transmission of Graphene-based carbon on quartz (blue line) and sapphire (red points).

Figure 7.9(b) shows the sheet resistance to transmission ratio of Graphene-based carbon on quartz and sapphire, using the PE-CVD process with varied process time. Both the coating on sapphire and quartz show a linear dependence of optical transmission and sheet resistance in logarithmic scale with the same slope. Hence no difference between the two substrate materials can be identified.

It can be concluded, that this process can work on different substrates and the quality is not influenced by the tested substrate material. The coatings on sapphire and quartz share the same properties.

7.2.5 Structural analysis

To investigate the atomic structure, roughness of the surface, and purity of the carbon coatings, a thorough characterization has been carried out using Raman spectroscopy, Time of Flight Secondary Ion Mass Spectroscopy (ToF-SIMS), STM imaging and TEM-cross section images. For this investigation, samples have been produced using optimized parameters derived from the previous optimization process. These parameters are summarized in Table 7.6.

Parameter	value
Plasma power (P_P)	1.0 W
Process time (t_P)	7.5 min
Gas atmosphere	$\dot{V}_{Ar} : \dot{V}_{Methane} = 90 : 20$
Working pressure (p_W)	71 Pa
Substrate temperature (T_s)	1050°C

Table 7.6: Deposition parameters for the structural analysis of the argon process.

Figure 7.10 shows a single Raman spectrum, the inset is a false color picture of the Raman 2D-intensity (mapping area 1 mm^2). The spatial resolution is given by the interaction volume of the laser spot. It has a diameter of about $0.6\text{ }\mu\text{m}$. Except the small scratch on the right side, the intensity of the 2D-peak is quite constant which indicates a homogeneous carbon coating. At the bottom of the picture, the sample is getting out of focus because of the large mapping area. This decreases the overall Raman intensity and causes that optical inhomogeneity.

Figure 7.10: Single Raman spectrum of a Graphene-containing carbon coating deposited on quartz glass using PE-CVD; inset: false color picture of the Raman 2D-intensity (mapping area 1 mm^2), resolution about $0.6\text{ }\mu\text{m}$.

Furthermore, the high resolution STM picture (Figure 7.11 a,b) provides a very flat surface with an average roughness lower than $1\text{ }\text{\AA}$. The film is closed and has neither holes nor any spikes or islands. This finding fits well to the previous Raman mapping.

Figure 7.11: a) 3D-STM image of a Graphene-like coating on silicon oxide, b) 2D-STM image of the same sample.

Furthermore, to analyze the crystallographic structure, the sample has also been measured by means of TEM (Transmission Electron Microscopy). Figure 7.12(a,b) shows a TEM cross-section image of a Graphene-based carbon layer, deposited at 1000 °C. The substrate material is a polished silicon wafer, covered with 300 nm thermal grown silicon oxide. In Figure 7.12(b) the Graphene flakes are color-marked for better visibility. This measurements illustrate that the orientation of the Graphene crystallites is mostly flat with respect to the substrate. However, the material consists of multi crystalline flakes with a lateral dimension of a few nanometers.

Figure 7.12: a) TEM cross-section image of Graphene-based carbon on silicon oxide deposited at 1050 °C using PE-CVD, (b) Graphene flakes color-marked for better visibility.

Moreover, the purity of the coating should be one of the most interesting properties of the current process, because no exfoliation process is necessary. However, there are some metals inside the chamber, which can accumulate inside the growing layer, for example iron from the walls of the chamber, copper and nickel from the plasma electrode, molybdenum from the heating element, and tin and lead from the cooling serpentine. With the aim to identify the metallic pollution, measurements using Time of Flight Secondary Ion Mass Spectrometry have been conducted. Figure 7.13 shows the result of this investigation.

As can be seen, no metallic pollution could be identified, neither nickel (top left) nor copper (top right). Only aluminum is visible (bottom right). This is a result of the scratch and represents the substrate material (sapphire).

In summary, the PE-CVD process produces flat and closed films which have a very low roughness and are nearly free of any metallic pollution. The Graphene flakes have a lateral dimension of several nanometers and they are mostly flat orientated with respect to the surface material.

Figure 7.13: ToF-SIMS measurements. Top left: nickel; top right: copper; bottom left: photomicrograph; bottom right: aluminum.

7.3 Optimization of the Φ -HCA process

7.3.1 Introduction

As mentioned above in section 6.2, the idea of the deposition process using the Φ -HCA technology consists of the thermal conversion of amorphous carbon into a predominantly sp^2 -hybridized Graphene-like structure. This thermal conversion can be done ex situ (annealing after deposition) or during the deposition process.

First, the effect of ex post heating (annealing) on ta:C coatings was studied. For that purpose, quartz substrates have been coated with a different number of arc pulses. The substrates were 70° tilted with respect to the plasma beam, and the argon pressure was about 1 Pa to decrease the effective kinetic energy of the carbon ions.

Secondly, the heating during deposition was analyzed. Therefore, to determine the effect of the different parameters on the quality of the Graphene-like carbon, different substrates (300 nm thermal grown silicon oxide on silicon, fused quartz, sapphire) have been coated under constant conditions by varying one of the deposition parameters. As described above in section 6.3, the quality of the carbon

coatings can be influenced by the following parameters, which are characteristic ones for the Φ -HCA technology:

- Plasma arc time (τ_p),
- Plasma arc current (I_{arc}),
- Filter current (I_F),
- Buffer gas pressure (Argon).

The duration of the plasma arc τ_p multiplied by the arc current I_{arc} determines the amount of carbon atoms, which were emitted in one pulse. Consequently, these two parameters influence the deposition rate. An increase of arc time will increase the rate of deposition (layer thickness per pulse), because the longer the arc is burning, the more carbon ions will be emitted into the filter arc. Moreover, the current of the plasma pulse (I_{arc}) influences the deposition rate as well, because it directly determines the plasma density during arc evaporation. By increasing the arc current the density of the plasma will increase as well. As a result, more carbon will be deposited at one plasma pulse.

The filter current (I_F) induces the magnetic field inside the filter arch. This magnetic field guides the electrons and subsequently the carbon ions through the filter arch. In high vacuum, the magnetic field has a significant effect on the transmittance of the magnetic filter. Switching off the filter current will set the deposition rate to zero, because all of the carbon ions will be adsorbed on the walls of the filter arch. Increasing the filter current will substantially increase the deposition rate. In the present case, this effect of the magnetic field can be superimposed by scattering of the emitted carbon ions in the buffer gas. Thus, the main effect of the filter current on deposition rate and quality of the coating has to be determined.

Moreover, one of the main parameters of the present process is the pressure of the buffer gas which significantly moderates the kinetic energy of the carbon ions due to multiple collisions. An increase of the background gas pressure will reduce the mean free path of the carbon ions and increase the number of scattering. Approximately, all carbon ions will be thermalized if the pressure of the background gas is high enough. It is probable that the argon pressure is one of the main parameters in the optimization process and therefore it has to be carefully examined. Additionally, the growth of the carbon coating can be influenced by adding hydrogen as a functional gas to the buffer gas atmosphere. It can be supposed that the reactive gas will fundamentally change the growth mechanism of the Graphene-like coating. Hence, the effect of the buffer gas and the hydrogen will be examined in a separate section. The investigation of the ex-post heating (annealing) of ta:C carbon will be described in the following section.

7.3.2 Thermal conversion of modified ta:C

The thermal conversion process of conventional ta:C into graphitic carbon is already well known and published e.g. by A. Ilie et al. [40]. To reproduce and verify the results, samples were coated using the following deposition parameters (Table 7.7). These parameters have been taken from previous investigations of homogeneously deposited ultra-thin amorphous carbon films. With the aim to moderate the effective kinetic energy of the carbon ions, the chamber was filled with argon; additionally, the substrate was tilted with respect to the particle beam. As mentioned in section 6.2, this should avoid deep implantation into the substrate material. Consequently, the starting point of the annealing process is not conventional ta:C but modified amorphous carbon.

Parameter	value
Arc current (I_{arc})	3000 A
Arc time (τ_p)	1 ms
Filter current (I_F)	600 A
Argon pressure (p_{Ar})	0.75 Pa
Substrate temperature (T_s)	Room temperature

Table 7.7: Deposition parameters for the investigation in the conversion process of modified ta:C into carbon with a higher electrical conductivity

Subsequently, the samples have been characterized to evaluate the quality and to compare the results with that which is published in literature. Figure 7.14 shows the Raman spectra of the ta:C coating before (blue line) and after temperature treatment (red line) at about 1000°C. Before the annealing process, no Raman activity of the ta:C coating can be measured. This is a result of the very high amorphous sp^3 -content without any crystallographic long range order, which is not Raman active.

In contrast, after the temperature treatment, the Raman spectrum is dominated by the characteristic peaks D and G, which are the typical signatures for sp^2 -bound carbon. Additionally, the morphology and homogeneity have been measured using AFM (Figure 7.15a)) and high resolution mapping of the G-intensity (Figure 7.15b)).

The AFM picture shows a very flat coating with a low roughness (RMS) of 0.9 nm. Additionally, the Raman mapping shows neither holes nor any inhomogeneities (e.g. island growth). That indicates, that this technology is suitable for homogeneous deposition of large areas of predominantly sp^2 -bound carbon. However, the sheet resistance of the coatings with technologically relevant transmissions of about 90% is in the range of 100 kΩ to 3 MΩ (cf. Figure 7.14, inset). Consequently, the resistance of the coatings is at least 2 orders of magnitude too high for any application. This quite low conductivity verifies the results of A. Ilie et al., where a specific resistivity of about 1 Ωcm could be found [40]. For one monolayer with a thickness of 3 Å this value is equal to a very high sheet resistance of $1 \cdot 10^8 \Omega_{\square}$. Furthermore, the missing 2D-peak in the Raman spectrum and the very broad D- and G-bands are

Figure 7.14: Raman spectra of a ta:C coating as grown (blue line) and after temperature treatment (red line); inset: Sheet resistance vs. transmission of thermal converted ta:C.

a sign of a predominantly amorphous character of the coating. It can be supposed that the ex post heating can convert the sp^3 -bonds into sp^2 -hybridized carbon, but it cannot dissolve the amorphous structure into ordered Graphene growth. Hence, the optimization of the Φ -HCA process will be done by parallel heating of the substrates with the goal to deposit a Graphene-containing carbon film directly on the insulating substrate material. This optimization process will be described by the following.

7.3.3 Optimization of the electrical deposition parameters

In this section, the different electrical parameters of the Φ -HCA technology (cf. section 7.3.1) will be analyzed and optimized. For that purpose, different substrates have been coated under constant conditions by varying one parameter. As mentioned above, for all investigations, the substrates have been heated during the deposition process. The electrical parameters of the Φ -HCA process are the filter current I_F , the arc current I_{arc} , and the pulse duration τ_p .

With regard to the filter current of the magnetic filter, the influence of the deposition rate and the growth process of the coating is approximately low because of the dominating scattering effect of the buffer gas. The argon atoms inside the filter arch are able to transport the carbon ions through the filter only by multiple scattering. For this reason, the filter current should have only a limited effect. Figure 7.16 a) shows the layer absorption (blue line) and the I_{2D}/I_G peak ratio from the Raman spectrum. This peak ratio is a sign of the Graphene character and increases by increasing the quality of the Graphene-like coating. In Figure 7.16 a) it can easily be seen that the I_{2D}/I_G peak ratio has an optimum between 200 A and 400 A and it decreases by increasing the filter current up to 600 A. The absorption of the carbon layer with 150 plasma pulses decreases slightly by increasing the filter

Figure 7.15: a) AFM picture of thermal converted ta:C. b) Raman mapping of the G-intensity of thermal converted ta:C.

current.

Figure 7.16: a) Absorption (blue line) and I_{2D}/I_G peak ratio (red line) vs. filter current. b) Resistivity vs. transmission by varying the filter current.

In contrast to that finding, the filter current should have an opposite effect on the deposition rate. As described above (cf. section 7.3.1), in vacuum a higher filter current causes a higher deposition rate. In the present case, this effect is superposed by the scattering on the buffer gas atoms. Nevertheless, this does not explain a lower deposition rate at a higher filter current. It can be supposed, that the higher magnetic field negatively influences the structure of the Graphene-like coating. This may cause a lower order of the Graphene flakes and subsequently a lower absorption. Nevertheless, Figure 7.16 b) shows the optical transmission at 600 nm vs. the sheet resistance by varying the filter current. In well correlation to Figure 7.16 a), the graph indicates an optimum between 200 A and 400 A. At 600 A the sheet resistance increases as well as at 0 A. The dashed lines show the expected linear behavior at logarithmic scale for different transmissions and resistivities by varying the filter current.

Overall, it can be summarized that with regard to the Figure 7.16a) and b) the optimized filter current

lies between 200 A and 400 A.

Another important parameter which should be optimized is the arc current (I_{arc}). This parameter can be varied between 0.5 kA and 3.0 kA. As described above (cf. section 7.3.1) this parameter determines the plasma density while the arc discharge is burning. Figure 7.17 a) shows the I_{2D}/I_G peak ratio and the absorption vs. the varied pulse current (I_{arc}). As expected, the absorption of the Graphene-like coating increases as the arc current increases because of the higher plasma density. The I_{2D}/I_G peak ratio rises to reach an optimum between 1.5 kA and 2.5 kA.

Figure 7.17: a) Absorption (blue line) and I_{2D}/I_G peak ratio (red line) vs. pulse current. b) Sheet resistance vs. transmission by varying the pulse current.

In perfect accordance with that finding, Figure 7.17 b) shows the resistivity vs. the transmission by varying the pulse current. As seen in Figure 7.17 a), the sheet resistance reaches an optimum between 1.5 kA and 2.5 kA as well. The dashed lines show the expected linear behavior at logarithmic scale for different transmissions and resistivities by varying the pulse current. To reach an acceptable deposition rate (e.g. for the mass production), the arc current should be as high as possible. Thus, the optimum value for the arc current is 2.5 kA.

As well as the arc current, the duration of the plasma pulse (τ_p) determines the deposition rate. But in contrast to the arc current, the pulse duration does not vary the plasma density during the arc discharge. For that reason, no significant effect on the quality of the Graphene is supposed. Figure 7.18 a) shows the Raman I_{2D}/I_G peak ratio from Graphene-like coatings, deposited by varying the pulse time. As expected before, no dependence of the I_{2D}/I_G peak ratio from the pulse time can be identified.

Also, the transmission vs. resistivity (Figure 7.18 b) shows only a slight increase of the resistivity at 5 ms pulse time. The dashed lines, which illustrate the linear behavior, are very close to each other. Overall, it is shown that the pulse time has no effect both on the growth mechanism and the quality of the carbon coatings.

Figure 7.18: a) I_{2D}/I_G peak ratio (black squares) vs. pulse time. b) Sheet Resistance vs. transmission by varying the pulse time.

7.3.4 Optimization of the buffer gas pressure

One of the most important parameters of the present process is the pressure of the buffer gas. It can be supposed that the amount of inert gas inside the chamber will fundamentally change the structure of the carbon coating. The pressure inside the chamber can be varied between 0 Pa (high vacuum at 10^{-5} Pa) and 200 Pa. A higher pressure above 200 Pa can disrupt the arc evaporation and ignite parasitic discharges (e.g. at the walls of the chamber).

It can be supposed, that the effect of the gas filled chamber on the deposition process depends on the ratio of the argon atoms and the injected carbon ions. The more argon atoms are inside the chamber, the shorter is the mean free path of the carbon atoms and the scattering effects increase (including losses of kinetic energy and charge exchange). To get an idea of the number of argon atoms and carbon ions inside the chamber, the ratio will be calculated by the following procedure. The number of argon atoms N_{Ar} can be calculated using the thermal state equation for gases:

$$\begin{aligned}
 p_{Ar} \cdot V_f &= k_B \cdot N_{Ar} \cdot T \\
 N_{Ar} &= \frac{p_{Ar} \cdot V_f}{k_B \cdot T} \\
 N_{Ar} &\approx 6.07 \cdot 10^{17} (1 \text{ Pa}) \\
 N_{Ar} &\approx 6.07 \cdot 10^{19} (100 \text{ Pa})
 \end{aligned} \tag{19}$$

In this equation, p_{Ar} is the argon pressure, k_B the Boltzmann constant ($1.38 \cdot 10^{-23} \text{ J/K}$), V_f the volume of the filter arch ($L_f \cdot \pi r_f^2 = 2.5 \cdot 10^{-3} \text{ m}^3$), and T is the temperature ($\approx 300 \text{ K}$). It can be seen that the number of argon atoms is between $6.07 \cdot 10^{17}$ for 1 Pa and $6.07 \cdot 10^{19}$ for 100 Pa.

On the other hand, the number of carbon ions, which were emitted with one plasma pulse, can be calculated using the following equation:

$$N_{C^+} = \frac{I \cdot \tau_p}{10e} \quad (20)$$

$$N_{C^+} \approx 1.87 \cdot 10^{18}$$

In this equation, $I \cdot \tau_p$ is the current integral of one pulse (3 As) and e is the elementary charge ($1.602 \cdot 10^{-19}$ C). Furthermore, the current integral is divided by 10 because approximately 10% of the current flows inside the plasma and generates carbon ions.

As a result, the number of buffer gas atoms and that of carbon ions are in the same order of magnitude at the given pressure. Consequently, the kinetic energy of the carbon ions (some tens of eV) will be widely transferred to the buffer gas. Moreover, the mean free path of the carbon ions is short in relation to its path through the filter arch (L_f). The mean free path λ_f of the particles can be calculated using the following equation, in which the diameter of the argon atom d_{Ar} is 0,376 nm

$$\lambda_f = \frac{V_f}{\sqrt{2} \cdot \pi \cdot d_{Ar}^2 \cdot N_{Ar}} \quad (21)$$

$$\lambda_f \approx 6 \text{ mm}(1 \text{ Pa})$$

$$\lambda_f \approx 0.07 \text{ mm}(100 \text{ Pa})$$

That means, that the number of collisions inside the filter arch is between ≈ 100 at 1 Pa and 10^4 at 100 Pa. As the result, the carbon ions will be thermalized after a small distance and lose their kinetic energy due to multiple collisions. Furthermore, there will occur a two-way charge transfer between the argon and the carbon. Thus the now thermalized and neutral carbon atoms can form agglomerations inside the gas atmosphere. This agglomeration process can be the basis of the subsequent deposition process.

To examine the effect of background gas on the carbon coating process, different quartz substrates have been coated under constant conditions, varying the pressure. Figure 7.19 (a) shows the I_{2D}/I_G peak ratio from the Raman spectrum and the absorption of the carbon layer vs. the argon pressure. This diagram illustrates, that the absorption of the carbon coating is highly dependent on the gas pressure during the process.

The influence of the buffer gas can be split into three sections. Between 0 Pa and 10 Pa the absorption decreases by increasing the pressure due to the multiple scattering of carbon ions on the argon atoms. In this case, the magnetic field is responsible for guiding the carbon ions through the filter. Second, if the pressure rises above 10 Pa, the effect of the magnetic field is increasingly superimposed by the transport effect of multiple scattering. The higher the pressure is, the higher is the probability of carbon ions to pass the filter only by multiple scattering. Consequently, the absorption (and probably the deposition rate as well) increases to reach a maximum between 100 Pa and 150 Pa. Third, at higher pressure, the density of the background gas is too high, which disrupts the propagation of the carbon ions. Thus, the absorption of the carbon coating decreases, if it is deposited under buffer gas pressure above 200 Pa. The I_{2D}/I_G peak ratio (Figure 7.19 (a)), blue squares) directly correlates with the absorption curve. Hence, a structural change of the carbon coating can be supposed.

Figure 7.19: a) I_{2D}/I_G peak ratio (blue squares) and absorption (red squares) vs. argon pressure. b) Sheet Resistance vs. transmission by varying the argon pressure.

To determine the quality of the transparent and conductive carbon coating, Figure 7.19b) shows the transmission vs. sheet resistance with a varied background gas pressure. Surprisingly, the diagram shows no significant dependence of the electrical and optical properties of the referring coating on the gas pressure during the process. The slopes of the linear fits in logarithmic scale of the data at 100 Pa and 150 Pa are nearly identical. All other data measured on coatings, deposited under different gas pressure (black triangle), show the same linear behavior. This finding is in contradiction to the absorption and I_{2D}/I_G peak ratio ((Figure 7.19 (a))). To clarify this conflict, more structural analysis is necessary and will be described as follows.

The main parameters for getting more information about the carbon structure are the specific resistivity ρ with $\rho = R_{\square} \cdot d$ (where d is the thickness of the coating). Moreover, the absorption coefficient α is given by the following equation, which is known as the Lambert-Beer equation:

$$I = I_0 \cdot e^{-\alpha \cdot d},$$

where I is the transmitted intensity of light, I_0 is the intensity of the incoming light, α is the absorption coefficient, and d is the thickness of the coating. The extinction coefficient k can be calculated using the following equation:

$$k = \frac{\alpha \cdot \lambda}{2\pi},$$

where λ is the wavelength of light, which is set to 600 nm to compare all samples. The optical transmission, which represents the ratio I/I_0 , is provided by spectral photometry. The thicknesses of the different samples have been measured at a step by means of Atomic Force Microscopy (AFM). By measuring the thickness of the sample, the absorption coefficient α and the specific resistivity ρ can be calculated. To clarify the topology of the surface, the samples have also been characterized using Scanning Tunneling Microscopy (STM). The STM provides pictures of the surface and the roughness (RMS, root-mean-squared roughness). Figure 7.20(a) shows the change of the thickness and the roughness as a function of argon pressure during deposition. It can easily be seen that both

the thickness and the roughness increase with rising pressure. Likewise, the extinction coefficient k dramatically decreases between 0 Pa and 0.75 Pa (cf. Figure 7.20(b)).

Figure 7.20: a) Roughness (RMS, red line) and thickness (blue line) vs. argon pressure. b) Specific resistivity (blue line) and extinction coefficient (red line) vs. argon pressure.

With regard to the absorption, it can be conducted that the mass density of the carbon coating significantly decreases at higher gas pressure, whereas the specific resistivity increases (cf. Figure 7.20(b), blue points) in nearly the same range. That explains why no change in the transmission/resistivity ratio can be identified (cf. Figure 7.19(b)) by changing the pressure of the noble gas atmosphere. It can be supposed that the changes in mass density and transmission at different gas pressure are caused by a structural variation in the respective coatings. To clarify this, a careful analysis of different coatings will be conducted in a separate section, which deals with the structural analysis (section 7.3.8).

Subsequently, after the optimization process, samples have been produced using the optimized parameters (cf. Table 7.8) to analyze the charge carrier mobility using the Hall-technique.

Parameter	value
Arc current (I_{arc})	2500 A
Arc time (T_p)	1 ms
Filter current (I_F)	200 A
Argon pressure (p_{Ar})	100 Pa
Pulses (N_p)	150
Substrate temperature (T_s)	1050°C

Table 7.8: Deposition parameters for Hall-analysis of the argon process.

For this purpose, the magnetic field was varied between 0 kG and 10 kG. Figure 7.21 shows the result of these measurements.

The measured mobility with a magnetic field with negative (red line) and positive (black line) sign is nearly symmetrical with respect to the average mobility (blue line). Consequently, the average

Figure 7.21: Measurement of the charge carrier mobility of a Graphene-like coating deposited using a Φ -HCA process with argon as buffer gas.

mobility is not influenced by the strength of the magnetic field. However, the mobility is much lower than that, when measured on high quality Graphene. This finding will be clarified by the structural analysis in section 7.3.8.

7.3.5 Hydrogen enriched atmosphere

It is well known in literature that hydrogen can improve the electrical properties of carbon coatings, when deposited using a high current arc evaporator [40]. In the current process, the hydrogen can be varied between 0 Pa and a few tens of Pa. In order to optimize the current deposition process, the possibility to add up to 20 Pa hydrogen to the noble gas atmosphere has been also investigated. However, it should be noticed that hydrogen decreases the deposition rate significantly. This effect is caused by the formation of C_xH_y -compounds, which are hardly involved in the deposition process. Thus, the hydrogen pressure should be carefully increased to determine the optimal parameter at suitable deposition rates. To illustrate the decrease of deposition rate by adding hydrogen, Figure 7.22 shows the deposition rate vs. varied hydrogen pressure.

The deposition rate in nm per pulse is determined by measuring the thickness after deposition using an AFM. Between 0 Pa and about 1 Pa, the rate is hardly influenced by the hydrogen. If the hydrogen pressure rises above 5 Pa, the deposition rate dramatically decreases in exponential scale. For that reason, only a few tens of Pa hydrogen are suitable for the current process. To determine the effect of a hydrogen containing atmosphere, the hydrogen pressure was first varied between 0 Pa and 35 Pa, whereas the argon pressure was set to 100 Pa, which is a result of the previous optimization process. All other deposition parameters (pulse current, pulse time, filter current) result from this optimization process as well. Figure 7.23(a) shows the sheet resistance vs. transmission at varied hydrogen pressure

Figure 7.22: Deposition rate vs. hydrogen pressure.

(blue points) in comparison with the results at 20 Pa (red line).

Figure 7.23: a) Sheet resistance vs. transmission at varied hydrogen pressure (blue points) and 20 Pa (red line), b) I_{2D}/I_G peak ratio (red line) and I_D/I_G ratio (black line) vs. hydrogen pressure.

The diagram illustrates, that the electrical and optical properties reach their optimum at a hydrogen pressure of about 20 Pa. If the pressure rises above 20 Pa, only the deposition rate decreases (cf. Figure 7.22), but no improvement of the properties can be reached. Figure 7.23(b) shows the I_{2D}/I_G Raman peak ratio (red line) and I_D/I_G Raman ratio (black line) vs. hydrogen pressure. In contrast to expectations, the I_{2D}/I_G ratio decreases significantly at higher hydrogen pressure and reaches its minimum at 20 Pa. At this hydrogen pressure, the best electrical and optical results can be reached. It can be concluded that this phenomenon shows the limitations of Raman spectroscopy for characterizing a multi-crystalline, Graphene-based film with different crystal orientations. Additionally, the I_D/I_G ratio shows no major dependence on the hydrogen pressure and the quality of the coatings as well. However, this is only the result at 100 Pa Argon in combination with hydrogen. To examine the influence of different argon pressures in a hydrogen containing atmosphere, the argon pressure was

subsequently varied as well. For that purpose, the hydrogen pressure was varied proportional to that of argon ($\dot{V}_{Ar} : \dot{V}_{H_2} \approx 5 : 1$). Figure 7.22 shows the specific resistivity (red line) and extinction coefficient (blue line) vs. different argon pressure in hydrogen-containing atmosphere.

Figure 7.24: Specific resistivity (blue line) and extinction coefficient (red line) vs. different argon pressure in hydrogen containing atmosphere.

It shows that the specific resistivity decreases by increasing the argon pressure. This is in good agreement with the findings from experiments without hydrogen. However, the extinction coefficient k increases simultaneously. This means that the resulting specific resistivity is lower, if the absorption is higher, meaning that no optimal parameter for the argon pressure results from that diagram.

Moreover, Figure 7.25(a) shows the specific resistivity vs. different argon pressure without hydrogen (blue line) and with hydrogen (red line). It can easily be seen that the addition of hydrogen to the gas atmosphere substantially decreases the specific resistivity of the carbon coating.

This effect is particularly strong between 50 Pa and 150 Pa. Surprisingly, no improvement can be seen if the hydrogen is added to high vacuum without any argon. The most important finding arisen from that diagram is that the optimal argon pressure is between 50 Pa and 150 Pa, if hydrogen is added to the gas atmosphere. A comparison of the coatings deposited with and without hydrogen is shown in Figure 7.25(b). It clearly illustrates that hydrogen greatly improves the process; it decreases the sheet resistance by at least half an order of magnitude at identical layer transmission.

Moreover, the mobility of the charge carriers has been measured and compared with the findings from the process without the addition of hydrogen. Figure 7.26 illustrates the Hall mobility vs. a varied magnetic field. The triangles represent the process with argon and hydrogen, while the points represent the process using pure argon as buffer gas. In both cases, the mobility with positive field (black line) and negative field (red line) are symmetrical with respect to the average mobility (blue line). Hence, the average mobility is hardly influenced by the strength of the magnetic field. However,

Figure 7.25: a) Specific Resistivity vs. different argon pressure without hydrogen (blue line) and with hydrogen (red line). b) Sheet resistance vs. transmission: Comparison of argon (blue line) and argon+hydrogen (red line).

the addition of hydrogen substantially increases the charge carrier mobility. This finding fits well to the previous investigation, where hydrogen decreases the sheet resistance at an identical layer transmission in comparison to the process with pure argon.

Figure 7.26: Comparison of Hall mobility vs. a varied magnetic field for the process with hydrogen (triangles) and without hydrogen (points).

7.3.6 Substrate temperature

With regard to any industrial application (e.g. transparent conductive coating, applications in microelectronics), the required substrate temperature is an important parameter. It would be desirable to deposit the transparent coating with a substrate temperature which is as low as possible. Thus,

this section is devoted to analyzing the dependence of the substrate temperature on the quality of the Graphene-like coatings. For that purpose, the temperature of the substrate has been varied between 500°C and 1050°C.

As a result, all coatings have no measurable conductance if they are coated at temperatures between 500°C and 700°C. However, the transmission of these samples is reduced by several percent as expected from the number of arc pulses. This indicates, that the substrate temperature plays a key role in forming Graphene-like coatings. Figure 7.27(a) shows the transmission vs. sheet resistance with a substrate temperature of 1050°C (red line) and with varied substrate temperature (blue points). The diagram illustrates, that the formation of conductive Graphene-like carbon starts at 750°C. However, at this temperature the resistivity is quite high in comparison to higher substrate temperatures.

Figure 7.27: a) Sheet Resistance vs. transmission at 1050°C (red line) and with varied substrate temperature (blue points). b) I_D/I_G ratio as a function of the lateral grain size in Raman spectrum from literature (black line) [49] and at varied temperature (black squares).

As described in section 7.2.3 in more detail, the grain size of the Graphene can be examined by measuring the I_D/I_G ratio in the Raman spectrum. Figure 7.27(b) shows the run of the I_D/I_G -curve from literature [49] (black line) and that at varied temperature (black squares). It shows clearly that the lateral grain size of the Graphene crystals increases at higher temperatures. This causes a better conductivity due to the lower density of the grain boundaries. However, at 850°C, the grain size reaches its maximum value of about 1.5 nm and higher temperature does not cause higher values. Hence, it can be supposed that the electrical properties of the coatings will be nearly constant at higher temperatures above 850°C. This is in good agreement with the findings from the transmission and resistivity measurements (cf. Figure 7.27(a)).

Additionally, the intensity of the 2D peak -which shows the Graphene-character of the coating- correlates with the substrate temperature. Figure 7.28(a) shows the 2D-intensity of the samples, coated under different temperatures (all spectra are normalized in order to the G-peak).

The 2D-intensity increases, if the substrate temperature increases and reaches its maximum at 900°C. This finding is in good agreement with all other measurements (D-intensity, conductivity), which has

Figure 7.28: a) 2D-intensity of the samples coated under different temperatures, b) Raman spectrum of the 2D-intensities.

been shown before. Furthermore, the mobility of the charge carriers has been determined under a varied magnetic field (Figure 7.29). In this figure, only the average mobility (average between negative and positive magnetic field) is plotted.

It indicates the strong dependence which the mobility has upon the substrate temperature. The lower the temperature is, the lower is the charge carrier mobility of the corresponding carbon coating after the process. This finding correlates well to the results from the Raman and conductivity measurements. It can be summarized, that the formation of Graphene-like coatings starts at 750 °C. Both the electrical conductivity and the grain size of the Graphene crystals reach their maximum at 850 °C. Only the charge carrier mobility increases if the substrate temperature rises above 1000 °C. However, this effect cannot be identified using either Raman analysis or electrical conductivity measurements only.

Figure 7.29: Average charge carrier mobility vs. magnetic field of carbon coatings, produced using the Φ -HCA technique.

7.3.7 Substrate material

One of the main aims of this process is to be nearly independent of the substrate material, because the carbon atoms and ions reach the surface and form an ordered graphitic structure without use of any catalytic effect. Thus, the process can work on arbitrary substrates which withstand the required temperature treatment. To prove these assumptions, another transparent and insulating material was tested. Sapphire (aluminum oxide Al_2O_3) withstands temperatures up to 2400 °C and it was already successfully used for Graphene synthesis [29, 34]. The substrates have been coated with different counts of plasma pulses (different thickness and transmissions) using the optimized parameters (Table 7.9), taken from the previous optimization process.

Parameter	value
Arc current (I_{arc})	2500 A
Arc time (T_p)	1 ms
Filter current (I_F)	200 A
Gas atmosphere	$p_{Ar} = 100$ Pa, $p_{H_2} = 20$ Pa
Substrate temperature (T_s)	1050°C

Table 7.9: Deposition parameters for the investigation in different substrate materials for the Φ -HCA process.

Subsequently, the carbon coatings have been analyzed by means of photometry, Raman spectroscopy and electrical characterization. Figure 7.30(a) shows a comparison between the Raman spectra of carbon coatings on sapphire and quartz. It illustrates that no changes in Raman intensity as well as peak ratios can be identified. The whole Raman spectrum for carbon on sapphire has slightly shifted

to a higher wavenumber with respect to the spectrum on quartz. This effect is described in literature and it is caused only by the interaction between the excitation laser and the substrate material [48]. With regarding to the comparison of the Raman spectra, no influence of the substrate material can be identified.

Figure 7.30: a) Comparison between the Raman spectra of carbon coatings on sapphire (blue line) and quartz (red line). b) Sheet resistance vs. transmission of Graphene-based carbon on quartz (red line), sapphire (blue line), BK7 (black triangle), and Quartz at 820°C (black squares).

Figure 7.30(b) shows the sheet resistance to transmission ratio of Graphene-based carbon on quartz, sapphire, normal glass (boron crown glass BK7) and quartz (coated at 820 °C). Both the coating on sapphire and quartz show a linear dependence of optical transmission and sheet resistance in logarithmic scale with the same slope. However, the coatings on sapphire have a slightly better transmission by identical resistance. Currently, the reason for that experimental result cannot be explained, especially because this effect does not occur using the PE-CVD process.

Moreover, based on the findings of section 7.3.6, it can be supposed that the process can also work on normal glass (BK7) because the process can be decreased to 820 °C without decreasing the quality dramatically. The black triangle in Figure 7.30(b) represents one experiment on BK7. The coating has the same quality like on quartz, deposited with the same substrate temperature which is shown by the dashed line with the same slope.

It can be concluded that this process can work on different substrates, and the quality is hardly influenced by the tested substrate material. The coatings on sapphire have slightly better properties than on quartz. One important finding is that if the substrate temperature is decreased to 820°C, standard glass samples can be coated as well.

7.3.8 Structural analysis

The crystallographic properties, the topography, and the roughness of the surface will be analyzed in this section with the aim to understand the growth of the carbon films. For that purpose, different methods of analysis have been used: TEM cross section image for measuring the thickness and illus-

trating the crystal orientation as well as the lateral size; ToF-SIMS for measuring the pollution and the purity of the carbon coatings, STM images to show the roughness and growth mechanism. In the first part, the coatings without hydrogen addition will be characterized. Subsequently, the optimized process using a hydrogen-containing atmosphere will be investigated followed by a comparison between both processes.

To examine the argon process, samples have been produced using the optimized parameters from the previous optimization process (cf. section 7.3.3). These parameters are summarized in the following Table 7.10:

Parameter	value
Arc current (I_{arc})	2500 A
Arc time (T_p)	1 ms
Filter current (I_F)	200 A
Argon pressure (p_{Ar})	100 Pa
Pulses (N_p)	150
Substrate temperature (T_s)	1050°C

Table 7.10: Deposition parameters for the structural analysis of the argon process.

To show the quality of the Graphene-containing coating, confocal micro-Raman spectroscopy and microscopy were used to accumulate single spectra and highly resolved Raman mappings. Figure 7.31(a) shows a single spectrum, (b) shows a high resolution image ($100\ \mu\text{m} \times 100\ \mu\text{m}$) with a laser spot size of about $1\ \mu\text{m}$.

Figure 7.31: a) Raman single spectrum of the Graphene-based coating. (b) Raman I_{2D} -mapping of the same coating as shown in a).

The high D-band centered at $1350\ \text{cm}^{-1}$ shows the presence of disordered carbon atoms and a high density of grain boundaries. For that reason, the G+D band at $2950\ \text{cm}^{-1}$ is also visible. The I_D/I_G ratio of 1.5 shows a distance between the defects (grain size) of a few nanometers [49]. The 2D peak

(Figure 7.31(a), inset) seems to be a convolution of four components: $2D_{1B}$, $2D_{1A}$, $2D_{2A}$, $2D_{2B}$. This is characteristic for multilayer Graphene, with a thickness between two and five layers [72]. Moreover the position of the 2D-peak at 2690 cm^{-1} has shifted to a higher wavenumber with respect to that expected for mono layer Graphene on silicon oxide [72, 48]. The homogeneity of the deposition was investigated by measuring the intensity of the 2D-band over an area of $(100 \mu\text{m} \times 100 \mu\text{m})$ (Figure 7.31(b)). The resulting false color picture shows neither holes nor any partial inhomogeneity (the diagonal line in the upper left corner is an artifact of the measuring device that appears on every scan at the same location). From that measurements it can be supposed that the coating, deposited with 150 arc pulses under optimized conditions, is several layers thick and homogeneously covers large areas. By contrast, Figure 7.32(a) shows a STM-image from the surface of a carbon coating with the same parameters. Surprisingly, it shows a rough and unordered carbon coating with a fractal cauliflower-shape structure comparable to that described in [73]. The thickness can be estimated to be about 27 nm and average roughness (RMS) has been measured to be 3.9 nm.

Figure 7.32: a) STM image of a Graphene-containing coating with 150 pulses, (b) Transmission spectra of different Graphene coatings (dashed lines) and one carbon coating (150 pulses, black line).

In Figure 7.32(b), the transmission spectrum of that coating is compared with different calculated transmission spectra. The calculation has been made using optical constants from literature [74]. The method of calculation includes multiple reflection losses, and uses the following equations to determine the overall reflection (R_t) and transmission (T_t). This method has been published and the calculations have been conducted by J. Bauer [75].

$$T_t = \frac{T_0 \cdot T_2}{1 - R_1 \cdot R_2} \quad (22)$$

$$R_t = \frac{R_0 - R_0 \cdot (R_2 \cdot R_0 - T_1 \cdot T_0)}{1 - R_1 \cdot R_2} \quad (23)$$

The variables R_0 , R_1 , and R_2 represent the reflection losses on the relevant interfaces (air-carbon, carbon-quartz, quartz-air), whereas the variables T_0 , T_1 , and T_2 represent the respective transmission.

It can be seen that the transmission spectrum fits to that of a Graphene coating, consisting of about eight layers (2.5 nm) and correlates to the Raman measurements. This finding is in sharp contrast to that from the STM image. To explain the very high transmission at high thickness, TEM cross-section images have been taken to determine the internal structure of the carbon coatings. Figure 7.33(a) shows the TEM image of the same Graphene-containing carbon coating, deposited under 100 Pa argon as buffer gas. In Figure 7.33(b), the Graphene flakes are color-marked for better visibility. The horizontal line in Figure 7.33(b) marks the end of the carbon coating.

Figure 7.33: a) TEM cross section image of a Graphene-containing coating. (b) Color-marked Graphene flakes for better visibility.

Inside the first 10 nm, the Graphene flakes grow almost perpendicular with respect to the surface. A flat growth of the Graphene-sheets occurs only inside the upper layers. The grain size of a few nanometers is consistent to the calculated data from the Raman spectrum (cf. section 7.3.3). It can be concluded that the perpendicular growth in the coating is responsible for the higher thickness and roughness than expected, because the extinction coefficient (k) of perpendicular grown Graphene is nearly zero with vertical incidence of light [76]. Consequently, the coating can be thicker than expected from the transmission spectrum. In contrast, the Graphene-like Raman spectrum and the relatively high electrical conductivity are caused by the flat Graphene growth inside the upper layers. These flat growing Graphene sheets can be displayed, if the same thick carbon film is measured using STM with high resolution. From several positions on the surface it is possible to measure the flat lying Graphene flakes on top of the mostly unordered carbon coating. To illustrate this, the Figures 7.34a),b) provide line-scans of different positions. Due to the very high resolution, however, the picture shows a lot of noise (horizontal lines). Furthermore, Figure 7.34c) shows an overview of the surface topography with lower resolution.

The height of the steps in the line scan fit well with the thickness of Graphene (0.33 nm). Furthermore, the lateral size of the flakes is measured to be about 4 nm. This measurement provides the same value as what has been obtained using TEM and Raman spectroscopy.

It can be concluded that the carbon coatings are inhomogeneous and consist of two different sublayers: one in horizontal orientation with an higher extinction, and another one in perpendicular orientation

Figure 7.34: a) STM line scan of a Graphene bi-layer flake, b) STM-line scan of a Graphene three-layer flake, c) STM image of a Graphene-containing coating with lower resolution.

with a low extinction. This can also be seen if the layer absorption is plotted vs. the number of plasma pulses (Figure 7.35). For that experiment, the deposition process was stopped after different numbers of pulses. It can be seen that the curve can be fitted using two different lines. These lines represent two different carbon coatings with different extinction coefficients.

Figure 7.35: Layer absorption vs. number of plasma pulses (pure argon atmosphere).

The linear slope between zero and one hundred pulses represents the flat growing Graphene flakes. The vertical oriented Graphene is represented by the slighter slope at more than 100 pulses. It should be noticed that both types of carbon seem to grow simultaneously, because at the end of the deposition

process, the flat lying Graphene is not located at the bottom but on the top of the carbon layer. However, it can be supposed from previous findings that the addition of hydrogen probably changes the structure of the carbon coating. This assumption is supported by the better electrical and optical properties of that coatings. Hence, the films produced using the hydrogen process will be carefully analyzed by the following as well. The referring Raman spectrum of such a sample is shown in Figure 7.36. It shows the characteristic peaks for multi crystalline Graphene-containing carbon coatings, such as the D-band centered at 1350 cm^{-1} and the G-Band at 1600 cm^{-1} . The 2D-Band at 2700 cm^{-1} is low, which is typical for coatings deposited under hydrogen-containing atmosphere (cf. 7.3.5).

Figure 7.36: Raman single spectrum (hydrogen process), insert: 2D-mapping of Graphene-containing carbon coating (hydrogen process).

The I_D/I_G ratio of 1.2 shows a distance between the defects (grain size) of a few nanometers [49]. The 2D-intensity mapping ($100 \times 100\text{ }\mu\text{m}$) (Figure 7.36, insert) shows an excellent homogeneity without any holes. However, the Raman spectrum does not contain more information about the structure of such multi crystalline Graphene-containing coating. Thus, to investigate the optical properties and the surface quality, measurements by means of STM and spectral photometry have been conducted. As shown in Figure 7.37(a), the coating is free of holes and no island growth can be identified. The surface has a very low average roughness (RMS) of 0.65 nm.

The spectral transmission (Figure 7.37(b)) fits well to that of 4-layer Graphene (calculated with optical constants from literature [74]). However, regarding to the previous results of this work, it can be supposed that the real thickness of that coating is much higher because of different optical constants. Therefore, measurements of the thickness using AFM have been carried out and provide a thickness of 4.7 nm. The extinction (k) has been calculated to be 1.1. Comparing to the values published for Graphene in literature ($k=1.8$ [74]), the extinction is too low. The reason for that can easily be seen in the referring TEM cross-section image (Figure 7.38(a,b), in (b) the Graphene flakes are color-enhanced

Figure 7.37: (a) STM image of a Graphene-containing coating with 400 pulses (hydrogen process). (b) Transmission spectra of different Graphene coatings (dashed lines) and one carbon coating (400 pulses, black line), hydrogen process.

for better visibility).

Figure 7.38: a) TEM cross section image of a Graphene-containing coating (hydrogen process). (b) Color-marked TEM-picture for better visibility.

Inside the first 3-4 layers, the Graphene flakes grow almost flat with respect to the surface. If the coating is getting thicker, a perpendicular and unordered growth of the Graphene sheets occurs. The grain size of a few nanometers is consistent to the calculated data from the Raman spectrum (cf. section 7.3.5). It can be concluded that the perpendicular growth in the coating is responsible for the higher thickness which is measured to be 4.8 nm. This result also fits to the data which was measured using AFM. Since the extinction coefficient (k) of perpendicular grown Graphene is nearly zero with vertical incidence of light, the extinction coefficient decreases. Consequently, the coating can be thicker than expected from the transmission spectrum. On the other hand, the relatively high electrical conductivity is caused by the flat Graphene growth inside the first 3-4 layers. It can be concluded that by adding hydrogen to the atmosphere, the carbon coatings are still inhomogeneous and consist of two different sublayers: one in horizontal orientation with a higher extinction, and another one in perpendicular orientation with a low extinction. This can also be seen if the layer

absorption is plotted vs. the number of plasma pulses. Similar to previous investigations above, the data can be fitted with two lines, which have different slopes (Figure 7.39).

Figure 7.39: Layer absorption vs. plasma pulses (argon atmosphere + hydrogen).

One line represents a layer with a high extinction (high slope, flat Graphene), and a second line correlates to a layer with a lower extinction (low slope, perpendicular Graphene).

Finally, the results of the structural analysis of both processes (pure argon atmosphere and hydrogen-containing atmosphere) will be compared by the following. First, the Raman spectrum (Figure 7.40(a)) of the two coatings show significant differences. In comparison to the Raman spectrum of the argon process, the 2D-band of the spectrum, referring to the hydrogen process is much lower. It is probable that this is a result of the lower carbon thickness using the hydrogen process, because the deposition rate is much lower (Figure 7.40(b)).

Figure 7.40: a) Comparison of the Raman spectra of both processes. (b) Comparison of the absorption after different plasma pulses (both processes).

The excitation laser of the Raman system integrates the Raman intensity of the material, which is located in the laser focus. Since the Rayleigh length of the focus is much longer than the thickness of the coating, the Raman spectrum contains the information of all the carbon material of the coating. Thus, the thicker the coating is, the more Graphene flakes are located in the laser spot. Consequently, the 2D-Band increases with higher layer thickness and cannot give any information about the crystallographic quality of Graphene-containing multi crystalline carbon. Nevertheless, the D-Band in the Raman spectrum can give information about the part of amorphous carbon and the density of the grain boundaries as well. As shown in (Figure 7.40(a)), the D-Band decreases if hydrogen is added to the atmosphere which indicates a better Graphene growth. This probably causes the higher conductance of the samples, which was already shown in section 7.3.5.

Additionally, the structure and orientation of the carbon changes by adding hydrogen to the gas atmosphere. Whereas in the argon process the growth starts in perpendicular orientation (Figure 7.41a)), the Graphene sheets lie flat in the first atomic layers (Figure 7.41a)) if hydrogen is added. Hence, the carbon coatings grow in a reverse order by adding hydrogen. Moreover, the TEM image illustrates that the number of ordered Graphene sheets increases in TEM picture which corresponds to a lower part of amorphous carbon.

Figure 7.41: a) TEM cross-section image of Graphene-based coating (+hydrogen). b) TEM cross-section image of Graphene-based coating (pure Argon).

Furthermore, the roughness of the surface differs in both processes as well. If hydrogen is involved in the process, the average roughness (RMS) decreases dramatically from 5 nm to 0.65 nm (cf. Figure 7.41(a,b)). The surface structure changes from a fractal cauliflower-shape structure into a closed, dense graphitic structure.

It can be concluded that hydrogen improves the coating with regard to its electrical and optical properties as well as the surface roughness. The number of ordered Graphene sheets increases, the roughness is lower, and the coatings are more dense than without hydrogen. Similar to the investigations in the PE-CVD process, ToF-SIMS measurements have been used with the aim to identify the metallic pollution. Several metallic impurities of the coating can be caused e.g. by parasitic discharges on the walls of the chamber (aluminum, iron, copper). In Figure 7.43, the results of the mass spectrometry

Figure 7.42: a) STM image of the carbon surface (+hydrogen). b) STM image of the carbon surface (pure argon).

investigation of some selected elements are illustrated. A photomicrograph of the analyzed region is shown in the top left picture .

As the result, nearly no metallic pollution can be identified, neither for potassium (top middle) nor for aluminum (top right), copper (bottom, left), natrium (bottom, middle), or iron (bottom, right). This result fits well to the findings from the measurements of the charge carrier mobility. Since the average mobility is independent of the strength of the magnetic field, this measurement does not indicate a p-type doping as it occurs in case of metal induced p-type doping. Hence, the carbon films contain only pure carbon. However, the grain size of the Graphene-flakes, measured using TEM, is only a few nanometers. This causes a high density of grain boundaries and subsequently a frequent electron scattering. That significantly reduces the conductivity, compared to pristine Graphene and explains the lower electron mobility.

Figure 7.43: ToF-SIMS measurements. Top left: photomicrograph of the analyzed region; top middle: potassium; top right: aluminum; bottom left: copper; bottom middle: sodium; bottom right: iron.

7.4 Comparison and discussion

In this section, the experimental results of the PE-CVD and the Φ -HCA technology will be compared. It has to be noticed that for both approaches, only the best results obtained from the optimized parameters will be compared. Therefore, the optimized parameters for both processes are shown in the following Table 7.11:

Regarding the substrate temperature, no differences between the two processes of deposition could be found. The optimum substrate temperature is about 1000°C . At this value, the coatings provide the best charge carrier mobility and the best ratio of transmission and sheet resistance. Decreasing the temperature significantly decreases the quality of the coatings, as well as the lateral size of the Graphene crystallites. The process of deposition starts at about 800°C in both cases and below 750°C , no Graphene-like film could be deposited.

Both processes are suitable for different substrate materials. To prove this, various materials have been tested (Sapphire, Quartz, Glass). In case of the PE-CVD process, no differences between the transmission-resistance-ratios of the carbon films on different substrates can be found. Both the coating on sapphire and quartz show a linear dependence on optical transmission and sheet resistance in logarithmic scale with the same slope. In contrast, using the Φ -HCA technology, the samples on Sapphire have slightly better properties than on quartz because the sheet resistance is lower at the identical optical transmission. Moreover, both processes are able to coat normal glass (e. g. BK7) with

Φ -HCA	
Arc current (I_{arc})	2500 A
Arc time (T_p)	1 ms
Filter current (I_F)	200 A
Gas atmosphere	$p_{Ar} = 100$ Pa, $p_{H_2} = 20$ Pa
Substrate temperature (T_s)	1050°C
PE-CVD	
Plasma power (P_P)	1.0 W
Gas atmosphere	$\dot{V}_{Ar} : \dot{V}_{Methane} = 90 : 20$
Working pressure (p)	0.7 Pa
Process time (t_P)	7.5 min
Substrate temperature (T_s)	1050°C

Table 7.11: Optimized parameters for both the PE-CVD and the Φ -HCA process.

a Graphene-containing conductive coating. However, the substrate temperature has to be decreased to 820°C in order not to melt the substrate material. This results in a lower conductivity and Hall mobility as well.

Additionally, to use these coatings in a field of application, they have to be clean without any metallic pollution. Hence, the carbon films have been characterized by means of mass spectroscopy (ToF Sims) to identify any chemical impurity. As a result, no impurity could be found in the coatings produced by means of PE-CVD and Φ -HCA. All coatings are nearly free of any metallic pollution coming from the walls of the chamber or the experimental setup.

The Raman characterization (Figure 7.44) of the samples, deposited using both processes, provides only weak differences. The I_D/I_G ratio is nearly identical, which indicates a similar grain size of the Graphene crystals. However, the 2D-peak of the coating using the Φ -HCA is slightly higher. This could be a sign of both a higher oriented graphitic carbon and a higher density of flat-lying Graphene. However, by interpreting the TEM measurements (Figure 7.45a,b,) this assumption can hardly be confirmed. In both cases, the TEM picture shows graphitic carbon with different orientations with respect to the surface.

However, the cross-section TEM-measurements provide a high percentage of flat lying Graphene sheets both for the PE-CVD and the Φ -HCA. From this investigation, no fundamental differences can be identified.

Furthermore, the topography of the samples has been investigated using STM measurements. Figure 7.46a,c shows a comparison of the roughnesses of the two different coatings with equal thickness. It can easily be seen that the roughness of the PE-CVD coating (Figure 7.46c,d) is much lower than that, deposited using Φ -HCA. Additionally, the PE-CVD coating is nearly atomically flat so that the

Figure 7.44: Comparison between the Raman spectra of carbon coatings deposited using PE-CVD (blue line) and Φ -HCA (red line), inset: Mapping of the 2D-intensity (left: Φ -HCA, right: PECVD).

measured RMS value of 0.9 pm does not reflect the physical reality.

In contrast, the Φ -HCA coating shows a higher RMS roughness of 0.64 nm (Figure 7.46,a,b). The STM picture indicates that the carbon grows in a preferential orientation, and that it forms sheets on top of the surface. However, regarding any optical application in both cases, the RMS roughness is much lower than the wavelength of light. Consequently, this low roughness cannot negatively influence the optical properties of the carbon coatings.

Finally, the electrical properties of the coatings have to be compared by plotting the transmission vs. the sheet resistance of coatings with different thicknesses (Figure 7.47). The average mobility of the charge carriers is shown vs. a varied magnetic field for both processes (Figure 7.47, inset).

The most striking result to emerge from this investigation is that the linear fits of the measured data from both processes are identical. This means that the coatings have the same sheet resistance at identical transmission. Additionally, the variation of the measured values is similar. This shows the excellent scalability of the two processes. Since the technology of the two deposition methods is completely different, this finding is very surprising. However, comparing the best achieved charge carrier mobilities, the PE-CVD process provides a higher value than the Φ -HCA. Nevertheless, this obviously has no effect on the sheet resistance.

Overall, it can be concluded that both processes are very similar regarding the electrical and optical properties. Furthermore, the requirements on the substrate material (temperature treatment) are the same. Both processes are suitable for different insulating substrate materials such as quartz, sapphire,

Figure 7.45: TEM cross-section image of a Graphene-containing carbon coating, deposited using a) PE-CVD and b) Φ -HCA.

glass. The comparison with other approaches, described in literature and an overview of possible applications, will be done in the following section.

Figure 7.46: STM image of a Graphene-containing coating, deposited using a) Φ -HCA and c) PE-CVD. Roughness histogram of a Graphene-containing coating, deposited using b) Φ -HCA and d) PE-CVD.

Figure 7.47: Sheet resistance vs. transmission of coatings with different thicknesses for the PE-CVD (red points) and Φ -HCA (black squares).

8 Comparison with literature

As described above, the two processes examined in the current work are able to produce transparent conductive carbon films with a high percentage of oriented graphene-flakes. To introduce this coating in any industrial application, it has to fulfill several requirements with regard to its optical and electrical properties and its purity. Using conventional CVD-graphene on copper substrates, the coatings have to be lifted off and applied to the area of usage. This causes p-type doping of the graphene, provoked by residual copper [77]. To verify the purity of the current coatings, the carbon films have been measured by means of mass spectrometry (ToF-SIMS). As a result, in contrast to the exfoliated graphene, no chemical impurity (e.g. residual metals) could be identified in both coatings deposited using PE-CVD and Φ -HCA. Moreover, the charge carrier mobility is not influenced by the strength of the magnetic field, which indicates a missing p-type doping and impurity as well.

Furthermore, the sheet resistance has been measured using the van-der-Pauw arrangement and the charge carrier mobility has been determined by means of Hall measurements. Additionally, the layer transmission has been determined using spectral photometry and reflectometry. These measurements can be plotted in a diagram which shows the sheet resistance vs. the optical transmission. To compare these findings with the current literature, Figure 8.1 shows the results from this work (red line) and from different established technologies described in literature (dashed lines). Since both examined processes (PE-CVD and Φ -HCA) provide the same result, all measured values are combined in one curve.

Figure 8.1: Sheet resistance vs. transmission of carbon coatings, which have been deposited using different processes: low-temperature PE-CVD on copper (black dashed line), coatings from this work (red line), annealed RGO (purple dashed line), and exfoliated high-quality graphene on copper (green dashed line). * [16], ** [14], *** [78].

Compared to the measurements on exfoliated graphene deposited by a low-temperature PE-CVD process [16], the sheet resistances achieved in the present work are significantly lower, and the reported results on annealed RGO are in the same range [78]. The resistivity of exfoliated high-quality graphene is much lower [14], which is a result of the much larger grains (lower density of grain boundaries) and the lower distortions as well. The small grain size also causes a much lower charge carrier mobility ($\approx 40 \text{ cm}^2/\text{Vs}$) than that reported for high quality graphene (up to $10^5 \text{ cm}^2/\text{Vs}$ [13]). However, one of the main advantages of the new approaches presented here is the avoidance of any exfoliation process. With regard to any industrial applications (e.g. transparent conductive coatings), the films have to fulfill the requirements in terms of sheet resistance and optical transmission. Figure 8.2 shows the sheet parameters of different possible applications and the result of the current work.

Figure 8.2: Requirements for different applications (gray recs) and the result of the current work (red circle).

It illustrates that the achieved conductivity can be suitable to produce conductive films for EMI shielding (e.g. mobile phone displays). However, it has to be noted, that the required substrate temperature of about 850°C makes the current process not applicable for coating polymers which were used for the production of displays. For other applications such as TCO, the current coatings can be compared with the conventional used material (ITO) as well as thin metal films. In case of thin sputtered metal films on dielectrics, the coatings usually pass different stages. The underlying principle is called Volmer-Weber-growth, in which the three-dimensional islands grow together and form a closed film at higher thicknesses. At the first stage the electrons are confined to the islands [79] and subsequently an incident electromagnetic field can excite surface plasmons, which are responsible for a higher light absorption [79]. Due to this plasmonic effect, the absorption of such a discontinuous film has a maximum and cannot be calculated using the Lambert-Beer-Law. To illustrate this, Figure 8.3 shows the absorption as a function of the layer thickness of a sputtered silver film (blue line) [80]

compared with a Graphene-like coating (red line) from this work. It can be seen that the silver film has an absorption maximum at a thickness of 4 nm (average coverage of the surface with Ag-islands) due to the described plasmonic effects.

Figure 8.3: Absorption as a function of the layer thickness of a sputtered silver film (blue line) [80] and a Graphene-like coating (red line)

In contrast, the absorption of the Graphene-like coating shows no local maximum or minimum. Hence, this indicates no island growth but a homogeneous coating even at ultra-thin layers. This finding is in good correlation with the results of the Raman-mapping and the STM measurements.

With regard to the sheet resistivity, the Vollmer-Weber-growth has a strong influence on the conductivity of the thin metal film. In the first stages the film is discontinuous, whereas only a non-metallic regime exists, consisting of metallic islands and a dielectric continuum. Hence, the resistance of this coating is very high [81]. The low residual conductance of this film is provided by thermally activated electron tunneling or hopping from particle to particle [81]. After increasing the sputter time, the film passes the second stage (semi-continuous) and subsequently the third state (continuous coating). At these stages, the island size increases and they join together. Consequently, the sheet resistance decreases and the conductivity is limited by the scattering effects of the electrons on the grains of the islands (grain boundaries). Figure 8.4a) shows the transmission vs. thickness of sputtered copper (red line) in comparison with a Graphene-like coating from this work (blue line).

The different stages for the copper film growth are labeled in the diagram and they can be easily identified. In contrast to that finding, the growth of the Graphene-containing carbon does not show such a behavior, resulting from island growth. The resistivity exponentially decreases if the thickness increases. The slope of the transmission-resistivity-curve is linear (in logarithmic scale) at all examined layer thicknesses. This indicates that no island growth appears by depositing thin carbon coatings using the current approaches. This finding fits well with the previous described measurements of the

Figure 8.4: a) Sheet resistance vs. thickness of sputtered copper [81] (red line) and Graphene-like coating from this work (blue line). b) Spectral transmittance of Graphene-based carbon (blue line) compared with copper (purple line [82]), gold (green line [82]), and ITO (red line [83])

absorption, the AFM- and STM-pictures, and high resolution Raman mapping. It can be supposed from that investigation that the carbon coatings are fully closed even in the stage of very small thickness.

Furthermore, if the optical transmittance of the carbon coatings (Figure 8.4b), blue line) is plotted and compared with different metals [81] and ITO [83], it can easily be seen that the Graphene-based film provides the best result of the optical transmission measurement. As mentioned above, the absorption is constant in a wide range between 350 nm and 1000 nm. In contrast to that finding, the thin film metals (gold and copper) show different local absorption maxima and minima. Moreover, the widely used ITO also provides an inhomogeneous transmission spectrum even at higher thicknesses of several hundreds of nanometer. It can be concluded that Graphene and Graphene-based materials have the best optical properties of all examined materials. However, with regard to the sheet resistance, the carbon film is still not suitable for a broad application. The sheet resistance ((Figure 8.4b), label) is several orders of magnitude higher than that for ITO with comparable transmission. Hence, according to Figure 8.2, the sheet resistance is currently still too high for applications such as TCO, used in FPD or PV.

9 Summary

For the current work, two processes (PE-CVD and Φ -HCA) for the production of transparent and conductive carbon films have been developed, analyzed and optimized with the aim to deposit such coatings directly on arbitrary substrates. The direct growth on functional substrates can avoid the exfoliation, which can damage the Graphene and leave contaminations such as metals, solvents, and polymers on the carbon material.

In the first part of this work, two vacuum chambers have been constructed, tested, and the plasma discharge of the PE-CVD process has been characterized using emission spectrometry.

Subsequently, in the experimental part, an optimization process has been described with the aim to achieve highly conductive and transparent carbon coatings. For that purpose, the different deposition parameters have been examined and test samples have been produced in both chambers and characterized using AFM, STM, Raman Microscopy, Hall measurements, spectral photometry, ToF-Sims, and TEM. The optimized process parameters arisen from this investigation have been used to prepare samples and to compare the properties with those, published in literature. Subsequently, coatings have been made to check the possibility of any application.

In summary, that the electrical and optical properties of the coatings described in the current work are comparable to those, reported in literature. In contrast, the mobility of the charge carriers is significant lower than reported in literature. That is a result of the multi-crystalline character with only small grains of graphitic carbon. Additionally, with regard to the requirements of several applications, the sheet resistance is still too high except for the application as EMI shielding. Consequently, the sheet resistance has to be decreased at the given transmission to reach a broader field of application. This could be done by doping the Graphene with HNO_3 or $AuCl_3$, as it has been used for the production of OLEDs [17]. Furthermore, the described processes can further be optimized, e. g. by using different buffer gases or functional gases.

However, a first application of the Φ -HCA films has been already realized by S. Feifel et al. by applying organic photo molecules on top of the conductive carbon coating. Subsequently, a significant photo current could be measured. This work will be published soon. Furthermore, the Φ -HCA process was applied for a patent (PCT/EP2013/061684) in 2012 and published in [84]. Further publications are in preparation [85, 86].

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