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Deposition and characterization of doped nanocrystalline diamond films and particles - toward applications in energy converters

by

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Abstract

Nanocrystalline diamond (NCD) thin films were produced by chemical vapor deposition (CVD) and doped by the addition of phosphine to the gas mixture. By carefully adjusting the influential deposition parameters such as C:H-ratio, working pressure, substrate temperature and dopant concentration, the process was optimized. The characterization of the films focused on probing the incorporation and distribution of the phosphorus (P) dopants. Electron microscopy evaluated the overall film morphology and revealed the interior structure of the nanosized grains. The homogeneous films with distinct diamond grains featured a notably low sp²:sp³-ratio as confirmed by Raman spectroscopy. High resolution spectroscopy methods demonstrated a homogeneous P incorporation, both in-depth and in-plane. The maximum obtained P concentration in the films was determined to be in the order of 10^{19} cm⁻³ with a significant fraction integrated at substitutional donor sites. XRD revealed that high doping levels in deposition conditions where the substrate temperature exceeds 800°C suppress the formation of (111)oriented facets. After H-termination, P-NCD obtained a negative electron affinity (NEA) surface. With n-type doping, this leads to a low effective work function, and efficient thermionic electron emission has been measured from all P-NCD films on metal substrates. Thermionic emission currents reached up to 1.4 mA $\rm cm^{-2}$ at 950 K. The emission characteristics vary in function of dopant concentration, film morphology and substrate material. Resistance measurements demonstrated a sheet resistance of approximately 5 G Ω at 500 K which drops to a few tens of $M\Omega$ at 900 K. In the context of the starting activities on thermionic energy conversion, a dedicated UHV system has been set-up for the measurement of thermionic emission properties.

The production of boron-doped diamond nanoparticles enabled the application of this material for a broad range of research fields. Here the production of highly boron-doped diamond nanoparticles using boron-doped CVD diamond films as a starting material is presented. In a multistep milling process followed by purification and surface oxidation, diamond nanoparticles of 10 to 60 nm with a boron content of approximately 2.3×10^{21} cm⁻³ were obtained. The B K-edge electron energy-loss near-edge fine structure demonstrated that the B atoms were tetrahedrally embedded into the diamond lattice. The boron-doped diamond nanoparticles have been used as nucleation seeds for the CVD of a boron-doped diamond film. Further experiments have evaluated the possibility to integrate diamond nanoparticles in thin films from doped Si/Ge-nanoparticles for thermoelectric measurements.

List of abbreviations

Abbreviations

AC	alternating current
ADF	annular dark field
AFM	atomic force microscopy
arb. u.	arbitrary units
ASU	Arizona State University
CF	conflat
CL	cathodoluminescence
CVD	chemical vapor deposition
DC	direct current
DI	deionized
DFT	density functional theory
DLS	dynamic light scattering
DND	detonation nanodiamond
EDX	energy dispersive X-ray
EELS	electron energy loss spectroscopy
ELNES	energy loss near-edge spectroscopy
EMAT	Electron Microscopy for Materials Science- University of Antwerp
FTIR	Fourier transform infrared
FWHM	full width at half maximum
GEMaC	Groupe d'Etude de la Matière Condensée - University of Versailles
HPHT	high pressure, high temperature
IMO	Instituut Voor Materiaalonderzoek (Institute for Materials Research)
IR	infrared
MATCON	Materials and Interfaces for Energy Conversion and Storage
MW PE	microwave plasma enhanced
NEA	negative electron affinity
NCD	nanocrystalline diamond
ND	nanodiamond
ppm	parts per million
PVD	physical vapor deposition
RF	radio frequency
rms	root mean square
rpm	revolutions per minute
sccm	standard cubic centimeters per minute
SEM	scanning electron microscopy
SIMS	secondary ion mass spectroscopy
STEM	scanning transmission electron microscopy

- TEM transmission electron microscopy
- UHV ultra-high vacuum
- UNCD ultrananocrystalline diamond
- UV ultraviolet
- VIS visible
- WD working distance
- WSI Walter Schottky Institute, Technical University of Munich
- XRD X-ray diffraction
- ZT thermoelectric figure of merit

Chemical elements and compounds

Al	aluminum
Al ₂ O ₃	alumina
Ar	argon
Au	gold
В	boron
BN	boron nitride
CH_4	methane
Ċs	cesium
Cu	copper
FS	fused silica
H ₂	hydrogen
HĈI	hydrochloric acid
H ₂ O	water
H ₂ O ₂	hydrogen peroxide
H ₂ SÕ₄	sulphuric acid
IP	iso-propanol
Мо	molybdenum
N ₂	nitrogen
Ňĥ₄OH	ammonium hydroxide
0,	oxygen
Ρ	phosphorus
PEI	polyethyleneimine
PH_3	phosphine
Pt	platinum
Re	rhenium
Si	silicon
TMAH	tetramethylammonium hydroxide
ТМВ	trimethylborane
TMP	trimethylphosphate
Ti	titanium
W	tungsten

Symbols and constants

A _R	Richardson constant
с	speed of light in vacuum, $c_0 = 299792458 \text{ m s}^{-1}$
d	interaction cross section
Ε	energy (eV)
E _C	energy of conduction band edge
E _F	Fermi energy
E _G	bandgap
Ev	energy of valence band edge
е	elementary charge, $e = 1.6022 \times 10^{-19} \text{ C}$
f	function
ħ	reduced Planck constant, $\hbar = 6.582 \times 10^{-16}$ eV s
Ι	current (A)
I_E	emitter current (A)
j	current density (A m ⁻²)
Κ	shape factor (\approx 1)
kв	Boltzmann constant, $k_B = 1.380658 \times 10^{-23}$ J K ⁻¹
ĸ	wave vector in momentum space
т	integer
m _e	electron mass, $m_{\rm e} = 9.109 \times 10^{-31}$ kg
<i>m</i> *	effective mass
n	index of refraction (real part); charge carrier density (m^{-3})
Ρ	power (W)
P _{EL,TL}	electrical or thermal losses (W)
р	pressure (Pa)
Ra	surface roughness (nm)
S	Seebeck coefficient (V K $^{-1}$)
Т	temperature (K, °C)
t _f	film thickness (m)
V	voltage (V)
V _{th}	thermovoltage (V)
ν	velocity (m s ⁻¹)
β	line broadening
Δ	mean size of grains (nm)
η	efficiency
θ_B	Bragg angle (°)
θ_i	angle of incidence (°)
κ	thermal conductivity (W m ^{-1} K ^{-1})
λ	wavelength (nm), mean free path (m)
μ	chemical potential
σ	electrical conductivity ($\Omega^{-1} m^{-1}$)
ϕ_C	collector work function (eV)
ϕ_E	emitter work function (eV)
ϕ_{vac}	electrostatic vacuum potential (V)
χ	electron affinity (eV)
ΧΕΝ	electronegativity

1 Preface

'The content of physics is the concern of physicists, its effect the concern of all men.'

Friedrich Dürrenmatt

The decline of fossil fuels has led to an increasing awareness of the need to find alternative energy supplies. As energy is critical to human development, the growing world population and the economic expansion will continue resulting in high demands of energy everywhere in the world. In order to prevent the negative impact on the climate change, research efforts focus on renewable alternatives and at the same time reducing the emission of greenhouse gasses, above all carbon dioxide. The most prominent, commercialized and competitive renewable energy technologies are wind and hydro power, solar and geothermal energy or biomass. However, there is a great number of emerging technologies such as artificial photosynthesis, biofuel cells, thermoelectric and thermionic conversion currently subject of intensive research that could find their way into dedicated applications in the future. The EU Seventh Framework Programme project 'Materials and Interfaces for Energy Conversion and Storage' ('MATCON') addressed fundamental research aspects of materials and interface for energy conversion as in storage. The project 'MATCON' concentrated on (I) the photo-electrochemical generation of H (II) the bio-inspired and bio mimetic as well as (III) thermoelectric and thermionic energy conversion involving primarily different forms of diamond. Besides the thorough study of the underlying physics and chemistry of the different conversion mechanisms, significant effort was put on the exploration and engineering of suitable materials for electrodes, substrates and interfaces. Within the consortium, IMO was in charge of the growth and doping of CVD diamond films and the activities in the scope of thermionics and thermoelectrics.

This thesis focuses on the deposition and characterization of P-doped nanocrystalline diamond which has been proven to be a promising material for thermionics. The main objective was to study n-type doped diamond films and to address electron emission properties of doped diamond surfaces in order to obtain maximum thermionic emission currents. Moreover, B-doped diamond nanoparticles in respect to potential applications in thermoelectrics, diamond CVD or fundamental characterization were fabricated and investigated.

After a general introduction to diamond as functional material in chapter 1, chapter 2 reviews the different possibilities to dope diamond. The focus lies on doping of polycrystalline diamond. The basic concepts of thermionic and thermoelectric energy conversion are presented in chapter 3. Chapter 4 outlines the experimental methods that were used throughout the studies. In chapter 5, the new set-up at IMO for thermionic emission experiments is detailed. Chapter 6 contains the main results of the growth and characterization of P-NCD. A number of spectroscopic techniques allowed to identify and quantify phosphorus dopants in the NCD films. The fabrication of the novel B-doped nanoparticles is explained in chapter 7. The thesis closes with the final conclusions and an outlook in chapter 8.

2 Diamond - a versatile material

'A diamond is a chunk of coal that is made under good pressure.'

Henry Kissinger

2.1 General properties

Diamond is an allotrope of carbon whose crystal structure is a face-centered cubic (fcc) bravais lattice with a two-atomic basis (Fig. 2.1). The atoms of the basis are located at (0,0,0) and (1/4, 1/4, 1/4). In consequence, there are eight atoms per unit cell which features a length of 3.57 Å. In the crystal lattice, each carbon atom is arranged symmetrically to four neighbors forming a tetrahedron. By virtue of symmetry the covalent, interatomic bonds are extended to 1.54 Å. The main crystallographic planes in diamond due to its cubic lattice are (100), (110) and (111). The four atomic orbitals orientate themselves towards each other to minimize electrostatic repulsion. These bonds, fully sp^3 -hybridized, inhere in a very high binding energy. As a result, diamond features a compact lattice with 1.76×10^{23} atoms cm⁻³ which makes it the hardest mineral found in nature. Its atomic density in the single crystalline state is 3.51 g cm⁻³. Dangling bonds at crystal surfaces are usually saturated by oxygen (O) or hydrogen (H). Bulk diamond is chemically and radiation inert, as well as bio-compatible. Carbon-based chemistry offers a large range of possible reactions for surface functionalization. Numerous molecules form stable covalent bonds with diamonds and make diamond an attractive chemical platform. Upon the incorporation of specific impurities (Ch. 3), diamond becomes electrically conductive and can reach metallic and even superconducting properties. Its semiconductor state is characterized by an indirect band gap of 5.47 eV and by high charge carrier mobilities for electrons $(2200 \text{ cm}^2 (\text{Vs})^{-1})$ and holes $(1800 \text{ cm}^2 (\text{Vs})^{-1})$ in single crystals [1, 2]. Furthermore, diamond features a high acoustic velocity as well as a thermal conductivity of 22 W (cm K)⁻¹ which is five times higher than that of Cu [3]. Diamond has an optical transparency greater than 60% for all wavelengths between 220 nm and 80 μ m and the highest value of Young's modulus (1000 to 1100 GPa).



Figure 2.1: Unit cell of the crystalline diamond lattice. Each carbon atom has a tetrahedral bond structure to four neighboring atoms.

As a result of those mentioned superior properties, diamond is today commercially used in cutting tools, abrasives or as heat sink, electrodes and has from the physics perspective the potential for electronic applications.

2.2 Monocrystals and polycrystals

Different sub-groups classify diamond in respect to its number of defects, crystallinity, grain size and sp²:sp³-carbon ratio. Single crystalline diamond exists in a variety of grades that principally refer to its nitrogen impurity level (Fig. 2.2(a) A). With the aim to obtain single crystals in wafer size, highly oriented epitaxial diamond layers, as depicted in Fig. 2.2(a) B, can be grown on foreign substrates only with the help of multilayer interlayers, that feature a similar crystalline lattice parameter and allow diamond nucleation [4]. When diamond is deposited on non-diamond substrates, one typically obtains polycrystalline films (Fig. 2.2(a) C-D). Many, by itself single crystalline grains of different orientations coalesce and form a closed film of diamond on the selected substrate material. The simplified scheme in Fig. 2.2(b) outlines the columnar growth that is typical for diamond polycrystals. The interfaces between the individual grains, the grain boundaries, are constituted of sp²-hybridized carbon. Grain boundaries considerably contribute to the characteristics of diamond thin films and impact on the interaction of electrons, photons and phonons. Moreover, they are known to incorporate hydrogen as well as dopants [5]. In respect to the grain size, three sub-groups of polycrystalline diamond are distinguished, (1) microcrystalline diamond (MCD), (2) nanocrystalline diamond (NCD) featuring grains up to several hundreds of nm and (3) ultrananocrystalline diamond (UNCD) with crystallites of a few tens of nm.



Figure 2.2: (a) Different kinds of diamond that were studied for this thesis. A: CVD single crystal, B: as-grown heteroepitaxial single crystal from Universität Augsburg, C: free-standing (14 μ m) microcrystalline diamond film, D₁: P-NCD on Si, D₂: P-NCD on FS. (b) Simplified growth scheme of polycrystalline diamond.

2.2.1 Microcrystalline diamond

MCD is polycrystalline diamond with grains of several μ m. The growth evolves from seed crystallites and proceeds along the fastest growing crystalline orientation which results in columnar grains. As a result, MCD is typically a few micrometer thick and mechanically stable to exist as free-standing films (Fig. 2.2 C). Preferential grain orientation can be achieved by the careful selection of deposition parameters.

2.2.2 Nanocrystalline diamond

NCD thin films of a few tens to hundreds of nanometers thickness are a driver for fundamental as well as application-oriented investigations exploiting the extreme properties of this material. The advantage of NCD is the possibility to cover large areas, however, the granular nature of NCD leads to properties based on the interplay between grains and grain boundaries [6–8]. In doped films, grain boundaries provide a competing pathway for the incorporation of dopant atoms and thus questions have arisen on the efficiency of the in situ doping process in nanocrystalline material. The choice of the deposition parameters such as gas composition and temperature controls the morphology, $sp^2:sp^3$ -ratio within the film and grain size. In order to initiate controlled diamond growth on a non-diamond substrate, nucleation seeds have to be provided. Mechanical abrasion, bias enhanced nucleation or nanoparticle seeding (Ch. 5.1.2) are methods to spread seed crystallites on the substrate surface. Elevated C:H-concentrations in the plasma affect the ratio of sp²:sp³-carbon in the film as well the deposition rate [9]. The grain size of NCD is thus primarily defined by the deposition time and carbon concentration. The higher the seeding density, the sooner the individual grains coalesce to form a continuous layer. With today's seeding densities of 10^{11} particles cm⁻², closed NCD films of less than 100 nm thickness can be grown [10].



Figure 2.3: Carbon phase diagram which indicates the regions of stability for diamond and graphite (after [12].)

2.2.3 Ultrananocrystalline diamond

UNCD refers to the smallest grain size diamond films. Adding Ar to the growth plasma, using C:H-concentrations above 10% or applying a continuous dc bias voltage during CVD induce this growth mechanism of continuous renucleation. Nanometric grains of around 10 nm develop in an abundant non-structured carbon matrix. For UNCD, the grain size does not increase but is uniform throughout the film thickness which results in microscopically smooth surfaces.

2.3 Diamond synthesis

Since the 1950s, diamond can be synthesized artificially [11]. The carbon phase diagram (Fig. 2.3) depicts the necessary conditions to obtain diamond with the different methods. The most prominent techniques are (1) the detonation synthesis which is primarily used for the production of diamond nanoparticles. (2) The high pressure, high temperature method (HPHT) reproduces the conditions under which natural diamond is created from sp^2 -carbon. Most of the industrial diamond is produced in large HPHT presses. (3) A small window for temperatures and pressures less than 1500 K and 1 GPa allows to prepare diamond by CVD. The conditions are close to the stability region of graphite, the thermodynamically stable carbon phase. The challenge in diamond CVD consists in suppressing the deposition of sp^2 -carbon besides the formation of stable sp^3 -bonds.



Figure 2.4: Microwave enhanced CVD plasma in the ASTeX PDS17 reactor. The feed gasses H_2 and CH_4 are dissociated into atomic hydrogen and reactive hydrocarbons.

2.3.1 Chemical vapor deposition

Eversole was the first to synthesize diamond from a carbon-containing gas mixture in the CVD regime at 900°C and 10000 Pa (100 mbar) [13]. The breakthrough of CVD diamond occurred in the 1970s when hydrogen was discovered to etch graphitic carbon that deposits simultaneously with sp³-carbon. Further technological advances were reported by Japanese research groups which optimized CVD diamond growth [14, 15]. In the following years, several CVD techniques using hot filaments, MW or RF plasma or even combustion flames developed to activate the gas phase. The principle of all techniques is identical and based upon a gas discharge that typically contains a few percent of carbon, e.g. CH_4 , in H_2 , optionally with additional O_2 or Ar. Today, the most common deposition technique is microwave plasma enhanced CVD (MW PE CVD) where the growth plasma is maintained by injected microwaves (Fig. 2.4). It offers several technological assets, such as low contamination and a good control of a dense plasma. Typical CVD plasmas contain C:H concentrations less than 10 %. The exact C-concentration is chosen in respect to the desired film charactistics. The gas discharge from H_2 and CH₄ is confined in a cloud that is tangent to the substrate holder.

Butler *et al.* investigated the growth chemistry and developed the today's standard model of diamond CVD in which atomic H and the methyl radical (CH_3) were identified as essential building blocks [16, 17]. The injected energy dissociates the molecular hydrogen feed gas into atomic H which is the main driver in the plasma chemistry:

$$H_2 + e^- \rightleftharpoons 2H + e^-$$
.

Further, hydrogen atoms induce the scission of methane molecules into reactive hydrocarbons:

$$CH_y + H \rightleftharpoons CH_{y-1} + H_2; \quad 1 \le y \le 4.$$

The hydrocarbons CH_y can recombine to acetylene C_2H_x which itself can undergo

the H-abstraction reactions. CH_4 , C_2H_2 and C_2H_6 have been detected as stable hydrocarbons in the plasma, besides previously mentioned CH₃-radical. The CVD process has not shown to be prone to the type of C-containing source gas but to the C to H ratio in the gas phase [18]. Hence, higher concentrations of acetylenemolecules require higher H concentrations, to induce the abstraction reactions. The longer hydrocarbons are dominant in the cool plasma regions where fewer Hatoms are available for the scission of C_2 -molecules. So, they do not participate directly in the growth process at the plasma-substrate interface. All reagents can exist in excited as well as neutral charge states which shows the complexity of the process. A diamond surface is typically passivated with H and stable at normal conditions. In the plasma, atomic H also abstracts the initial H passivation creating radical sites at the sample surface. C-radicals from the gas phase will adsorb to the active sites at the surface. After further H-abstractions and CH-bond rearrangements, a C-dimer bridge can form. This reactions eventually incorporates the new C-atom in the crystal. Surface migration of adsorbed molecules is not predominant as deposition temperatures above 700°C rather lead to desorption. Moreover, migration requires an adjacent active site that is easier to be occupied with a free radical from the gas phase than by a covalently bonded molecule. Plasma statistics illustrate that only very few reactions are successful radical adsorptions. Many reactions are simply H-adsorption and desorption processes that do not involve any C-containing molecule. Spectroscopic measurements have revealed the number of possible reactions in the plasma.

3 Doping of diamond

'Better a diamond with a flaw than a pebble without.'

Chinese proverb

Intrinsic diamond is a dielectric material. However, when defined impurities are incorporated into the crystalline lattice, diamond can become a semiconductor. Its band gap at room temperature is 5.45 eV, therefore diamond belongs to the group of wide band gap semiconductors, such as SiC, BN, AIN or GaN. Those materials are candidates to be used in high-power electronics or light-emitting devices in the UV range. Besides the need of diamond substrates in sufficient size and quality, suitable dopants for p-type as well as n-type conductivity have to be investigated. The typical technique to incorporate dopants in diamond is during the CVD process. Top-down methods, such as implantation are not suitable, as the crystalline lattice undergoes serious degradation. The high physical impact of the ion bombardment damages the sp³-bonds that, in contrast to other semiconductors, cannot be healed by annealing. High temperature treatments rather lead graphitization which presents an additional detrimental effect on the crystal lattice.

3.1 p-type doping

3.1.1 Boron doping

Boron has been shown to be a shallow p-type dopant that incorporates readily at substitutional lattice positions in diamond. As group-III element, boron acts as an acceptor for electrons that originate from the valence band. Few natural diamonds contain boron impurities, the most famous ones being the 'Wittelsbacher' and 'Hope' diamond which impress by their blue color [19]. Highly doped CVD diamonds, typically doped by diborane (B_2H_6) or trimethylborane (TMB, B(OCH₃)₃), also feature an intense blue color. The doping of single crystals with different crystalline orientation has been studied during many years. Typically, the boron incorporation in (111)-oriented surfaces is higher than in (100)-substrates whereas the (100)-orientation is preferred due to a better surface morphology control. Lagrange *et al.* investigated the conductivity behavior of B-doped homoepitaxial layers at different temperatures and reported an acceptor activation energy of 0.368 eV [20]. Ambient conditions are sufficient to thermally activate the carriers. For good electrical conductivity at room temperature boron concentrations in the range of 10^{19} cm⁻³ are required. The possible doping levels range between 10^{14} B cm⁻³ to 10^{21} B cm⁻³. The critical boron concentration to exceed the metal-insulator transition threshold lies around 10^{20} B cm⁻³ when the boron impurity band overlaps with the valence band and therefore induces metallic characteristics in terms of electrical conductivity [21]. Since a number of years, also polycrystalline thin films have been successfully doped with boron [7, 22]. This breakthrough has boosted many research fields as large doped films can be deposited. Besides the evident relevance for electronic devices and hard coatings, boron-doped thin films, nanocrystalline thin films in particular [23], are widely used as conductive, functional substrates. Thorough optical [24] and electrical studies [25, 26] have presented the characteristics of B-doped NCD. Boron incorporation both in the nanoscale grains and the grain boundaries has been evidenced by atomic resolution TEM spectroscopy [27]. Surface scientists appreciate the widest known electrochemical potential window of B-NCD which makes it an ideal material for electrochemical electrodes [28–30] and a stable platform for carbon chemistry [31–33]. In order to maximize the load with selected molecules for functionalization and charge transfer investigations, a high surface-to-volume ratio is required. Nanostructuring of thin films or the use of nanoparticles are the most common strategies to enhance the surface area [34, 35].

3.2 n-type doping

While p-type doping of NCD with boron is well-studied and widely used, n-type doping of diamond in general remains challenging. One present and still significant issue is to dope diamond efficiently with shallow donors.

3.2.1 Nitrogen doping

The most common impurity in diamond and so far the only known natural n-type impurity is nitrogen (N). The lattice distortion resulting from substitutional N is relatively weak, as the covalent radii of N (r(N) = 75 pm) and C (r(C) = 77 pm) atoms only differ by 2.6%. N-incorporation has been reported on all types of diamond from single crystals to ultrananocrystalline (UNCD) thin films where it sits predominantly in the abundant grain boundaries. N is physically considered a donor, however its ionization energy at a substitutional position is 1.7 eV [36]. For semiconductor applications this is far too deep to be of significant interest as the N-dopants are not electrically active at room temperature. Yet, N-incorporation in diamond is widely studied. The luminescence characteristics of the so-called nitrogen-vacancy colour center (NV-center) in single crystalline diamond and particles has been subject of extensive research in the field of electron spin related phenomena, such as spintronics and quantum optics [37, 38]. With respect to deposit diamond coatings at lower cost, N-doped UNCD and novel hybrid materials

have been investigated [39, 40]. Finally, N-doped NCD has been proven to be an efficient electron emitter and could be reconsidered for co-doping studies [41].

3.2.2 Phosphorus doping

Phosphorus (P) is a popular and certainly the most-studied candidate for n-type doping. As group-V element it provides an additional electron in the diamond lattice which contributes to the electrical conductivity. However, due a difference of 43% between the covalent bond lengths of P (r(N) = 110 pm) and carbon, the lattice is highly strained upon incorporation. First calculations predicted trigonal bonding symmetry for a P-atom at a substitutional site, later tetragonal incorporation was confirmed [42]. In any case, the distorted site symmetry certainly impacts on the donor activation energy. P-doping can be realized with different source gases, *e.g.* the organophosphorus substances, tertiarybutylphosphine (TBP, P(C₄H₉)H₂) and trimethylphosphine (TMP, P(CH₃)₃) or phosphine (PH₃). The decomposition temperature of all source gases is inferior to the gas temperature during the deposition. So, there is almost no dependence of the precursor on the P-containing radicals available for incorporation [43]. Despite its high toxicity, PH₃ is preferred for the deposition of high quality films due to its purity.

First successful P-doping of diamond was reported in 1997. Using PH_3 as doping source, Koizumi et al. achieved the incorporation in a CVD film deposited on a (111)-oriented HPHT substrate [44]. Compared to the typical growth conditions for undoped layers, the optimum conditions for successful P-incorporation are CH_4 concentrations of less than 0.15% and deposition temperatures around 950 °C. N-type conductivity was proven by Hall measurements and initially an activation energy of 0.43 eV was deduced [44]. At even lower C-concentrations (0.05% C:H), substrate temperatures between 850 and 930 °C and using liquid TMP as precursor, the group at GEMaC obtained (111)-oriented films of similar characteristics [45]. Electrically active P-donors were identified by Hall measurements and CL [46]. To date, the incorporation in (100)-oriented surfaces still remains challenging. In a P-containing plasma, (100)-substrates often develop hillocks and unepitaxial crystallites whereas (111)-surfaces grow in a step-flow way which results in smooth surfaces. Typically the experimental conditions for (100) deposition differ considerably from depositions on (111)-surfaces. Layers of (100)-orientation are deposited both in higher C:H ratios and P:C concentrations. As the incorporation efficiency into (100)-surfaces is only about 0.02% and hence two orders of magnitude smaller than for (111)-facets, P:C ratios up to 10% are used during deposition. In order to overcome the issue of non-epitaxial growth, often substrates with a defined off-angle (2° to 10°) towards the exact (100)-plane are used [47]. In combination with C:H-ratios up to 3%, preferential P-incorporation along [110]aligned steps was observed [48]. Kato et al. were the first to achieve n-type conductivity on (100)-oriented substrates [49, 50]. The films were grown between 850°C and 950°C in C-concentrations up to 1% C:H with high concentrations of PH₃ as doping precursor. SIMS proved and quantified the P-incorporation at a level

greater than 10^{18} atoms cm⁻³. Hall measurements evidenced n-type conductivity, and allowed to deduce the room temperature carrier mobility which was about $350 \text{ cm}^2(\text{Vs})^{-1}$.

Spectroscopic techniques, such as FTIR and CL, have specified activation energy more accurately [51, 52]. Nowadays, the P-donor ionization energy in diamond is experimentally determined and confirmed to be 0.56 eV [53]. Controlled moderate P-doping on (111)-substrates led to doping levels as low as 10^{16} atoms cm⁻³, the highest doping levels were 2×10^{20} atoms cm⁻³. For (100)-substrates doping levels between 5×10^{16} atoms cm⁻³ and 2×10^{19} atoms cm⁻³ were reported. The highest reported Hall mobility values at room temperature were 660 cm² (Vs)⁻¹ for (111)-orientation and 570 cm² (Vs)⁻¹ for films grown on (100)-oriented substrates [47, 49, 54].

Electrical conduction is suggested to be deteriorated by the simultaneous incorporation of H [55]. H is believed to passivate the P-atoms leading to a reduced electron conduction. In order to obtain efficient conductors, H-incorporation should be minimized. Deposition at elevated temperatures is favorable to dissociate possible P-H bonds at the surface potentially improving the issue.

At room temperature the donor ionization energy is still very high for a significant free carrier concentration, hence conductivity. Therefore P-doped films feature a sheet resistance of several hundreds of M Ω . The highest P-concentration reported is 10^{20} atoms cm⁻³ [49, 56], so far no metal-insulator transition has been reported on n-type diamond.

P-doping of polycrystalline diamond - Status quo

The advantage of micro- or nanocrystalline diamond is the possibility to cover large areas. The granular nature of polycrystalline films leads to properties based on the interplay between grains and grain boundaries [6–8]. Therefore, polycrystalline P-doped diamond is unlikely to become ever a performing material for electronic devices. Due to grain boundaries and a large number of crystalline defects, the electron mobility will always be extremely low. In the case of B-doping, the B-NCD hole mobility of $\leq 0.77 \text{ cm}^2(\text{Vs})^{-1}$ is in stark contrast to 1800 cm²(Vs)⁻¹ reported for single crystals [26]. However, the benefit of large surfaces, satisfactory film quality and dopant incorporation make it suitable for applications as detectors or electron emitters. The interest in P-doped NCD (P-NCD) emerged, after N-doped NCD with H surface termination was proven to be a promising material for thermionic energy conversion applications [41]. The lower activation energy of P in comparison to the deep N donor level makes P-NCD an attractive alternative. Elaborate engineering of the surface properties is certainly going to optimize the materials towards efficient electron emission.

One of the first strategies to deposit P-doped polycrystalline diamond was to overgrow a free-standing and polished substrate of undoped polycrystalline diamond with predominantly (111)- and (110)-facets [57, 58]. The epitaxial growth on each of the facets resulted in a film with differently oriented grains. Later, research focused on the overgrowth of primarily (110)-textured polished undoped polycrystalline templates [59]. Raman and CL spectroscopy revealed considerable doping inhomogeneities between the different grains [60]. The P-doped layer featured tensile strain along the grain boundaries and relative to the undoped substrate. Moreover, increasing strain upon high P incorporation was correlated to structural degradation.

Not many reports of P-doped polycrystalline films on foreign substrates have been published so far. The early work of Schauer et al. presents P-incorporation in microcrystalline films on Si of several μ m thickness that were grown in dc and MW PE CVD plasmas [61]. (P:C)_{gas}-concentrations less than 2000 ppm were used which resulted in a doping level of 7.0×10^{18} atoms cm⁻³. Their observations of ten times higher P-contents in polycrystalline films compared to homoepitaxial films give reason to the assumption that most of the dopants incorporate in grain boundaries. All samples showed linear I-V characteristics and conductivities of approximately 2.0 \times 10⁻⁹ (Ω cm)⁻¹ were deduced. The impact on growth rate, morphology, film quality and grain orientation of microcrystalline diamond upon P addition was investigated by Bohr et al. [62]. Ghodbane et al. investigated the CVD of microcrystalline n-type P-doped diamond on Si substrates. Nucleation sites were induced by mechanical scratching; the films deposited in low CH₄ concentration (0.15%) in a plasma with 1000 ppm (P:C)gas. SIMS and CL confirmed the presence of active P-dopants at a level of 7.0×10^{17} atoms cm⁻³ in the grains of 1 to 6 μ m sized grains [63]. Without any further morphological characterization of the emitter material, P-doped NCD was successfully used as anode for thermionic emission experiments [64].

Other dopants

In search of shallow donors for the fabrication of electronic devices, theoretical calculations have considered Li, Na, K, Al, S, As or Sb as dopants. Figure 3.1 depicts the position of the donor level relative to the conduction band minimum. Many of these alternative doping candidates lack gaseous precursors, so for experimental routes new methodes would have to be established. Ab-initio calculations for the alkali metals have shown that the incorporation at different sites leads to different activation energies [65]. Li and Na atoms are small in size, so they preferably occupy interstitial sites in the compact diamond lattice. Li has been under discussion and subject of calculations with promising results both as a possible dopant as well as surface termination [66]. Surface-bound Li induces an electric dipole resulting in a negative electron affinity ideal for electron emission applications. Simultaneous N and Li-incorporation up to 10¹⁹ cm⁻³ was recently shown experimentally in single and polycrystalline diamond [67]. A suspension from solid Li_3N was used as precursor and drop-cast prior to growth. In order to prevent earlier published issues of electrically inactive sites and the diffusion of Li in the lattice, N is expected to stabilize Li dopants and to improve charge transport. Yet, despite the demonstration of Li-N-incorporation, the macroscopic conductivity in the film remained low.

Sulphur was considered early to be a possible donor. In its ionized state calculations predicted a position at around 0.5 eV below the diamond conduction band minimum [68]. Other research groups computed similar levels, however the results of the different calculations have always been controversial. Sulphur incorporation was evidenced experimentally [69], however electrical activity originating from the S-dopants has never been proven. Kalish *et al.* raised the doubt on the donor activity of S and attributed the conductivity in S-doped samples to B-contamination [70].

Kasu *et al.* reported n-type doping of CVD-grown homoepitaxial layers with arsenic [71]. SIMS quantified the As-doping level to be in the range of 10^{19} cm⁻³. Both Hall measurements and the I-V characteristics of a pn-junctions revealed n-type conductivity of the incorporated donors. DFT calculations had predicted an carrier activation energy of 0.4 eV [72]. The experimentally deduced values range between 0.8 eV and 1.6 eV depending on the doping concentrations.

For a short-period, boron-deuterium complexes were thought to result in n-type conductivity. In 2003, Teukam *et al.* discovered shallow donor states in B-doped diamond after deuterium plasma treating the single crystals for several hours [73]. Ab-initio calculations of Kumar *et al.* suggested the BH—2-complex to be a donor with an activation energy of 245 meV. Eventually, the controversial results were explained by inhomogeneities in the doping distribution across the sample that identify the wrong majority carriers using transport measurements [74].



Figure 3.1: Overview of the activation energies of different suggested dopants in diamond. Reproducible doping has been experimentally confirmed for B, P, and N. Li and As are currently under investigation. The measured ionizations energies of Li and As differ from the suggested *ab-initio* calculations.

4 Thermionic electron emission and thermoelectrics

4.1 Thermionic electron emission

Thermionic emission implies the heat-induced emission of charge carriers over a surface-potential barrier typically into a vacuum space. In practice, a device consists of a hot side with the thermionic electron emitter separated from the collector electrode by a vacuum gap (Fig. 4.1). Thermal electrons originating the hot electrode cross the gap and are captured by the cold collector.

Today's research focuses on increasing the power output of the devices by engineering materials with low work functions. Moreover, new strategies to optimize the charge transfer from the emitter towards the collector are considered. Recently, photo-induced emission processes that have been reported to enhance pure thermionic emission are also under intense investigation [75, 76]. Challenges such as the relevance and stability of the negative electron affinity (NEA) (Ch. 4.1.1) or space charging (Ch. 4.1.2) are current fields of research.

The emission of charges from heated metals was discovered in the late 19th century. Edison found that hot metal filaments emit negative charges. His findings led to the most known application of thermionic emission - the incandescent lamp. That the emitted electrical charges are carried by particles could only be understood after Thompson's discovery of the electron in 1897. In 1928, Richardson's contribution in respect to the thermionic phenomenon and the corresponding law that he deduced was granted the Nobel Prize in Physics. He demonstrated that the emission current j relates exponentially to the work function of the material ϕ and the temperature T. The interest in thermionic emission was pushed by the achievements in semiconductor technology and material engineering when doped materials appeared and emission at significantly reduced temperatures was measured. N- and P-doped NCD films on Mo substrates have been proven to be good emitters [41, 64]. In the particular case of diamond thermionics, a negative electron affinity induced by H surface termination results in a low potential barrier for emission. With today's knowledge of solid state physics and quantum theory of electrons, the current *j* can be readily derived from Fermi-Dirac statistics [77]. Prior to emission, the system of electrons with a particular energy state inside a material in thermodynamical equilibrium is described by the Fermi-Dirac distribution,



Figure 4.1: Scheme of an thermionic emission converter. Electrons are thermally emitted from a hot cathode and cross the vacuum gap before they are captured by the collector.

$$f(k) = \frac{1}{\exp(\frac{E(k)-\mu}{k_BT}) + 1}.$$
 (4.1)

where *E* is the energy, μ refers to the chemical potential which in a semiconductor at the given conditions is approximated by the Fermi energy E_F, *k* stands for the momentum, k_B is the Boltzmann constant and *T* describes the absolute temperature. The energy for a free electron in the vacuum space is given by:

$$E(k) = \frac{\hbar^2 k^2}{2m_e} - e\phi_{\rm vac}.$$
 (4.2)

This equation is derived from quantum mechanical considerations with \hbar being the reduced Planck constant and m_e the electron mass. The additional constant $e\phi_{vac}$ originates from the vacuum electrostatic potential near the material surface which results from the calculations for electrons in a finite periodic potential [77]. In solid state physics the work function ϕ is defined as the work that is necessary to remove an electron from the solid to a point in the surrounding vacuum, hence

$$\phi = (-e)\phi_{\text{vac}} - E_F. \tag{4.3}$$

In a semiconductor, the charge carriers are statistically situated at E_F . The work function ϕ is dependent from the crystal face, surface termination, potential contamination or the doping level. For the case of an electron outside the emitter surface, taking into account the energy of a free particle and the definition of ϕ , equation (4.1) becomes:

$$f(k) = \frac{1}{\exp\left(\frac{\frac{\hbar^2 k^2}{2m_e} + \phi}{k_B T}\right) + 1}.$$
 (4.4)

Assuming a typical work function in the order of a few eV, equation (4.4) simplifies

$$f(k) = \exp\left(-\frac{\frac{\hbar^2 k^2}{2m_e} + \phi}{k_B T}\right).$$
(4.5)

The emission current j is the sum of all electrons with a net movement away from a solid along the surface normal (cf. Fig. 4.1). Assuming the current to flow into positive x-direction, one obtains:

$$j = (-e)nv_{\chi}. \tag{4.6}$$

The integration over the reduced k-space leads to

$$j = (-e) \int_{\substack{k_x > 0 \\ k_x > 0}} v_x f(\vec{k}) \frac{d^3 k}{4\pi^3} = (-e) \exp\left(-\frac{\phi}{k_B T}\right) \int_{\substack{k_x > 0 \\ k_x > 0}} \frac{\hbar k_x}{m_e} \exp\left(-\frac{\hbar^2 k^2}{2m_e k_B T}\right) \frac{d^3 k}{4\pi^3} = -\frac{em_e k_B^2}{2\pi^2 \hbar^3} T^2 \exp\left(-\frac{\phi}{k_B T}\right) = A_R T^2 \exp\left(-\frac{\phi}{k_B T}\right).$$
(4.7)

The factor $A_R = 1.20 \times 10^6$ A (mK)⁻² is the Richardson constant. The Richardson-Dushman equation eq. (4.7), allows to deduce the work function and Richardson coefficient A_R from experimental data by exponential fitting. At the same time it evidences that enhanced emission currents require materials with a low work function and a high A_R . From many studies it has become clear that the exponential dependence of the work function from the current fits very well, however A_R often varies significantly between materials and experiments. Several adaptations have been suggested to theoretically comprehend the discrepancy. Different correction factors try to account for material properties such as band structure and morphology as well as the possible electron reflection from the surface as a consequence of the wave properties of electrons [78]. Yet, a full universal term has not been derived.

For maximum power output, the work function needs to be minimal and at the same time a maximum potential drop between emitter and collector electrode is required. The potential drop V across the gap marked in Fig. 4.1 refers to the work functions difference ($\phi_E - \phi_C$) plus the applied bias voltage and a possible potential

induced by the temperature difference. Neglecting the applied bias, one obtains for the device power output:

$$P = I \times V = I_E \left(\phi_E - \phi_C\right) = A_R T_E^2 e^{-\frac{\phi_E}{\kappa_B T}} \left(\phi_E - \phi_C\right)$$
(4.8)

Moreover, it is assumed that no significant current is originating from the collector. A minimum collector work function ϕ_C will significantly boost the power output. In order to maximize equation (4.8), $\frac{\partial P}{\partial \phi_E} = 0$, *i.e.*

$$\frac{\partial P}{\partial \phi_E} = A_R T_E^2 \exp\left(-\frac{\phi_E}{k_B T}\right) \left(1 - \frac{1}{k_B T} \left(\phi_E - \phi_C\right)\right). \tag{4.9}$$

One finds the optimum emitter work function to be $\phi_E = k_BT + \phi_C$. The efficiency of a thermionic converter depends on electrical (EL) and thermal losses (TL), *i.e.* dissipated heat, radiation loss from the electrons or losses from electron activation over the surface barrier. Tanner *et al.* derived a term to quantify the device performance η by taking into account all occurring power losses, however not considering space charging:

$$\eta = \frac{I_C \left(\phi_E - \phi_C\right) - P_{\mathsf{EL}}}{I_C \phi_E + P_{\mathsf{TL}}} \tag{4.10}$$

More detailed studies, assuming the thermal losses to be dominant, evidence that it is not possible to have optimised power output and a peak efficiency at the same time. Therefore, future thermionic experiments will have to find the best compromise and certainly further efficiency considerations are needed [79].

4.1.1 Negative electron affinity

A key parameter for thermionic emission is the potential barrier that the electrons have to overcome with the up-take of thermal energy. The height of this barrier defines the activation energy that is necessary to emit electrons from the surface. In solid state physics, the electron affinity χ is defined as the energy difference between the conduction band minimum $E_{\rm C}$ close to the surface and the vacuum level $E_{\rm vac}$.

$$\chi = E_{\text{vac}} - E_{\text{C}}$$

$$= \phi + (E_{\text{F}} - E_{\text{V}}) - E_{\text{G}}$$
(4.11)

The absolute measure of the electron affinity χ is not straightforward to determine. It is typically derived from the values of the work function ϕ and $(E_F - E_V)$ (cf. eq. 4.11). In the case of diamond, the surface termination tunes the energy



Figure 4.2: Simplified energy band diagram for a H-terminated P-doped diamond surface.

bands and hence the surface potential barrier. Energy band bending occurs when the energy level defined by the doping in the bulk and the states at the reconstructed surface do not coincide. The internal electric field in the material due to the alignment of the Fermi level reorganizes the charge distribution which results in the band bending. An O-terminated diamond surface features a positive electron affinity [80]. The upward bended energy bands increase the effective surface barrier for electrons in the crystal. H-terminated undoped diamond has been proven to feature a true NEA which is stable up to 800°C in UHV [66]. The H-passivation of the surface results in an approximately 0.1 nm wide layer of polar CH-bonds [81]. As a result of the higher carbon electronegativity ($\chi_{EN-C} = 2.55$) in comparison to H χ_{EN-H} = 2.20, the binding electrons are slightly shifter towards the C-atoms in these surface dipoles. The effect is a downward band bending for electrons which facilitates electron emission. Vice versa, the electron affinity is a function of the H-coverage, *i.e.* a fully saturated surface features the lowest NEA value while χ increases with H-desorption. For (111)-surfaces the minimum NEA was quantified $\chi_{min} = (-1.27 \pm 0.07)$ eV [81]. On H-terminated n-type single crystals upward band bending was reported which was attributed to a depletion layer of ionized P-donors [82, 83]. A simplified energy band diagram for a H-terminated surface of P-doped diamond is shown in Fig. 4.2. Also theoretical considerations suggest an energy barrier that results from ionized donors [84, 85]. Besides the saturation with H, Li-deposited oxygenated diamond has been demonstrated a stable NEA platform recently [66]. Surface defects and traps will present an additional barrier that needs further excitation. So far, electron emission from hydrogenated surfaces has been measured from temperatures around 400°C [64].

4.1.2 Space charges in the inter-electrode gap

A phenomenon that reduces the power output of thermionic devices is the accumulation of charges in the inter-electrode gap. Emitted but not collected electrons stay in the gap as a negative charge cloud and present an additional potential barrier for following electrons. Only the most energetic electrons will pass on to the collector while low energy charges accumulate in the gap. There are three strategies in order to overcome this issue: (1) Typically, a slightly positive suction potential (10 to 20 V) is applied to the collector electrode. In the electric field, electrons are accelerated across the gap. (2) By reducing the gap width to 3 to 5 μ m, the collector would be close enough to the charge cloud to capture the emitted electrons [79]. However, technologically a realization of micrometric gaps without electrical shortage is challenging. (3) Gaseous molecules with an appropriate ionization energy, such as methane, are used to mitigate the space charge. Transient negative ions, transport the charges across the gap [86]. Similar neutralizing effects have been observed upon introduction of Cs-vapors [87]. On the other hand, reducing the gap as well as the introduction of gases enhances the heat transfer from emitter to collector which in consequence will reduce the temperature difference between the electrodes and finally the device efficiency.

4.2 Thermoelectrics

Thermoelectrics is considered a second possibility to use waste heat for energy conversion and to become an alternative in the development of sustainable energy sources. In the scope of this thesis only a brief discussion about thermoelectrics is given in order to set the experiments in Sec. 8.3.2 in an appropriate context. The underlying phenomena of thermoelectrics are described by the Seebeck and the Peltier effect. In a nutshell, a thermal gradient across a material gives rise to a thermovoltage $V_{\rm th}$ and vice versa a current through a material interface induces cooling or heating.

Seebeck discovered the voltage build up between two points in a material when those two points are kept at different temperatures. In an open circuit ($\vec{j} = 0$), a temperature gradient across a semiconductor induces an electric field $\vec{E} = S\nabla T$. This effect is relatively small in metals. However in doped semiconductors thermovoltages V_{th} up to several hundreds of μV can be reached. In the steady state, the differential Seebeck coefficient *S* is defined as the ratio of V_{th} to ΔT . For a thermocouple-like configuration, as depicted in Fig. 4.3, the resulting thermovoltage V_{th} is a contribution of the two metal contacts (A) in addition to the voltage across the material (B) itself:


Figure 4.3: Scheme illustrating the Seebeck effect: A voltage is induced due to a temperature gradient across the material B.

$$V_{\text{th}} = -\oint S(\nabla T) \, \mathrm{d}\vec{s}$$

= $-\int_{T_0}^{T_1} S_A(T) \, \mathrm{d}T - \int_{T_1}^{T_2} S_B(T) \, \mathrm{d}T - \int_{T_2}^{T_0} S_A(T) \, \mathrm{d}T$ (4.12)
= $\int_{T_1}^{T_2} S_A(T) \, \mathrm{d}T - S_B(T) \, \mathrm{d}T$

This is also the experimental configuration that was used for the measurements at WSI presented in section 8.3.2. In the case of material A being a metal and material B being a semiconductor, it is $|S_B| \gg |S_A|$. In semiconductors, charge carriers are thermally activated into the conduction band at the heated end. Thus, an increased number of charge carriers is present and diffuses to the colder end where they accumulate. In order to obtain a precise value for S_B , the measured value of V_{th} needs to be corrected by the contribution of the metallic contact.

Today's research activities focus on maximizing the so-called ZT-value,

$$ZT = \frac{S^2 \sigma}{\kappa} T,$$
 (4.13)

the figure of merit in thermoelectrics. According to equation 4.13 high performance thermoelectric materials have ideally to feature a high Seebeck coefficient, a good electrical conductivity σ whereas the thermal conductivity κ should be low at the same time. The highest ZT-value, reported in spring 2014, was (2.6 ± 0.3) at 923 K for SnSe single crystals [88]. To date, many of the efficient thermoelectric materials are tellurides and antimonides [89] which are hazardous to health and rare elements, so there is an increased interest to find alternatives. By materials engineering through doping and nanostructuring, the thermoelectric properties can be significantly improved [90]. A variety of suggestions has been reported with the aim to decouple σ and κ . Since porous and nanostructured material morphologies have been reported to lower the thermal conductivity, group-IV semiconductor thin films have developed into a promising alternative [91]. Further improvements are expected from composites that could be realized by alloying nanoparticles of different materials. To use diamond with its high thermal conductivity in thermoelectrics seems contradictory, however in a composite material, interfaces and the nanometric dimensions are expected to impact σ and κ . This is the approach whose investigation was started within MATCON.

Seebeck measurements can also be used to determine the majority charge carriers in a highly doped semiconductor. Thermally activated charges diffuse to the cold end, and the sign of V_{th} indicates the type of the majority carriers in the material. Under the assumption of a parabolic band structure, the doping concentration *n* can be deduced from the Seebeck plots by [92]:

$$S = \frac{8\pi^2 k_B^2}{3eh^2} m^* T \left(\frac{\pi}{3n}\right)^{2/3}.$$
 (4.14)

Here, *e* the elementary charge and *h* the Planck constant, m^* refers to the effective hole mass in case of p-type semiconductors. In polycrystalline material, equation (4.14) is associated to the average carrier density within the grains.

5 Materials and experimental methods

5.1 Substrates and preparation

In the scope of this thesis, NCD was deposited on highly resistive (100)-Si (10-20 k Ω cm) or fused silica. These materials are easily available at low cost, in high purity, and with a smooth surface finish. They are suitable for the deposition processes that require high temperatures. While Si substrates are used for morphological and spectroscopic studies, fused silica is needed as substrate for electrical characterization. The standard in-house substrate size is 1x1 cm² and 500 μ m thickness. Samples dedicated to thermionic emission experiments require an electrically conductive substrate for the back contact. Circular (1 inch or 2 cm) Mo, Re coated Mo or highly conductive Si substrates were used here.

5.1.1 Cleaning

In order to obtain uniform NCD films, the substrate cleanliness prior to deposition is crucial. Si and fused silica substrates are cleaned in two steps in a widely used state-of-art procedure (RCA clean) [93]. RCA-1, a mixture of DI water, NH₄OH and H₂O₂ at the ratio of (5:1:1), removes organic contaminants. Metallic residues dissolve in RCA-2 solution, *i.e.* DI water, HCl and H₂O₂ at the ratio of (6:1:1). The mixtures are heated to 80°C before the substrates are immersed in each of the solutions for about 10 min. Finally, they are thoroughly rinsed with DI water and N₂ blow-dried.

Many metals are strongly oxidized in H_2O_2 , hence RCA cleaning is not suitable. Metallic substrates such as Mo and Re coated Mo, were therefore sonicated in Acetone, IP and ethanol for respectively 5 min before a H_2 plasma clean for another 10 min.

5.1.2 Seeding

Diamond CVD on non-diamond substrates, hence heteroepitaxial deposition, requires the provision of seed crystallites or a bias enhanced nucleation step. To enhance diamond nucleation, the substrate is treated with a water-based state-ofthe-art colloidal suspension of detonation nanodiamonds (ND). The suspension is prepared from ND powder provided by the NanoCarbon Institute Co., Ltd., Japan. Sonication of the suspension (ND in DI water at a concentration of 0.33 g I^{-1}) for 3 h ultra-disperses the powder and creates a colloid that is chemically stable for several months. Dynamic light scattering determined the maximum of the particle size distribution to be between 5 to 10 nm. The zeta-potantial at 4.8 pH is (49 ± 5) mV.

In order to obtain a homogeneous ND seed coverage, the substrate is placed on a spin-coater and a drop of the seeding suspension is applied with a pipette. After approximately 20 s of contact time, the sample is flushed with DI water and spin-dried at 4000 rmp. The surface chemistry between the ND particles and the substrate strongly influences the seeding density. Attractive van der Waals and electrostatic forces lead to ND adhesion, hence dense seeding.

5.2 ASTeX-type reactor and CVD

All P-doped diamond thin films were grown in a commercial ASTeX-type microwave plasma enhanced CVD reactor of the type ASTeX PDS-17 (ASTeX 1) which is used for n-type doping, predominantly for P-doping. Figure 5.1 shows the installation at IMO. The reactor consists of a cylindrical steel chamber. The energy needed to maintain the plasma is coupled into the chamber as electromagnetic waves via a top window. The microwave generator operates at the standard frequency of 2.45 GHz and outputs between 500 and 5000 W. Microwaves that are generated in the magnetron propagate along the rectangular waveguide. A circular waveguide, sitting just above the deposition chamber, deflects the microwaves into the vacuum chamber. The plasma ignites where the electric field has a local maximum. Hence, the adjustment of stage height and optimum microwave tuning are crucial to obtain a stable plasma tangent to the substrate surface. A set of three manual standard rod microwave tuners allows to adjust the impedance and to minimize the reflected power. The plasma ball size, power density, gas discharge color is controlled mainly by microwave power, working pressure and gas composition. The deposition chamber is connected to an oil-free pumping system consisting of a membrane pump and a turbomolecular pump. This configuration reaches a base pressure down to 3.5×10^{-8} Torr (4.7 $\times 10^{-8}$ mbar). For P-doping, a clean environment *i.e.* especially the minimization of N contamination is mandatory for the growth of high quality and electrically active films. Therefore, the vacuum chamber is vented with Ar.

The samples, diamond single crystals as well as non-diamond substrates are positioned centered on dedicated Mo substrate holders. Due to the size of the vacuum chamber, mostly only one sample is grown at the time. Homogeneous depositions of P-NCD up to 1 inch in diameter are possible.

The substrate stage is water cooled which allows to work with highly energetic plasmas without an uncontrolled increase of the substrate temperature. The height-adjustable stage offers a high flexibility for different experiments. However, the



Figure 5.1: ASTeX PDS-17 CVD reactor used for P-doping experiments at IMO. The optical bench with the components for reflectance interference is marked.

plasma stability is best at the stage height display value of 63.8 mm. The system disposes six gas channels in total with each of them having an individual mass flow controller: Channel 1 with a maximum flow rate of 500 sccm is fed by H. H is provided by a hydrogen generator with a purity of 7N. Methane (CH_4) enters the chamber via channel 2 (20 sccm) or 3 (50 sccm). Depending on the growth conditions, the user selects the appropriate channel. Channel 4 is dedicated for O_2 which is used *e.g.* for etching as surface defect reducing pre-treatment for homoepitaxial growth. Phosphine (PH_3), as the doping source is connected to the channels 5 and 6. For CVD in highly P-concentrated plasmas, subject of this thesis, mainly channel 6 with a possible maximum flow of 500 sccm was used. For reasons of security, the total gas flow into the system is typically set to 500 sccm. A stable plasma can be obtained at pressures between 20 and 200 Torr (26.7 and 267 mbar). A throttle valve controls the working pressure during the deposition. NCD deposition requires adapted deposition conditions. Throughout the present work, the working pressure was set to 50 Torr (66.6 mbar) or 67 Torr (89.3 mbar). The C:H concentration ranged between 1% and 3%, substrate temperatures of $(810 \pm 10)^{\circ}$ C were achieved with 950 W.

5.2.1 In-situ thickness measurements

For the NCD experiments, the reactor was upgraded with an optical *in situ* thickness monitoring tool. The optical components were installed on a bench that was fixed to the horizontal wave guide. A He-Ne laser (633 nm) and a diode pumped



Figure 5.2: In situ laser reflection interference for thickness monitoring of NCD growth.

solid state laser of 473 nm are directed on the substrate through the top windows of the chamber. The relationship between the angle of incidence (θ_i) and refraction (θ_r) of light that passes an interface of two isotropic media of different indices of refraction, *e.g.* NCD of n_{NCD} and Si ($n_{\text{substr.}}$), is given by Snell's law:

$$n_{\rm NCD}\sin\theta_i = n_{\rm substr.}\sin\theta_r.$$
(5.1)

The interference signal of the laser beam that is reflected (1) from the substrate and (2) from the surface of the NCD film is measured by a Si photodiode. An interference filter in front of the photodiode minimizes the radiation background.

The light reflected from the substrate and the growing film will interfere. Constructive interference occurs in case of no phase difference between the two waves. If the reflected waves have a phase difference of $\frac{\lambda}{2}$, the interference is destructive. Fringes of constructive and destructive interference, a result of the increasing optical path in the growing film, allow to determine the film thickness with time. Figure 5.2 shows a reflected laser signal as a function of deposition time. The intensity decline is due to scattering induced by the increasing surface roughness. When multiple reflections are neglected and only the real part of the refractive index is considered, basic geometrical optics provide a relation to evaluate the film thickness. For integer multiples of the incident wavelength, the constructive interference conditions are fulfilled when

$$2n\frac{t_{\rm f}}{\cos(\theta_i)} = m\lambda. \tag{5.2}$$

For NCD deposition on Si, a $\lambda/2$ -phase shift occurs for reflections at an optically denser material ($n_{substr.} > n_{NCD}$) which means an interference minimum for $\lambda/2$:

$$2n\frac{t_{\rm f}}{\cos(\theta_i)} = \left(m + \frac{1}{2}\right)\lambda.$$
(5.3)

In the above equations t_f represents the film thickness, θ_i is the angle of incidence measured to the surface normal, m the order of wavelength multiples that fit in the optical path difference, λ refers to the laser wavelength, n is the real part of the refractive index.

In the present case the angle of the lasers towards the surface normal θ_i is approximately 0°, hence equations (5.2 and 5.3) simplify:

$$t_{\rm f} \approx \frac{{\rm m}\lambda}{2n},$$
 (5.4)

$$t_{\rm f} \approx \frac{1}{2n} \left({\rm m} + \frac{1}{2} \right) \lambda.$$
 (5.5)

In dispersive media, the refractive index *n* is wavelength and temperature dependent. For diamond and the given wavelengths it is $n_{\text{NCD,633}} = 2.412$ and $n_{\text{NCD,473}} = 2.439$ at room temperature. The real time monitoring of the reflection signal during deposition also reports changes of the growth rate in time. Due to scattering and absorption within the film, the interference read-out signal typically decreases with time. The columnar growth regime of NCD results in increasingly rough surfaces.

5.2.2 Optical emission spectroscopy

The presence of the gaseous species in the diamond CVD plasma can be monitored by optical emission spectroscopy (OES). In the scope of this work, OES experiments focussed on the detection of P-fingerprints in the growth plasma. An optical fiber (*Avantes* FC UV600-2) collected the light via one of the lateral viewports. The spectra were recorded by an AvaSpec-2048 (*Avantes*) spectrometer which comprises a 2048 pixel CCD detector array and covers the range of wavelengths between 200 and 1100 nm. Due to the absorption of the quartz windows we focused on wavelengths between 300 nm and 800 nm. The overall spectra were recorded without optical filters. With additional shortpass filters cutting at 450 nm or 525 nm, the dominant H_{\alpha} and H_{\beta} emission lines can be filtered which allows a more detailed investigation of the PH line. The resolution of the detector limits the set-up for more detailed investigations.

5.3 Boron doped diamond - as raw material for nanoparticles

5.3.1 Bias enhanced CVD of UNCD

In a hybrid NIRIM-type CVD reactor with a 5 cm diameter quartz tube as reaction chamber UNCD deposited on solvent-clean, circular (1 cm diameter) Si substrates by argon free plasma enhanced CVD under a continuous DC bias. The bias voltage is applied between the axially symmetric, metallic substrate holder and a cylindrical counter electrode that is placed around the substrate. In a first step (1) the substrates were heated in a pure hydrogen plasma (50 mbar, 275 W) to approximately 700°C. (2) Diamond crystallites nucleated in a plasma of 1% C:H during 10 min., while the substrate is negatively biased at 260 V_{dc} . (3) B-doped layers are grown at 50 mbar for maximum 3 h in a TMB containing plasma (1% C:H, 5000 ppm B:C) at 425 W microwave power under continuous DC bias of 260 V_{dc} during the entire deposition time. The resulting dc current increases linearly in the early stage of growth, until it stabilizes at (0.35 ± 0.05) A after around 30 min. Carbon soot deposited on the quartz tube walls when high B-concentration were used in the depositions. The substrate temperature is monitored by an optical pyrometer via the top view port. Substrate temperatures of 1000°C and the acceleration of the plasma ions toward the substrate result in a high deposition rate, around 5 μ m h⁻¹. The deposition time is limited by the increasing mechanical stress in the substrate which often results into convex deformed substrates.

5.3.2 B-doped microcrystalline diamond

A 14.5 μ m thick microcrystalline film was deposited on a standard cleaned, doubleside polished, seeded (100) Si wafer (2 inch) in an ASTeX 6500 series reactor at 3% C:H-ratio and 5000 ppm B:C-ratio during 24 h. Throughout the growth process the plasma power was maintained at 4000 W, the working pressure was kept at 45 Torr (6666.1 Pa), while the total gas flow was 500 sccm. These conditions resulted in an appropriate deposition rate of (11.8 ± 1.1) nm min⁻¹ not having a negative effect on the diamond quality. The initial deposition temperature was 750°C which further decreased to 700°C during the growth. The temperature drop is common in long deposition during which (1) increasing surface roughness induces scattering of the IR emission towards the pyrometer and (2) thermal conduction of the growing film reduces the overall substrate temperature. In order to obtain free-standing diamond, the Si substrate was entirely etched in an aqueous 25% tetramethylammonium hydroxide (TMAH) solution at around 80°C during several hours. The polished substrate facilitates considerably the wet-etch process as the anisotropic TMAH etch rate on (100)-oriented substrates is reasonably high (0.9 μ m min⁻¹).

5.4 Raman spectroscopy

Raman spectroscopy is amongst the most adapted techniques for identifying various forms of carbon. It is a flexible and non-destructive method to evaluate the diamond quality in terms of sp^2 - and sp^3 -hybridized carbon. Detailed analysis of the spectra helps to evaluate phase purity, stress or doping effects, requires however caution and awareness for quantification.

The monochromatic laser beam interacts with crystal phonons and lattice abnormalities resulting in energy shifts of laser photons. The Raman-effect refers to inelastic scattering of incident photons with matter. Atoms in the crystal lattice can either absorb or release energy in the interactions. In relation to the incident energy, the energy of scattered light is shifted to higher (Stokes-Raman-scattering) or lower (Anti-Stokes-Raman-scattering) energy. To fulfill energy conservation, the difference between absorbed and emitted energy, creates a phonon.

Energy dispersion of laser photons collected by the detector carries thus information about the sample, e.g. lattice strains or dopants. Signals from non-diamond phases (sp²-carbon) are more distinct at low energy photon excitation. The strong wavelength dependence of the Raman scattering for diamond and graphitic carbon respectively, renders an excitation in the visible range a good compromise. A pure diamond spectrum consists of a single line at 1332 cm^{-1} . It refers to a triply degenerate optical Brillouin zone center phonon where two diamond sublattices vibrate against each other. Lattice strains and crystal defects downshift or upshift the characteristic peaks. Polycrystalline diamond features additional bands attributed to graphitic carbon. The most prominent signatures of amorphous carbon are the D-band at 1350 cm^{-1} and the G-band between 1550 and 1600 cm^{-1} . Moreover, a large peak attributed to sp^2 -carbon is detected at 1480 cm⁻¹ [94]. Bormett et al. studied Raman scattering efficiencies of the carbon allotropes upon excitation with different wavelengths. The intensity ratio difference between diamond and non-diamond carbon signals was identified to be a factor of ≈ 25 higher for UV excitation [95]. Being aware of possible inaccuracy of absolute values, peak ratio comparisons throughout this thesis were necessary to assess optimum deposition parameters. Without consideration of the higher sp²-interaction at 488 nm excitation, the presented ratios are potentially overrated.

The spectra recorded in the scope of this thesis were obtained at room temperature and ambient pressure under blue excitation of a *Lexel* SHG-95 Ar-ion laser (488 nm) via a confocal microscope with a *Horiba Jobin-Yvon* T64000 micro-Raman spectrometer. Second harmonic generation allows measurements with light of 244 nm. The sample area designated for spectroscopy is selected by a camera mounted on the microscope. A x-y-stage allows a coplanar displacement. An optical grating (1800 lines mm⁻¹) enables the dispersion of the beam on the charge coupled device (CCD) detector cooled by liquid nitrogen. The notch filter cuts the backscattered beam. The beam intensity is controlled by width of a slit situated above the microscope's front lens. As a rule, intensity is reciprocal to resolution. Using the blue laser, the objective magnification is typically x100. The pinhole was 200 μ m, each scan took 60 s. One set contains the data of at least 3 scans to improve the signal-noise-ratio and to average possible film inhomogeneities.

5.5 X-ray diffraction

X-ray diffraction (XRD) assessed the structural properties of P-NCD films as a function of the P-level in the CVD gas phase. From peak intensity differences, it is possible to evaluate preferential grain orientations. A *Siemens* D5000 Bragg-Brentano diffractometer collected the data upon irradiation of the samples with Cu-K_{a1} line ($\lambda = 0.15406$ nm). The samples were positioned with an angle of 0.6° towards the substrate surface to minimize the prominent diffraction signal from the Si substrate. Due to the polycrystallinity and the irregular grain orientation, the offsetangle will not influence the result.

5.6 Scanning electron microscopy

Scanning electron microscopy (SEM) offers high resolution imaging of solid surfaces by electron beam scanning. In contrast to optical microscopy, SEM features a high depth of field as well as a large magnification range. For diamond thin film research, it is an indispensable tool for visualizing morphology, grain size, film continuity and uniformity at nanoscale. Throughout this thesis a FEI Quanta 200 FEG SEM was used. The field electron gun of the microscope emits a high energy beam between 200 eV and 30 keV, however for measurements on NCD samples, it was typically operated at 15 kV at 10 mm working distance (WD).

5.7 Transmission electron microscopy

Transmission electron microscopy (TEM) offers a number of tools with high spatial and spectroscopic resolution. Sophisticated techniques such as STEM-EDX are able to probe the local elemental composition within nanometric objects. In a typical experiment, the electron beam is scanned over the sample and an EDX spectrum is obtained simultaneously in each point, allowing a correlation of the morphology with the spectroscopic data from EDX. All TEM studies on P-NCD as well as on UNCD films were conducted in cooperation with the Electron Microscopy for Materials Science (EMAT) facilities of University of Antwerp. Following the established procedure, an electron transparent sample for (S)TEM imaging was prepared by ion-milling [96]. STEM-EDX was carried out on an aberration-corrected Titan 'cubed' microscope operated at 120 kV and equipped with a Bruker 'super-X' four quadrant windowless EDX detector. Imaging and spectroscopy were performed using a convergence semi-angle alpha of 22 mrad, and an acceptance inner semiangle beta for annular dark field (ADF) imaging of 33 mrad. The beam current for imaging was 40 pA, for EDX 250 pA was used.

5.8 Secondary ion mass spectroscopy

Secondary ion mass spectroscopy allows to determine the composition of a solid material with high sensitivity. In semiconductor research it serves to identify impurity atoms and to profile doping concentrations. Our co-workers at GEMaC, Versailles operate a *Cameca* IMS 4f set-up with a primary Cs⁺-ion beam for experiments on diamond. The highly energetic ion beam impinges the surface and ejects particles that are analyzed in a mass spectrometer. SIMS is a destructive method that leaves a crater where the sample has been hit by the ion beam. As a result, SIMS evaluates the absolute concentration of the detected species without any further information about its bonding configuration or electrical activity. SIMS quantification is possible by comparison with calibrated standards.

5.9 Cathodoluminescence

Cathodoluminescence (CL) means the emission of photons from a material upon electron excitation. Through the recombination of electron-hole pairs, the characteristic emission lines can be attributed to defects. Diamond features an indirect bandgap. As a result most transitions between conduction band and valence band are assisted by phonons. In order to analyze the coordination of the P-atoms in diamond thin films, CL spectroscopy was used. CL allows to: (1) investigate the optical activity of incorporated P-dopants in diamond and (2) to quantify the donor concentration. The spectra were taken at GEMaC in a *JEOL* 7001F SEM at 30 K in order to minimize phonon-related line broadening. The electron beam was operated at 10 keV resulting in around 900 nm electron penetration depth.

5.10 Thermionic emission measurements

Thermionic emission currents were measured in a dedicated UHV system with load lock at Arizona State University with a base pressure smaller than 5.0×10^{-9} mbar. The system comprises a radiatively heated stage with a W-coil. P-doped NCD films on Mo and Re/Mo substrates (1 inch) were used as emitters. The samples were exposed to a hydrogen plasma (900 W, 5 min.) for a fresh H-termination before being transferred into the vacuum chamber. The collector was a polished Mo plate of 1 inch which is contacted by an air-cooled Cu rod. The two electrodes were sandwiched and firmly tied together in a dedicated holder. An electrical feedthrough transfers the emission current signal to the amperemeter. Free-standing alumina

pieces of 50 μ m thickness were used as spacers between the electrodes. A *Mikron* 2-color pyrometer read out the emitter temperature through the lateral viewport. The temperature of the heater was monitored by a thermocouple in the center of the coil. A DC bias voltage of 20 V at the collector anticipated space charging. The emission current is determined by a *Keithley* 2400 source-measure unit. Typically, several measurement cycles between 250°C and 800°C are repeated to create a stable emitter surface and to evaluate the emission current as a function of temperature.

5.11 High resistance measurements

P-NCD films for electrical measurements were deposited on FS substrates. Wet chemical oxidation in H_2SO_4 with added KNO_3 guaranteed an O-terminated surface and hence no surface conduction. The high P-donor activation energy requires measurements at elevated temperature, additional scattering effects are expected from grain boundaries. A micrometric 6-contact Hall bar structure improved the experiments by avoiding material effects or the buildup of inhomogeneous electric fields. State of the art photolithography and the standard recipe for the negative photoresist NR9 was used to define the bar pattern. After deposition of a Cr hard mask, the pattern was O-plasma etched for 10 min in a capacitivelycoupled configuration of a home-built PVD system (300 W, 30 sccm O₂, 50% valve, 3.5×10^{-3} mbar). The contacts are e-beam evaporated Ti/Pt/Au-pads, known for ohmic behavior on n-type diamond. Annealing of the contacts at 800 K in vacuum improves the physical contact between the metal and the diamond surface. The distance between two lateral contacts is (0.88 ± 0.02) mm (Fig. 5.3), the effective bar width is (0.48 ± 0.02) mm, the total length (1.97 ± 0.04) mm. A home-designed vacuum oven with four BNC feedthroughs provides a stable environment between 300 K and 900 K for the measurements. At the same time, the vacuum casing serves as electrical shielding. The heater is a pyrolytic BN disc whose temperature is controlled in a loop of a type N thermocouple and a Eurotherm PID device. Ceramic clamps hold the sample in place and assure good thermal contact. By means of wire bonding, one connects the sample to the external electrical feedthroughs with a 25 μ m diameter Au wire. Ideal settings for Au-bonding at the bonder are 4.5 to 5 units ultrasound power, 4.5 ms pulse for both bonds with enabled wire bonder tool heating. The presented measurement configuration is not ideal for measurements on highly resistive NCD samples. However, it may result in first indications on the electrical properties of P-NCD.

Alternating polarity method In materials with a high resistivity, background currents may significantly distort the measurements. They may originate from charge trapping at material defects, charge accumulations or piezoelectric effects. By alternating the voltage polarity during the measurements, background currents can be eliminated. The *Keithley* Electrometer/High Resistance Meter 6517A features a built-in test sequence. A constant bias voltage of \pm 70 V



Figure 5.3: The four inner contacts of the P-NCD bar structure that was used for high resistance measurements.

was applied for 15 s at the outer contacts of the bar structure, before the read-out was taken. Typically, 10 iterations were taken per measurement, the first 3 read-ings were discarded. For each temperature, the resistance values are calculated from the source voltage and the measured current by Ohm's law. Assuming a linear voltage drop across the bar, the voltage between the inner contact pads was calculated.

Current-voltage-sweeps Standard current-voltage (IV)-sweeps also allow to assess the conductivity. Moreover, this method reveals potential diode or Schottky characteristics at the contact-NCD interface. For each temperature, several sweeps between -50 V and +50 V ($\Delta V = 5$ V) were recorded with a *Keithley* Electrometer/High Resistance Meter 6517A. Each measurement was taken after a stabilization phase of 10 s.

6 Thermionic electron emission measurement set-up

"It is easy to see," replied Don Quixote, "that thou art not used to this business of adventures; those are giants; and if thou art afraid, away with thee out of this and betake thyself to prayer while I engage them in fierce and unequal combat."

from Don Quixote, Miguel Cervantes

Within the framework of the MATCON Initial Training Network workpackage D 'Nanocomposite Materials for Thermoelectric and Thermoionic Heat Conversion', an experimental set-up for measuring thermionic electron emission was designed and assembled. The design of the set-up realized at IMO bases upon the device at NanoScience Lab, Arizona State University (ASU) dedicated for the same type of measurements. The group at ASU pioneered the field of heat induced electron emission from diamond surfaces and has gained a great experience over the last years. Their know-how and the collaboration were extremely helpful for the starting activities on thermionic emission at IMO.

6.1 The vacuum system

Thermionic emission is a surface process that involves free electrons crossing a vacuum gap (Ch. 4). In order to reduce the probability of collisions with other particles and to keep the emitter surface in a defined state, ultra high vacuum conditions (UHV) are required. The mean free path defines the average distance that a particle can travel between two successive collisions. For UHV applications this distance typically needs to be larger than the vacuum vessel dimensions. Following the kinetic theory of gases and assuming a Maxwellian velocity distribution, the mean free path λ depends on the temperature *T*, pressure *p* and the effective cross section *d* linked to the particle size:

$$\lambda = \frac{k_B T}{\sqrt{2\pi} d^2 p}.\tag{6.1}$$



Figure 6.1: Technical drawing of the thermionic emission measurement set-up realized at IMO. Load lock and main chamber are separated by a manual gate valve.

In ambient conditions (10^5 Pa, 20° C), the mean free path of a N₂ molecule is smaller than 100 nm. At a base pressure of 10^{-9} Torr, the mean free path increases to approximately 35 km.

In order to meet the required UHV standards, the system is entirely built from state-of-the-art conflat (CF) flange components. Cu gaskets seal the joints between the different components and oil-free vacuum pumps are used to prevent contamination from pump oils. The set-up has been built in a modular way and is mounted on a frame on wheels, so that future adaptations, extensions and connections to other UHV systems, such as XPS, are easy to realize. Figure 6.1 shows the technical drawing of the set-up without its base frame. The set-up is an assembly of two connected 6-way crosses, the bigger one (CF 100) being the main chamber while the second cross (CF 63) serves as load lock. The two crosses are separated via a manual UHV gate valve and a CF 100-63 reducer nipple. Each cross is connected to a pumping system and can therefore be evacuated independently. In this configuration the main chamber does not need to be vented when a sample is introduced into the system which minimizes contamination and saves time. A check with the He leak detector prior to baking measured 10^{-9} mbar ls⁻¹ and confirmed UHV quality. All other necessary components are fixed to the six arms of the crosses.

Load lock

The *Edwards* EXT DN40 turbopump evacuates the load lock to minimum 2.0×10^{-8} mbar. An *Edwards* XDD 1 diaphragm pump which at the same time backs the turbopump reaches 1.5 mbar as fore vacuum. Due to its small volume, the pumping of the load lock is quick. A combined Pirani/ionization gauge (*Oerlikon* Ionivac ITR 90) measures the pressure and a view port at the top flange enables to see inside the lock which facilitates the loading. Through the viton-sealed loading port, the emitter cell is clamped to the grabber of the transfer rod (Ch. 6.4). The magnetically coupled rotary transfer rod sitting in main axis of the system and allows to insert and retract the emitter cell into and from the main chamber.

Main chamber

The main chamber comprises the heated sample stage (Ch. 6.3) and the movable top contact assembly which are the central parts for thermionic measurements besides the emitter itself. A water-cooled *Edwards* nEXT240 turbopump which is backed by a *Edwards* xNDS 6i scroll pump maintains the UHV in the main chamber. A glass fiber-coated heating tape wound around the main chamber is used for bakeout. The outside wall temperature has to be monitored by *e.g.* a thermocouple as non-steel components are specified for 200°C maximum. After extensive baking for several days at 180°C and multiple heating-cool down cycles between 200 °C and 600 °C of the heater, the system reached a base pressure of $\leq 5.0 \times 10^{-10}$ mbar. Just as in the load lock, a combined Pirani/ionization gauge covering the full range from 1000 mbar to 5.0×10^{-10} mbar measures the pressure. While the Pirani measuring system is used for pressure > 5.5×10^{-3} mbar, the ionization switches on when pressures drop below 2.0×10^{-2} mbar. A viewport facilitates the sample transfer allows to monitor the experiments *e.g.* by an additional temperature evaluation by a pyrometer.

The control units for the turbomolecular pumps, the read-out displays of the pressure gauges as well as the PID controller, heater power supply and *Keithley* measurement unit are grouped in a metal blind and accessible from the front.

6.2 Top contact assembly

All components mounted to the top flange of the main chamber are linked to the read-out of the emission current. The unit that electrically connects to the collector electrode of the emitter cell is approached and retracted with a UHV Z-manipulator of 50 mm travel length. In order to ensure that the collector is not grounded via the steel chamber, a ceramic insulator break separates the main chamber electrically from the top contact unit. In the current configuration, this piece is obsolete, it assures that the top electrode is electrically floating. The topmost component of the column is a CF40 4-way cross that holds the electrical and thermocouple



Figure 6.2: Details of the technical drawings: (a) U-shaped cooling lines with the contact rod that realizes the electrical contact with the collector. (b) Heater (red) and tilting mechanism.

feedthroughs as well as the top contact water-cooling. The vacuum side of the top flange holds two parallel tubes that end in a steel coupler piece to form a U-shaped cooling line for the collector contact. A close-up view is shown in Fig. 6.2(a). Via a *Swagelok* connector the lines are coupled to the external water cooling circuit. A macor[®] block electrically insulates the Mo contact rod from the water lines. A type K thermocouple connected to the macor[®] piece monitors the temperature of the top contact assembly. The electrical contact to the collector electrode is realized via a small Mo pin that sits at the lowermost end of the assembly. A silver coated Cu wire (0.6 mm diameter) connects the Mo pin to the electrical feedthrough at the 4-way cross.

6.3 Heater and sample holder

The heater and sample holder are mounted to the bottom flange of the main chamber. Their exact position and adjustment are crucial as the top contact assembly and particularly the transfer rod connection do not allow mechanical play (Fig. 6.3). A 1 mm diameter thermocoax heater cable with insulating Inconel[®] 600 coating is tightly coiled up between two countersunk steel discs, see Fig. 6.3. A few weld spots hold the discs together and the wire in place. The wire has a heated length of 75 cm and approximately 30 cm of cold ends which are connected via the electrical feedthrough at the bottom flange to the *TDK* Lambda Z+, 60-7 AC/DC power supply. At 20°C, the resistance of the wire is 9.4 Ω . According to the specifications, a thermocoax cable with the mentioned dimensions in good thermal contact with a heat sink can be operated at maximum 45 V which results in a power output of



Figure 6.3: View inside the main chamber along the transfer axis: The heater sits in the center of the chamber. By lowering the top contact assembly, the electrical contact with the collector is established. In the background, one discerns the bottom of the emitter cell.

200 W. The heater temperature is controlled by a PID device which monitors the read-out from a type K thermocouple. The *Eurotherm* 3504 PID (loop 1) controls the AC/DC power supply that feeds the heater. The PID outputs analog 4 to 20 mA with 4 mA representing the lowest and 20 mA the highest point of the range used. In order not to run the thermocoax cable at its limit, the maximum output voltage was set to 40 V which thus corresponds to the 20 mA high signal. The PID control loop was tuned at 600°C, which means a medium value of the expected measurement range. For the 600°C output, the heater wire was operated at 1.7 A and 17.5 V. In general, the *Eurotherm* controller is a capable device that offers a number of features for future experiments. Besides the simultaneous temperature read-out of the two thermocouples, it can control the heater by the use of predefined heating ramps.

The heater sits in a holder that at the same time supports the tilt mechanism for the emitter-collector cell (Fig. 6.2(b) and Fig. 6.4). A rotational manipulator levers the cell from the horizontal position on the heater to a vertical position for loading and unloading. In the upright position (90° towards the heater surface) the cell, sitting on the transfer rod grabber, can be screwed to the ring holder. Once removed from the grabber, the cell is tilted onto the heater for the experiment. The design for the grabber mechanism with the four spring clips, see Fig. 6.6, was adapted from older UHV systems at IMO.



Figure 6.4: Lateral inside view of the main chamber: The emitter cell is screwed into the ring of the tilt mechanism, yet still attached to the grabber. At the lower left the heater with its thermocouple is visible. The top contact is retracted opening enough room for the tilt.



Figure 6.5: Exploded view of the individual parts and the stacking order in the emittercollector cell.

6.4 Emitter-collector cell

In this project the electron emitting thin films are P-doped NCD layers deposited on a conductive, typically metal, substrate. However, any other type of material with suitable dimensions is possible to be measured in the presented set-up. The emitter-collector cell is designed to hold circular samples of 2 cm in diameter. A crucial aspect of thermionics to avoid space charges is the distance between collector and emitter which at the current stage still presents a challenge for experiments. This gap should (1) be ideally a few μ m only to extract as many emitted electrons as possible and (2) be uniform over the whole emitter surface without shorting the two electrodes. To meet these requirements, emitter and collector are fixed in a dedicated carrier cell that allows convenient handling and guarantees a constant spacing.

The emitter-collector cell consists of a steel cup and a steel ring in between which emitter, spacers, insulators and collector are stacked and bonded together with a wire. Figure 6.5 pictures the exploded view of the cell and the stacking order of the different parts. The cup has an external thread to be screwed into the tilting mechanism of the heater. The ring has grooves which fit the grabber of the transfer rod. Figure 6.6 shows the emitter cell clipped to the grabber ready to be transferred into the main chamber.

The bottom cup holds the sample whose emitting surface is facing upwards. Spacer pieces of approximately 2 mm² from alumina (Al₂O₃) that are placed on top of the emitter sample define the gap width between the electrodes. The use of alumina is convenient as it exists as free-standing pieces in different thicknesses. Moreover, alumina is electrically insulating and has a low thermal conductivity which reduces thermal conduction towards the collector. A macor[®] ring with an inner diameter



Figure 6.6: The grabber (right) holding the emitter-collector cell (left).

of 2 cm holds the Mo collector in place and avoids therefore short-circuits with the side walls. A polished Mo disc (2 cm in diameter) with a protruding rod is used as collector electrode. Another ceramic ring insulates the collector towards the upper metal ring. The entire stack is bonded together with a wire that runs at four positions through the cup and the top ring. Tight wiring results in a rugged cell with firmly clamped spacers. The collector is electrically contacted when the assembly is lowered and enters in contact with the rod that protrudes the cell.

6.5 Future perspectives

The presented set-up is versatile and can also be used for other type of measurements. Field emission and cross plane resistance studies would need only few minor adaptations. The design is such that also thermionic experiments under low pressure gaseous atmosphere are possible. Additionally, the height of the set-up was adjusted to be compatible to available XPS systems. This opens up a variety of possible research projects.

7 Phosphorus doped NCD films - growth & characterization

'There is something fascinating about science. One gets such wholesale returns of conjecture out of such a trifling investment of fact.'

Mark Twain

Research on thermionic and photo-enhanced emission processes using n-type diamond as emitter material has been gaining more and more attention. Dedicated sessions at several large conferences focused on the science and application of diamond junction cathodes evidence the emerging interest in the field. For these intensifying activities especially phosphorus doped nanocrystalline thin films are of particular significance. Besides efficient doping, thermionic electron emission is expected to relate to a number of materials' characteristics such as surface electron affinity, defect density, sp²:sp³-ratio within the film and the NCD-substrate interface. The recent progress using P-NCD as thermionic emitter requires a fundamental analysis of the emitter material. Therefore, the motivation for the presented study lied in the investigation of the crystalline quality and the role of the local dopant distribution.

7.1 Optical analysis of the CVD plasma

CVD of diamond is a process that involves excited gaseous species such as H, different hydrocarbons and possible dopants. The injected microwaves maintain the plasma state, which is characterized by permanent molecular excitation and de-excitation processes. Each of the mentioned molecules presents characteristic optical emission lines when electrons transit from a high energy to a lower energy state. By the collection of molecular emission spectra during a CVD process, it is possible to identify *in situ* the chemical composition of the plasma.

The presence and concentration of reactive plasma species strongly define the possible reactions during the deposition. Chemically active molecules of the dopant carrying feed gas are necessary in order to incorporate the dopant into the growing film. For P doping it is hence crucial to have a sufficient number of excited PH_x , $x \leq 3$ molecules ready to bond to active sites at the plasma-substrate interface. The reported incorporation ratio of P into (100)-oriented diamond is

0.02% [49] whereas 15% has been measured for (111)-surfaces [44]. For polycrystalline films with a typically random grain orientation, the ratio is expected within these limits. Accordingly, highly doped films require a high number of excited PH-molecules that are available for CVD.

7.1.1 Optical emission spectroscopy of P-containing CVD plasma

A typical CVD growth plasma contains more than 90% of H_2 , less than 10% of CH_4 and only low concentrations of dopant carrier gasses. This fact represents in the peak intensities of OES spectra which are highly dominated by the distinct lines of the Balmer serie. The H_{α} (656.3 nm), H_{β} (486.1 nm) and the H_{γ} (434.1 nm) lines and the bundle of molecular transitions between 550 nm and 600 nm evidence H. Figure 7.1 presents an overall emission spectrum normalized to the dominant H_{α} -line. Hydrocarbons are identified by CH and CH⁺ at 431.5 nm and 422.2 nm respectively. A change of relative intensities with increasing plasma power is not identified for H nor the hydrocarbons with our experimental arrangement. The relative line intensities do not shift proportionally to the plasma power. A detailed look on the P-related spectral line reveals a relative increase with the injected energy. Figure 7.2 shows spectra recorded from a PH_3 plasma corrected by the data from a pure H_2 -plasma for an enhanced signal affiliated to P. For security reasons, PH_3 used at IMO is diluted in H_2 at a concentration of 200 ppm, *i.e.* the spectra always reveal clear H₂ signatures. Normalization to the H_{γ}-peak allows a comparison of the different measurements. The presence of P in the plasma is evidenced by the spectral line at 344.4 nm that is attributed to PH. Due to the limitations of the optical set-up, no absolute quantitative conclusion can be drawn. No spectral line from CN, typically present at 388.3 nm is detected. Even though, this does not rule out the presence of N, it suggests a low N-contamination level that lies below the optical detection limit of the used set-up.

The rising PH-concentration with increasing plasma power in PH₃-H₂ plasmas is in agreement with reports of Bruno *et al.*. Based on combined OES and mass spectroscopy, a decomposition process of PH₃ into PH and H₂ through dissociation upon electron impact or through molecular processes has been suggested [97]. The above results from diamond CVD follow the same trend at far lower Pconcentrations. Besides the plasma-activated PH₃ decomposition into PH, solid red and black P forms and deposits on the reactor walls. Aiming at high P-incorporation it is advantageous to use high plasma powers, *i.e.* temperatures, in order to supply sufficient PH-radicals. These findings are agreement with the successful P-doping of single crystals at elevated temperatures [50, 98].



Figure 7.1: Normalized overall OES spectrum of a CVD plasma for P-NCD deposition. The most prominent emission lines associated to H and CH are indicated. No changes of the relative line intensities with the injected plasma power are resolved.



Figure 7.2: Detailed view of the PH emission line at 344.4 nm. The spectrum is normalized to the H_{γ} -line. The number of PH radicals increases with the injected microwave power.

7.2 Identification of optimum CVD conditions for P-NCD growth

The concentration of activated chemical species in the plasma is function of the plasma temperature and gas composition [99]. This fact provoked several experimental series to gain insight into the influence of the different experimental parameters of CVD. At the same time this study served to establish the process for P-NCD growth in the ASTeX PDS17 reactor that had been used only for homoepitaxy. Cleaned and seeded Si (Ch. 5.1) was used as substrate. The characteristics of P-NCD deposition and the resulting films are presented through the results of four selected experimental series listed in Tab. 7.1: In series (I) the plasma power was varied between 800 W and 1500 W while the carbon concentration was kept constant at 1% C:H. The effect of the C:H concentration in plasmas of high density was studied in (II). (III) investigated the impact of the PH₃ concentration on morphology and growth of NCD films. Conditions for the growth of P-NCD were optimized in (IV). For all experiments the total gas flow was set to 500 sccm, the working pressure was 50 Torr (66.7 mbar). The power and pressure ramp up until reaching the final set point for a respective deposition took typically few minutes. For the subsequent characterization, thin films from experiments with the improved parameters were used.

Series	Plasma power (W)	C:H conc. (%)	P:C conc. (ppm)
I	1500	1.0	500
	1200	1.0	500
	1000	1.0	500
	900	1.0	500
	800	1.0	500
11	800	0.5	500
	800	1.0	500
	800	3.0	500
	1000	1.0	500
	1000	1.0	1000
	1000	1.0	2000
	1000	1.0	5500
IV	850 → 950	1.0	0
	850 → 950	1.0	1000
	850 → 950	1.0	5000
	850 → 950	1.0	10,000

Table 7.1: Overview about the experimental series with the aim to evaluate optimum parameters for P-NCD growth.

7.2.1 Influence of plasma power

The injected microwave power controls the plasma chemistry and temperature (Ch. 5.2.2) which in consequence affects the substrate temperature. Samples grown in plasmas of different power densities feature considerable variations in their morphologies resulting from the chemical processes at the surface. Figure 7.3 presents the sequence of films. At 1500 W injected MW power resulting in substrate temperatures of 1000°C individual grains with a crumbly substructure develop (Fig. 7.3(a)). The initial power density estimated from the plasma geometry is approximately 106 W cm $^{-3}$. The highly energetic plasma partly etches the nucleation seeds, and leads to diamond chunks instead of a continuous film. Only films grown at 700°C are characterized by a coating with uniformly sized faceted grains (Fig. 7.3(e)). The intermediate films Fig. 7.3(b) to (d), few containing pinholes, depict the trend to (1) a more defined crystallinity and (2) smaller grains toward lower deposition temperatures. All films were grown for 30 min. and despite their different morphologies and thicknesses prudent comparisons are legitimate. Background corrected and normalized Raman spectra evidence a clear sp³-carbon signature at 1333 cm⁻¹ and a notably low sp²:sp³-ratio. A plot of the treated data, exemplary for all following studies, is given in Fig. 7.4(a). The general increase of non-diamond carbon as function of the plasma power, *i.e.* substrate temperature is illustrated in Fig. 7.4(b). The graph presents data from Lorentz fitted spectra of the diamond peak ((1333.3 \pm 0.5) cm⁻¹), the G-band at (1565 \pm 15) cm⁻¹ and a second sp²-related band at (1480 \pm 10) cm⁻¹. The black data points refer to the sp²:sp³-ratio evaluated from the G-band while the red data shows the trend when the band at 1480 cm^{-1} is considered. The curves are a guide for the eye. Higher deposition temperatures lead to an enhanced sp²-content. This fact is in agreement with the poor crystalline quality seen by SEM. Since better phosphorus incorporation has been reported at temperatures greater than 800°C for single crystals [44, 49], the incorporation into NCD is expected to be a function of the substrate temperature too. The following experiments were conducted between 900 and 1000 W which was a convenient compromise for good quality films and elevated substrate temperatures.

7.2.2 Influence of CH₄ concentration

Series II (Tab. 7.1) considers the effect of the C:H-ratio in the plasma. A moderate plasma power and a low P:C concentration were chosen to minimize their impact on the film morphology. Figure 7.5(a) shows that low (0.5%) C:H concentrations lead to inhomogeneous grain sizes up to 500 nm. At higher C-rates, *i.e.* 1.0% or 3.0% (Fig. 7.5(b) and (c)), the grains develop more uniformly in size. The comparison of the Raman diamond peak with the G-band, displayed in Fig. 7.6, states the increase of graphitic carbon in the film with the (C:H)_{gas}-concentration. Moreover, enhanced CH_4 -concentrations up to 3% C:H lead to higher growth rates. The presented results are in positive agreement with experiments of B-doped and intrinsic NCD. Detailed studies have shown the impact of the C:H-ratio in the CVD plasma



Figure 7.3: SEM images of P-NCD films grown at different microwave powers (series I) which directly influence the substrate temperature: (a) 1500 W, (b) 1200 W, (c) 1000 W, (d) 900 W, (e) 800 W.



Figure 7.4: (a) Raman spectra of P-NCD films (series I). The spectra feature all known peaks for NCD. (b) The $sp^2:sp^3$ -ratio in P-NCD films evaluated by the peaks ratios from the G-band and the band at 1480 cm⁻¹ with the diamond line is function of plasma power. The curves are guides for the eye.



Figure 7.5: Top-view images of series II showing the impact of the C:H concentration on the film morphology: (a) 0.5%, (b) 1.0% and (c) 3.0%.



Figure 7.6: The development of the $sp^2:sp^3$ -ratio in P-NCD films with increasing C:H-ratio in the gas phase. The curve is a guide for the eye.

on the sp²:sp³-ratio in the grown film [9, 100]. C:H-ratios above 3% are certainly not beneficial due to the development even smaller grains. In case of P-doping, the dopants are expected to incorporate at a considerable rate in the grain boundaries where strain is more efficiently buffered. For further experiments, 1% C:H was chosen which is a satisfying compromise for all experimental parameters. It allows high dopant concentrations keeping the maximum gas flow at the standard limit of 500 sccm and renders excellent quality NCD at the same time.

7.2.3 Influence of PH₃ concentration

The low incorporation ratio of P into diamond compared to B-doping requires elevated PH₃ concentrations in the plasma in order to grow highly doped NCD films. The comparison of deposited films of series III in 500 ppm (P:C)_{gas}, 2000 ppm (P:C)_{gas} and 5500 ppm (P:C)_{gas} respectively (Fig.7.7) reveal the impact of the PH₃ concentration. While the film grown in the lowest PH₃-concentration featured faceted grains, Fig.7.7(a), the degree of crystallinity considerably decreased when



Figure 7.7: Series of SEM images presenting the influence of the P:C ratio in the gas phase on the film morphology without taking care of an appropriate ramp up: (a) 500 ppm, (b) 2000 ppm, (c) 5500 ppm.

up to 5500 ppm (P:C)_{gas} were used. Figure 7.7(c) shows individual 'cauliflower'type grains. In between those protruding features, the material appears to be of poor crystallinity. The morphology featured similarities to the films grown at high temperature (cf. Fig. 7.3(a)) and suggested the experimental conditions to be close to the diamond region in the carbon phase diagram. Figure 7.7(b) visualizes the gradual degradation of the grains for the intermediate film.

Due to morphology similarities to the plasma power series I, all follow-up experiments aimed at reducing the temperature in the initial growth stage for depositions in highly P-concentrated plasmas in order to prevent the nanometric seed crystals to be etched. A series (IV) of four samples was prepared in nominal (P:C)_{gas} concentrations of 0 ppm, 1000 ppm, 5000 ppm and 10,000 ppm. The deposition temperature was kept at 700°C (850 W) during the first 5 min before being set to the final value of $(810 \pm 10)^{\circ}$ C attained by 950 W. Reflection interference of the He-Ne laser (633 nm) allowed *in situ* thickness monitoring of the growing film and to stop the process at a film thickness of 320 nm. The evolution of the growth rate with increasing (P:C)_{gas} is presented in Fig. 7.8. In the selected experimental conditions, the growth rate for depositions in 10,000 ppm P:C was (10.5 ± 0.6) nm min⁻¹, being double in respect to nominally undoped films (5.2 nm min⁻¹). The shaded band represents the growth rate fluctuations resulting from similar experiments, not part of the series presented here, in identical conditions.

The above mentioned conditions allow to deposit homogeneous and uniform NCD films with pronounced grains of random orientation for all PH₃ concentrations (Figs. 7.9(a)-(d)). The grains are crystalline with lateral grain sizes ranging from 50 to 200 nm for the films of 320 nm thickness. The average grain size decreases from 250 nm to approximately 150 nm as function of P:C-ratio. While grains with defined edges of random orientation are observed for the nominally undoped film (Fig. 7.9(a)), a preferential orientation of the grains develops toward (100)-facets at a higher PH₃ levels. SEM images of the intermediate films (Fig. 7.9(b), (c)) present the changeover to cubic facets that are typical for the (100)-orientation. Fig. 7.9(d) features primarily (100)-facets. Moreover, morphological imperfections, such as notched edges and facets, are revealed with rising (P:C)_{gas} ratio. In be-



Figure 7.8: Evolution of the growth rate as a function of the (P:C)_{gas} ratio. All other experimental parameters were kept constant: P = 1000 W, p = 50 Torr, C:H = 1%.

tween the prominent grains, crystallographically undefined granules of a few tens of nm developed. Small grains in consequence mean more grain boundaries, hence an elevated concentration of sp²-carbon. Film depositions in C:H concentrations $\leq 0.2\%$ based on the findings of diamond homoepitaxy with PH₃ added for doping did not provide successful results. Despite standard cleaning, the films reproducibly peeled off the Si substrates which indicates high compressive stress. As a consequence, growth at extremely low C:H-ratios was not further studied.

Figure 7.10 presents the background corrected and normalized Raman spectra of series IV. Overall, all samples feature an excellent film quality. A pronounced peak, a known feature from Raman spectra of NCD films assigned to deformed CH_{x} bonds, is present at 1138 cm^{-1} and therefore reveals the presence of H [101]. Broader modes around 1480 cm^{-1} and 1550 cm^{-1} evidence sp²-carbon in the grain boundaries. The significantly higher peaks relating to P-NCD illustrate the higher ratio of graphitic carbon, in comparison to its intrinsic counterpart. The P-NCD peaks positioned between 1333.1 cm⁻¹ and 1333.9 cm⁻¹ for the highest doped film, suggest a distorted lattice. For measurements on different spots, the diamond peak shift towards higher wave numbers with its corresponding statistics is shown in Fig. 7.11(a). The dashed line at 1332.7 cm^{-1} references the signature of sp³-hybridized carbon and refers to scattering in an undisturbed diamond lattice [94]. At this point the observed blueshift with increasing PH₃ concentrations cannot be explained. Commonly redshifts due to tensile stress in micro- and single crystalline P-doped diamond layers have been reported [60, 102]. In the present case, the shift possibly relates to a shorter phonon lifetime due to the P-induced structural defects or to intrinsic micro-stress. For most films, the peak shift is accompanied by peak broadening which is a second indicator for degrading crystallinity. Just as for in the previous sections, the relative sp²:sp³-ratio was evaluated from the normalized Raman spectra. Figure 7.11(b) clearly states the progressive increase of sp^2 -carbon as a function of the P-concentration.



Figure 7.9: P-NCD films of series IV (320 nm thick) grown at 1% C:H at nominal (P:C)_{gas} concentrations of (a) 0 ppm, (b) 1000 ppm, (c) 5000 ppm and (d) 10,000 ppm.



Figure 7.10: Normalized Raman spectra of series IV. The sharp peak at 1333 cm⁻¹ evidences P-NCD of excellent quality. With increasing $(P:C)_{gas}$ the content of graphitic carbon (bands around 1480 cm⁻¹ and 1550 cm⁻¹) visibly increases.



Figure 7.11: (a) Evaluation of the diamond peak position in function of the $(P:C)_{gas}$ ratio. The peaks shift to higher wave numbers, the position in an undistorted lattice is indicated by the dashed line. (b) Trend of the sp²-content evaluated from the Raman spectra of 7.10 as function of the augmenting doping level.

7.3 Structural analysis of highly doped P-NCD

For the different spectroscopy studies, films with a potentially high phosphorus content were selected. The aim was to identify and locate the incorporated P-dopants within the films and to compare the results to the findings of homoepi-taxial layers. For the following experiments, P-NCD films of 320 nm thickness, identical to series IV, were grown under the optimized conditions (Ch. 7.2.3) in 10,000 ppm (P:C)_{gas} concentration.

7.3.1 Transmission electron microscopy

TEM studies are an appropriate technique to assess structural defects within the grains and at grain boundaries after the CVD of P-NCD had been developed. The SEM image of the film, Fig. 7.12(a), prior to TEM sample preparation shows the typical grain morphology of highly doped P-NCD presenting notched grains and edges.

Randomly oriented and densely packed diamond grains are shown in the low magnification ADF-STEM image, Fig. 7.12(b), which confirms the previously deduced grain size of 50 to 200 nm. From the shaded contrast, structural defects within grains are already discernible at low magnification. Figure 7.12(c) presents a randomly selected grain at higher magnification showing the elevated concentration of planar defects, mainly $\Sigma = 3$ {111} twin boundaries (cf. arrows). The $\Sigma = 3$ {111} twin is considered a low angle boundary with a high degree of symmetry and is the most prominent planar defect in CVD diamond [77]. Dopant induced strain in the crystalline lattice is accommodated via the atomic relaxation at the twin boundaries which are easily recognizable by their characteristic intersection angle of 71° [103]. Elevated PH₃ concentrations during CVD and the high



Figure 7.12: (a) SEM image of a 320 nm thick P-NCD film grown at 10,000 ppm P:C in the gas phase. (b) Low magnification ADF-STEM image showing randomly oriented diamond grains. (c) ADF-STEM image of a selected diamond grain. Arrows indicate $\Sigma = 3$ {111} twin boundaries.

growth rates certainly contribute to the formation of additional structural defects and strain upon the dopant incorporation [104].

7.3.2 X-ray diffraction

The decline of (111)-facets qualitatively observed in SEM, was semi-quantified by XRD. Marginally shifted in comparison to its literature value of 43.91° the diamond (111)-diffraction peak appears under 44.0°. For diffraction experiments with polycrystalline diamond thin films, long acquisition times are necessary. Figure 7.13(a) displays the background-corrected scans for the P-NCD samples of series IV. Thorough peak analysis by pseudo-Voigt peak fits and subsequent integration confirms (1) the decrease of (111)-facets and reveals (2) the crystalline degradation for P-NCD grown in highly P-concentrated plasmas. The upright triangle indicates the peak center. Figure 7.13(b) presents the trends of the (111)-cutback (black data points) and the peak-broadening which indicates grain size reduction and crystalline deterioration (red data points). The film grown at 10,000 ppm P:C features a 34% drop of (111)-peak intensity and a 16% increase in peak width in comparison to the nominally undoped sample. XRD proves that P-NCD deposition in the selected conditions, considerably impacts the crystalline configuration. Already much weaker in absolute intensity, the (220)-diffraction is observed at 75.3°. Enhanced doping levels lead to peak broadening and an increased (220)-signature, however the clear evolution deduced for the (111)-peak is not strictly traceable here.

7.4 Localization and quantification of phosphorus dopants

SIMS as well as cathodoluminescence measurements were conducted by courtesy of our collaborators at Groupe d'Etude de la Matière Condensée (GEMaC) of University of Versailles. For a better signal-to-noise ratio, a P-NCD film of 1.1 μ m thickness was deposited. Colleagues at EMAT, University of Antwerp assisted with high-resolution spectroscopy measurements. Following the established procedure, an electron transparent sample for STEM was prepared for the experiments by ion-milling a 320 nm thick P-NCD film [96].

7.4.1 Secondary ion mass spectroscopy on P-NCD

SIMS quantification occurred through comparison with calibrated standards. The measurements evidence the PH₃-driven plasma chemistry that leads to a P content of 1.0×10^{19} cm⁻³ near the surface of the film (Fig. 7.14). The linear decline in concentration throughout the $1.1 \,\mu$ m thick film to 7.5×10^{18} cm⁻³ at the diamond-substrate interface suggests a hindered incorporation in the early growth stage.



Figure 7.13: (a) XRD $\theta - 2\theta$ -plot of the diamond (111)-diffraction peak. Peak heights and pseudo-Voigt fits display the decline of the (111)-fraction when the NCD is P-doped. (b) Evolution of the fit area (black) confirming the disappearing (111)-phase and the peak width (red) demonstrating the crystalline deterioration.


Figure 7.14: SIMS data of the 1.1 μ m thick P-NCD layer on Si. The dotted horizontal line marks 7.5 × 10¹⁸ cm⁻³.

Despite the initial abundance of grain boundaries in comparison to the grains, phosphorus does not preferentially incorporate in sections of non-diamond carbon. The binary representation of the silicon and carbon signal at the top of Fig. 7.14 indicates the position of diamond substrate interface. Besides the identification of phosphorus, a constant level of 10^{21} cm⁻³ of incorporated H was measured. A considerable percentage of it should be located at the grain boundaries [5]. During the deposition, grain boundaries present dangling bonds that passivate easily with H. Due to the characteristics of dynamic SIMS, the identified concentration values present an average over the sputtered area. In the case of polycrystalline material such as P-NCD, this involves grain and grain boundary regions, so that the assessed P-concentration refers to a mean value in the material. The ratio of incorporated P detected by SIMS and the P-concentration, the mean incorporation ratio is 2.7×10^{-4} . This estimate is comparable to results previously published for the growth of P-doped (100)-oriented single crystals [105].

7.4.2 STEM characterization on P-NCD

The average EDX spectrum summed over the whole region displayed in Fig. 7.15(a) shows clearly the P K-line at 2.01 keV and therefore confirms the presence of the dopant in the material. The extremely low P signal meant a high beam current (250 pA) and an acquisition time of 90 min. needed to be used. The detected Si signal is a contaminant, arising from the substrate during sample preparation. Oxygen contamination is present in the form of oxides. Based on the summed EDX-data the P content was quantified to 0.02 at.% which corresponds to

 3.5×10^{19} P cm⁻³. This result is in good agreement with the quantification by SIMS and supports the earlier assumption that P incorporates in the developed grains rather than in grain boundaries. Within a selected grain, the elemental composition could be mapped. Figure 7.15(b) presents an ADF-STEM image of the scanned area, together with the corresponding C- (Fig. 7.15(c)) and P-map (Fig. 7.15(d)) obtained by STEM-EDX. The selected grain features a fivefold twin. Despite the low signal and in consequence of the low number of counts, the P map displays a uniform distribution of P throughout the sample. The P related signal follows the C signal, indicating an incorporation of P into the diamond lattice. At some measurement spots, a small enrichment of P was detected at grain boundaries, which was certainly not systematic, as displayed by the data here.

7.4.3 Cathodoluminescence on P-NCD

The method of Barjon et al. to evaluate the doping level from CL spectra was already used on thick P-doped microcrystalline films, evidencing crystallographic orientation dependent incorporation of the donor. It can therefore serve as a auideline in the analysis of P-NCD films [46, 106]. The normalized CL spectrum (Fig. 7.16) presents one dominant peak at 5.16 eV related to the neutral P-bound exciton recombination assisted by a transverse optical phonon (BE_{D}^{TO}). This clear signature confirms P-incorporation as donor, thus at substitutional sites in the diamond lattice. P-atoms that sit at lattice positions locally deform the electronic structure of the covalent bonds. A small band at around 5.33 eV refers to nonphonon assisted P-bound exciton (BE_p^{NP}) recombinations. With respect to epitaxial layers, both peaks feature large line-widths indicating a lower crystalline quality of the grains. The FWHM of BE_{P}^{TO} is 82 meV which is clearly larger than the reported values (12 meV) for single crystalline diamond measured in the same conditions [98]. The absence of the free exciton peak, normally found at 5.27 eV, indicates a donor concentration greater than 10^{18} cm⁻³. As consequence of the polycrystallinity, no finestructure in the bound exciton peaks, as reported for single crystals, was resolved [107]. Yet, the spectrum allows to assess the phonon energy from the non-phonon and phosphorus bound exciton recombinations as well as from the TO+O replica and its main peak. Table 7.2 summarizes the peak positions and lists the corresponding phonon energies. By means of Gaussian peak fits, the TO phonon energy is estimated to be 131.8 meV ($BE_p^{PP} - BE_p^{TO}$). For the optical phonon involved in the replica, 152.7 meV ($BE_p^{TO} - BE_p^{TO+O}$) was deduced. The latter value implies a wave number of 1234 cm⁻¹ which means an error of 8% to the diamond specific peak at 1332.7 cm^{-1} measured by Raman spectroscopy. The discrepancy is certainly due to imprecise peak fitting of the broad peaks.

All peaks are slightly down-shifted in comparison to reported values of (111)- and (100)-oriented single crystals [47, 108]. The exciton energies presented here are in good agreement with the data of a 2.5 μ m microcrystalline film from Ghodbane *et al.* who reported peak shifts to lower energies with increasing film thickness for polycrystalline films [63]. Deviations from the known exciton energies originate from the polycrystallinity and the twins. Due to the elevated number of crystal



Figure 7.15: P and C distribution in a selected, single diamond grain. (a) Summed EDX spectrum of the grain. The peak indications correspond to the colors in the elemental maps. (b) ADF-STEM image of the mapped region presenting the diamond grain, (c) corresponding C map and (d) P map.

Transition	Associated energy in CL (eV)	Phonon energy (meV)
BEPP	5.287 (5.331) [*]	
BE _P TO	5.155 (5.191)*	131.8
BE _P TO+O	5.002 (5.027) [*]	(131.8 + 152.7) = 284.5

Table 7.2: Exciton recombinations and calculated phonon energies (at 30 K) in P-NCD. In values in brackets refer to reported values of (111)-single crystals.

^{*}Phonon energies from measurement at 38 K in P-doped (111)-single crystals [107].



Figure 7.16: Normalized CL spectrum of the P-NCD film acquired at 30 K.

imperfections, excitons are likely to be associated to defects resulting in the mentioned line broadening. A more efficient incorporation into (111)-facets of microcrystalline diamond films has not been evidenced here. The volume of NCD grains is likely to be too small to resolve possible crystallographic effects in nanometric dimensions.

7.5 Thermionic characterization of P-NCD

P-NCD for thermionic characterization requires a conductive substrate to provide the electrical back contact. In order to investigate what properties and growth parameters lead to enhanced emission characteristics, a set of films was deposited on both bare Mo and Mo with an evaporated Re layer (Re/Mo) of \approx 10 nm. The Re interlayer was intended to improve the charge transfer across the substratediamond interface as Re is known not to form carbides [109]. As a result, P-NCD on Re/Mo is fragile and readily chips off. Table 7.3 summarizes the C:H- and P:Cratios of the series. The P-NCD films were deposited at 50 Torr (66.6 mbar) and temperatures of (750 ± 20)°C. All P-NCD films were approximately 300 nm thick.



Figure 7.17: Raman spectra of P-NCD on Mo and Re/Mo substrates respectively. Films on Re interlayers are characterized by an enhanced sp²-phase.

P-NCD on a Re interlayer features a generally higher sp²-content than films on bare Mo. Figure 7.17 evidences the higher sp²-content in Raman spectra for two selected sample sets.

ample	C:H conc. (%)	P:C conc. (ppm)				
10-1	1.0	5000				
10-2	3.0	5000				
10-3	0.4	10,000				
10-4	0.5	10,000				
e/Mo-1	1.0	5000				
e/Mo-2	1.0	10,000				
е/Мо-З	0.5	10,000				
e/Mo-4	0.5	10,000				
	ample lo-1 lo-2 lo-3 lo-4 e/Mo-1 e/Mo-2 e/Mo-3 e/Mo-4	ample C:H conc. (%) Io-1 1.0 Io-2 3.0 Io-3 0.4 Io-4 0.5 e/Mo-1 1.0 e/Mo-2 1.0 e/Mo-3 0.5 e/Mo-4 0.5				

Table 7.3: Overview about the series of P-NCD on Mo and Re/Mo substrates whose thermionic emission properties were measured at ASU.

Emission from P-NCD on Mo

All films emit thermionic currents that follow an exponential curve as a function of temperature. Thermionic emission is a mechanism that is very sensitive and readily impacted by surface adsorbates. In the following discussion, only data after a run for surface stabilization is considered. Richardson-Dushman fitting (Ch. 4.1) over the entire measurement range gives work functions of 1.20 eV (*Mo-2*), 1.69 eV (*Mo-3*) and (*Mo-4*) and 2.02 eV (*Mo-1*). Typically, the values for a freshly hydrogenated sample converge to their final value after a few measurement cycles. For some measurements the Richardson-Dushman equation, does not fully satisfy the trend of the data points. A more susceptible view of the evolution of the emission current is obtained when $\ln (i/\tau^2)$ is plotted versus $1/\tau$:

$$\ln\left(\frac{j}{T^2}\right) = \ln A_R - \frac{\phi}{k_B}\frac{1}{T}.$$
(7.1)

Figure 7.18 depicts the emission characteristics for P-NCD on bare Mo on e logscale as to eq. 7.1. The distinction of a) and b) in the graph's legend refers to different measurements. A dependence from the doping level is distinct. The emission current density of the sample grown under 5000 ppm P:H (Mo-1) is approximately two orders of magnitude smaller than for films grown at 10,000 ppm P:H (Mo-3). For a pure Richarson-Dushman behavior, the graph should be linear over the entire temperature range. Most of the curves, however, reveal a change of slope or break at around 667 K (394°C). The dotted line marks the transition zone. Based on eq. 7.1, this indicates a development of the surface work function. Fitting of the data in the low temperature region result in work functions between 0.16 and 0.4 eV. As surface adsorbates desorb when the sample is heated, not much importance should be given to these values. However, the data set suggests a second mechanism that dominates the emission characteristics in the temperature range between 523 K (250°C) and 673 K (400°C). For temperatures above this threshold, the measurements of the individual samples are reproducible and the Richardson-Dushman equation is a good approximation. Fitting of data in this reduced temperature range yields work functions of 0.36 eV (Mo-4), 0.79 eV (Mo-2), 0.90 eV (Mo-3) and 0.95 eV (Mo-1) which contrast significantly to the results from the full fit. Despite the more accurate fitting procedure, the deducted values for the work function are extremely and unrealistically low.

So far, there is not enough information to understand the origin for the discrepancy. Desorption or reconstruction processes at the surface are likely to play a role before the thermionic emission initiates. Different contributions from grains and grain boundaries are not expected to be significant, thermionic emission from Ndoped NCD has been recently reported to be spatially uniform [110]. The nanometric Mo₂C layer that forms at the substrate-diamond interface in the early growth is likely to influence the cross-plane charge transfer and Richardson constant, however should not impact the surface emission barrier [111].

Emission from P-NCD on Re/Mo

The emission currents from P-NCD on Re/Mo are marginally higher than the most powerful emitter on Mo. Figure 7.19 depicts the thermionic performance in the logarithmic plot. The emission curves hint at a better measurement reproducibility for temperatures above 650 K. Some of the emission curves feature a bend at 667 K (394°C), as previously mentioned for films on Mo substrates. From full exponential Richardson-Dushman fits, low work functions of 1.94 eV (*Re/Mo-1*), 1.77 eV (*Re/Mo-2*) and 1.3 eV (*Re/Mo-3*, *Re/Mo-4*) are obtained. Partial linear fits in the log-representation between 670 K and 950 K result in work function values of 0.45 eV (*Re/Mo-2*), 0.78 eV (*Re/Mo-3*), 0.81 eV (*Re/Mo-4*) and 0.91 eV (*Re/Mo-1*). Just as for Mo, partial fitting yields extremely low work functions. To date, there is



Figure 7.18: Emission current densities for P-NCD on Mo substrates. For some measurements the log-representation exposes a bend whose origin is not yet clarified. The referencing of the different samples is according to Tab. 7.3.

no final conclusion about the real work function value. A systematic error linked to the of current meter's measurement range is excluded, as the observation is valid for several current ranges. It is justifiable to take the full-fit data as upper estimation. However, given the impact on the fits, the observation of the emission current change cannot be neglected. For both types of substrates, the emission is impacted by two contributions (1) the enhanced sp²-carbon in the P-NCD films and (2) by the presence and resistance of the interlayer itself. Even though there is no obvious trend for optimized emission currents from Re/Mo films, the currents visibly scale with the doping level. Carbide interlayers e.g. Mo₂C limit the emission current density which has been observed in similar studies with N-doped NCD. Besides the enhanced emission, Koeck et al. noted increased values for the Richardson constant with Re interlayers [112]. According to the above observations, the high density of grain boundaries is likely to compensate the effect of the resistive carbide layer on Mo substrates. Table 7.4 presents an overview of the work function and Richardson values deduced from the full exponential fits as well as the linear approximations in the reduced range. The comparison of the data clearly states the discrepancy of up to almost 80% between the different work function values. The most powerful emitters present the best agreement of above 60%. The series on Re/Mo reveal consistent trends: the work function scales with (1) the sp^2 -content in the film and (2) the P-doping level. The tendency of enhanced Richardson constants for NCD on Re interlayers, recently published, has not been confirmed here [112]. The present study does not enable any further insight in the significance of the Richardson constant.

Figure 7.20(a) plots the emission current density of the leading samples, *Re/Mo-4* and *Mo-2*. The highest emission current for bare Mo was measured for films on *Mo-2* grown at 3% C:H. Expanded grain boundaries provide more efficient conduc-

Sample	Work function (eV)		
	full fit (ff)	limited fit (lf)	ratio $\left(\frac{\phi_{\rm lf}}{\phi_{\rm ff}}\right)$
Мо-1	2.02 ± 0.15	0.95 ± 0.05	0.47
Mo-2	1.20 ± 0.07	0.79 ± 0.01	0.66
Мо-3	1.69 ± 0.04	0.90 ± 0.003	0.53
Mo-4	1.69 ± 0.06	0.36 ± 0.02	0.21
Re/Mo-1	1.94 ± 0.01	0.91 ± 0.01	0.47
Re/Mo-2	1.77 ± 0.09	0.45 ± 0.03	0.25
Re/Mo-3	1.30 ± 0.05	0.78 ± 0.01	0.60
Re/Mo-4	1.30 ± 0.04	0.81 ± 0.01	0.62

 Table 7.4: Comparative overview of work function and Richardson constant values deduced from full and limited fits.



Figure 7.19: Emission current densities for P-NCD on Re/Mo substrates. The referencing of the different samples is according to Tab. 7.3.

tion paths for emission electrons. Besides the sp²:sp³-ratio, high P-concentrations enhance the current which was the case for *Re/Mo-4*. The present emission record data of P-NCD (*Mo2009*, $\phi = 0.9$ eV) and data from N-doped film (*N-Mo2006* $\phi = 2.0$ eV; *N-Mo2009*, $\phi = 1.29$ eV) is given for comparison [41, 64, 113]. Both of the recent P-NCD samples feature an emission improved by a factor of approximately two (*Mo-2*) and five (*Re/Mo-4*) respectively. The experiments and elaborated control of P-NCD deposition, a considerable achievement of this thesis, result in an improved thermionic performance of the films. The emission characteristics of the presented P-NCD films excel the present P-doped state-of-the-art emitters. However, the full fit work functions of the IMO P-NCD, being the reference characteristics to date, are slightly greater. The highest emission currents have been measured from N-doped NCD on an optimized (N)UNCD sublayer and a Re/Mo substrate [112]. Superior to the presented P-NCD characteristics, the enhanced Richardson constant is most significant contribution for the performance. This fact



Figure 7.20: (a) Comparison between the most efficient emitters from this study and data previously published in [64] (b) Emission curve illustrating the effect of H-desorption from 1000 K inducing an increase of the surface potential barrier.

shows the need of further studies and at the same time the existing room for the development of efficient P-doped material.

The effect of the H-termination on the thermionic emission is shown in Fig. 7.20(b). Starting from 1000 K, H desorbs from the surface. Due to the loss of the NEA, the surface potential barrier for electrons increases which instantly induces a drop in the emission current (Ch. 4.1.1).

7.5.1 High resistance measurements of P-NCD

The electrical characterization of P-NCD is not straightforward due to the high resistance of the films at room temperature. The resistance of an O-terminated 150 nm thick film (1% C:H, 10,000 ppm P:C) on FS was measured between 550 K and 900 K $(\Delta T = 50 \text{ K})$ by the alternating voltage method and IV-sweeps. As deposited under identical conditions as P-NCD from series IV (Tab. 7.1), similar characteristics are assumed. Prior to the measurements, the wire-bonded sample was annealed in the vacuum oven for several hours to create good electrical contacts. At each temperature, the system was left to stabilize for approximately 20 min before the measurements were taken. The corresponding P-NCD sheet resistance as a function of temperature is presented in Fig. 7.21. It was calculated taking into account the dimensions of the bar structure. An additional factor corrected the applied voltage at the outer contacts. The black data points refer to direct resistance measurements by means of the alternating polarity method reviewed in Ch. 5.11. Below 550 K the current was of the noise level and not reliable. The resistance values deduced from IV-sweeps are represented by red points. The straight lines are guides for the eye. Both methods yield consistent results. The general behavior of the P-NCD film is of a typical semiconductor. The resistance drops with increasing temperature which indicates the thermal activation of charge carriers.



Figure 7.21: Sheet resistance as a function of temperature of P-NCD. The black points refer to data that was collected by the alternating polarity method. The values deduced from IV-sweeps are represented by red points.

The sheet resistance is around 5.0 G Ω at 500 K and drops to a few tens of M Ω at 900 K. The high temperature settings required long stabilization times before the measurements could be started. For all temperatures, the measured resistance values initially drifted downwards until they eventually saturated. The data presents the measurements to be extremely sensitive to temperature instabilities. Temperature sweeps from low to high or high to low temperatures with alternating intermediate steps result in resistance values with a considerable variance. Despite annealed Ti/Pt/Au-contacts, some of the IV-sweeps feature a weak double Schottky-behavior. A tremendous challenge was to obtain stable measurements over a period of time. So far, the drift is assumed to relate to trapping or passivation at defects. Likewise, it is possible that the annealing effect is connected to the release or re-arrangement of H in the grain boundaries. Moreover, H which is localized at the grain boundaries could act as an electron trap hindering the charge transport [114]. Ballutaud et al. using deuterium as a tracer, reported bond modifications upon annealing [115]. The deuterium diffusion is governed by the sub-surface defects that are characteristic for polycrystalline diamond. Even after 12 h of annealing at 1050°C, H is still measurable in NCD films. Changes in the bonding configuration of polycrystalline diamond surfaces between H and C were evidenced upon low temperature vacuum annealing [116]. As a result it is deduced for the present study that H induced trapping or diffusion will consistently play a role in the transport process.

Moreover, grain boundaries and numerous crystalline defects at the grain-grain boundary interface as well as within the grains hinder the in-plane charge carrier transport.



Figure 7.22: P-NCD grown with 10,000 ppm P:C after the substrate cooling had been improved at the ASTeX reactor. In comparison to previous results (Fig. 7.9(d)), the film is visibly composed of (111)-faceted grains.

7.6 Recent improvements

In conjunction with a technical intervention at the substrate cooling water lines of the ASTeX reactor, the thermal coupling to the substrate holder and the substrate itself improved. As a result the deposition conditions for P-NCD needed an adjustment. As in earlier experiments, the total gas flow was 500 sccm. In order to reach substrate temperatures of 800°C, the working pressure had to be increased to 67 Torr (89.3 mbar), the plasma power was 2000 W. With the new CVD conditions highly doped P-NCD films with an enhanced number of (111)-oriented facets (Fig. 7.22(b)) can be deposited. The decline of (111)-oriented grains observed on P-NCD grown in highly P-concentrated plasmas which was discussed in detail in Sec. 7.3 is now significantly amended. Figure 7.22 depicts P-NCD which was grown with 10,000 ppm P:C in the gas phase. The impact of P is visible from the notched and stepped grain facets. This fact is expected to be beneficial for the incorporation of P into the diamond lattice. Research on (111)-oriented single crystal has proven to be advantageous for the incorporation of large dopants [44, 117]. At the same time these result show that slight changes in the deposition conditions can notably impact the NCD morphology and properties.

7.7 Conclusion

NCD films have been deposited by CVD under optimized experimental conditions and in plasmas containing high concentrations of PH_3 . Spectroscopic measurements of the plasma emission reveals a concentration dependence of PH-molecules with the injected microwave power. Aiming at high P-incorporation, deposition at powers above 900 W are preferred. High PH₃-concentrations deteriorate the P-NCD crystallinity and impact strongly the morphology. The observations from the CVD provoke the assumption that PH₃ impacts the plasma chemistry which reflects in enhanced deposition rates. Homogeneous NCD films were deposited at P:C-ratios up to 10,000 ppm in the plasma and temperatures of around 810°C. Despite the presence of numerous defects within the grains, primarily twin boundaries, the overall film quality as confirmed by Raman spectroscopy and electron microscopy was good. Detailed evaluation of Raman spectra has proven the impact of substrate temperature, C:H-ratio and the plasma dopant concentration on the sp²:sp³-ratio in the film. These findings will play a role in on-going thermionic characterization. P was effectively incorporated into the crystalline lattice of nanoscale diamond grains. High resolution spectroscopy techniques evaluated a concentration of around 1.0×10^{19} P cm⁻³. Although systematic preferential incorporation was not evidenced, fully developed grains featured an enhanced P content compared to sp²-carbon dominated regions. The doping level values resulting from SIMS, STEM-EDX as well as CL measurements are consistent and reveal an incorporation at substitutional lattice sites at a high rate. P-NCD on Mo substrates some with an additional Re layer have been characterized in terms of thermionic emission. All films featured measurable emission currents between 500 K and 1000 K. The optimized CVD of P-NCD for thermionic yielded high emission currents up to 1.4 mA (cm⁻²) at 900 K. From the results is deduced that emission current density scales with sp²-content and the doping level. The role of the Re interlayer as well as the deviation from the Richardson-Dushman relation is not fully understood. From resistance measurements semiconductor properties were deduced. Due to the dopant activation energy and numerous crystal defects the sheet resistance for P-NCD is high. For temperatures above 800 K, it ranges around 100 M Ω .

8 Routes toward boron doped diamond nanoparticles fabrication and applications

Diamond nanoparticles are developing toward a platform at the edge of nanotechnology, chemistry, physics and medicine [118–121]. Their high surface-to-volume ratio combined with their chemical and mechanical stability suggest a variety of applications spanning from magnetic sensing on single defects for quantum computing to surface-modified particles for biomarkers and drug-delivery. Most of the results reported have been conducted on undoped or nitrogen doped particles, however there is a large interest in electrically conductive, notably B-doped, nanoparticles. Fundamental and applied studies addressing nanoscale superconductivity or imaging and electrochemistry upon surface functionalization with suitable molecules will open up. Improved seeding of moulds has been reported promising for the making of conductive probing tips made from diamond [122]. MATCON envisaged to study the integration of conductive diamond nanoparticles into Si or Ge based composite materials for thermoelectric energy conversion. Moreover, doped nanodiamonds could be used as seeding crystals during CVD to avoid a first insulating layer between the substrate and the growing diamond films, which often is undesirable as it increases the interface resistance. To date, the synthesis of nanoscale diamond particles bases on (1) a bottom-up approach from typically sp²-carbon that transforms and crystallizes in a diamond configuration when the correct conditions are applied. The most prominent bottom-up technique is the detonation synthesis which refers to an oxygen-deficient mixture of carbon and solid explosives that is detonated resulting in typically 5 to 10 nm sized particles in a considerable volume of soot [123, 124]. (2) The ball-milling technique means the grinding of larger HPHT or CVD crystals into nano or micrometric shivers. In the meantime more techniques have been developed to produce nanodiamonds, particularly doped nanodiamonds [125]. The most straight-forward method is to coat undoped particles. Overgrown undoped diamond particles feature a conductive shell with a nonconductive center [126]. Boron doped ultrananocrystalline diamond was reported by the modification of glassy carbon powder [127]. Boron is still the only well-controllable shallow dopant for diamond resulting in p-type conductivity. Few attempts have been reported to obtain boron doped nanodiamonds. Ion implantation, although a successful method to control nitrogen incorporation for NV center studies [128], is not suitable to produce highly boron doped particles. The highly energetic ions impact the lattice inducing irreversible damage that rather leads to graphitization [129].

8.1 Ultrananocrystalline diamond

Ultrananocrystalline diamond films (UNCD) consist of nanometric diamond grains that are typically embedded in an abundant matrix of sp²-carbon. Instead of columnar grains that grow out of diamond seeds, UNCD growth is characterized by permanent re-nucleation resulting in nanograins without any preferred orientation throughout the entire film thickness [10]. Our interest in studying doped UNCD was twofold: (1) Diamond nanoparticles could be obtained with little technological effort from UNCD. The covalent bonds of the abundant grain boundaries are expected to be readily disaggregated by the mentioned top-down procedure. (2) As a consequence, we were interested to investigate the boron incorporation in UNCD films addressing the fundamental question of *in situ* doping efficiency of nanometric diamond grains. The films deposited in a home-built NIRIM-type CVD reactor which is presented in Ch. 5.3.1. In case of preferential incorporation in the amorphous phase, large quantities of the dopants are likely to be washed out after ball-milling. Prior to milling, the films underwent a thorough characterization in the material.

8.1.1 Characterization of the UNCD film

SEM images visualize a uniform film with a granular microstructure (Fig. 8.1(a)), the surface featured an average roughness R_a of approximately (3.0 ± 0.8) nm (Fig 8.1(b)). Films grown under 260 V bias are not crystalline at microscale and are under high compressive stress which manifests in convex bending of the substrate (Fig. 8.2(a)). The nucleation process under continuous bias voltage (bias-enhanced nucleation, BEN) is known to strongly influence the grain size and concentration of non-diamond carbon in undoped films [130]. The morphology of UNCD films grown in B-containing CVD plasmas at 260 V dc bias voltage did not significantly differ from the undoped counterpart.

Raman excitation at two different wavelengths assesses the film properties in respect to sp^2 - and sp^3 -hybridized carbon. The spectrum recorded at 488 nm excitation features two large bands (Fig. 8.2, red curve). The D-band at 1361 cm⁻¹ and G-band at 1600 cm⁻¹ confirm the presence of disordered and graphitic carbon [94]. No clear diamond signature is detected which is expected to be weak and probably masked by the intense bands. A pronounced peak, a known feature from Raman spectra of NCD films assigned to deformed CH_x-bonds [130], is present at 1170 cm⁻¹ and therefore reveals the presence of H [101]. As the interaction cross section of sp^3 -hybridized carbon increases with energy, excitation in the UV is expected to shed more light presence of sp^3 -carbon. The appearance of a minor peak at 1338 cm⁻¹ (Fig. 8.2, blue curve) next to the previously mentioned G-band (1594 cm⁻¹) upon excitation at 244 nm reveals the diamond in the film. The spectra in Fig. 8.2 are in agreement with previously published Raman studies of UNCD [131, 132].



Figure 8.1: (a) Top-view SEM image of a UNCD film grown at 5000 ppm B:C in the gas phase. The film does not feature crystallinity. (b) AFM images of a UNCD layer on Si. The gray scale bar refers to the height variation, the scan area covered $(1000 \times 1000) \text{ nm}^2$.



Figure 8.2: (a) Several μ m thick UNCD on Si, the film is highly stressed which manifests in the convex deformation of the substrate. (b) Raman spectra of a doped UNCD film acquired at 488 nm (red curve) and 244 nm (blue curve) excitation wavelength reveal an abundant sp²-matrix.



Figure 8.3: (a) HR TEM image of UNCD. Selected diamond grains are highlighted and their crystal planes indicated. (b) C K-edge of a EELS spectrum from a UNCD film featuring a clear π^* - as well as σ^* -peak. An exponential background signal (blue curve) is subtracted for B quantification.

The X-ray diffraction detects diamond (111) and (200) oriented crystal planes besides an intense Si (400) peak originating the substrate. A straight forward evaluation of the average grain size using the Scherrer equation (8.1)

$$\Delta(2\theta) = \frac{K\lambda}{\beta\cos\theta_B} \tag{8.1}$$

with the parameter Δ being the particle size, the shape factor K (\approx 1), the line broadening at FWHM β and the Bragg angle θ_B . Peak fitting yields grains between (8.3 ± 0.3) nm and (10.5 ± 0.1) nm in size. TEM and EELS measurements within a collaboration with EMAT helped to gain insight into the local boron distribution. High magnification bright field TEM images confirm nanometric diamond grains (Fig. 8.3(a)) that are embedded in an amorphous carbon matrix. The highlighted zones indicate the crystalline planes of the grains while the amorphous regions do not feature any regular substructure. The presence of a peak at 285 eV at the C K-edge in the EELS spectrum of Fig. 8.3 is the fingerprint of the 1s $\rightarrow \pi^*$ transition in sp²-hybridized carbon. The σ^* -peak refers to sp³-bonded carbon. EELS measurements proved boron incorporation of approximately 3.2 at.% in a film grown at 5000 ppm B:C in the gas phase. From the fine structure analysis preferential incorporation into the amorphous material was shown. Elemental mapping by STEM-EELS evidences the amorphous regions to be enriched with boron. The colour map (Fig. 8.4) clearly states the anti-correlation in counts of diamond-carbon and boron, while the boron maps correlates with the amorphous carbon signal [27]. The preferential boron dopant incorporation in the non-diamond phase, signalizes that the presented material is not appropriate for the production of doped diamond particles. Most of the dopants would be removed during the milling process.



Figure 8.4: Boron, sp^2 -C and sp^3 -C STEM maps (scan area: 150 nm × 150 nm) that illustrate the local bonding structure. The anticorrelation of the B and diamond signal is visualized in the overlay map.

8.2 Nanoparticle fabrication - from micro to nano

Within a collaboration between the research groups at IMO in charge of the diamond deposition, University of Würzburg experienced in bead-assisted desintegration and the research of diamond colloids and the high-resolution microscopy facilities at University of Antwerp we intended to produce highly boron doped nanoparticles by grinding a highly boron doped free-standing microcrystalline CVD film. Boron incorporation into polycrystalline diamond grains has been proven [27] and thoroughly studied, so grinding a doped microcrystalline film is expected to overcome the issues associated with doped UNCD as presented in Ch. 8.1.

8.2.1 The starting material: B-doped microcrystalline diamond

B-doped microscrystalline films, described in Ch. 5.3.2, were used as starting material for the grinding approach. The film featured randomly oriented microcrystals with an average crystal size around 7 μ m, with single grains measuring up to 20 μ m (Fig. 8.5(a)). Raman spectroscopy ($\lambda_{exc.} = 488$ nm) reveals a clear peak at 1325 cm⁻¹ related to sp³-bonded carbon (Fig. 8.5(b)). The peak shift between the front and back side is explained by the smaller grain size and higher grain boundary ratio. The Fano resonance as well as the band at 1311 cm⁻¹ confirm boron doping above 10^{20} cm⁻³. Nanosized grains of the early deposition, hence a high density of sp²-containing grain boundaries, justify the presence of the intense G-band at 1550-1570 cm⁻¹ visible in the spectrum from the backside of the film.

8.2.2 Bead-milling and purification

Crushing of the film was carried out at University of Würzburg using a vibration mill and grinding balls made of tempered steel which offer a satisfying compromise between sufficient hardness and easy removal of abrasion debris. In order to avoid material heating and subsequent graphitization, the film was milled in multistep way. Milling resulted in a mixture of diamond powder and iron abrasion which was removed in concentrated hydrochloric acid at elevated temperature (125°C) during 16 h. The remaining contaminants, mainly sp²-carbon and metallic residues, were dissolved during an oxidative treatment in a (9:1) mixture of concentrated sulfuric and nitric acid. Dispersion of the material after the chemical workup and a number of purification cycles yielded a deep blue colloidal solution of boron-doped diamond particles (Fig. 8.6(a)). Three fractions of different nanodiamond particle size distributions were obtained by centrifugation.



Figure 8.5: (a) Top view SEM image of the microcrystalline diamond film, the primary material for nanoparticles. (b) Raman spectra (red: front side; black: back side) of the free-standing film, prior to milling.

8.2.3 Nanoparticle characterization

Dynamic light scattering evaluated the distribution profile of the three fractions (Fig. 8.6(b)): BC1 contains coarse bulk particles evidenced by the broad distribution over several orders of magnitude. Particles with an average diameter of around 102 nm are found in BC2. The fraction BC3 features the narrowest distribution with the smallest particles (50 nm). Due to the technological interest in small nanoparticles, all further characterization focused on BC3.

Raman measurements on each of the fractions revealed the same features as described in Fig. 8.5(b). This hints at a high doping level of the particles. The harsh acid treatment formed carboxylic acid and other oxygen-containing surface groups which resulted in a negative zeta-potential of all fractions. The zeta potential varied between -37 meV (BC3) and -50 meV (BC1) in slightly acidic environment (pH 5.3 to 5.8). Different particle sizes, concentration and the remaining sp²-carbon are probably the origin of the difference in absolute values. Hence, all fractions yield a good chemical stability, however they are prone to agglomerate after several weeks. Sedimented clusters were deagglomerated by ultrasonification using a Hielscher UP400S sonotrode at minimum power and 0.5 s pulse.

TEM studies executed at EMAT on particles of *BC3* confirm the size range of 30 to 70 nm and their high purity, sp²-carbon was not evidenced in large quantities. As a result from milling, many particles being chips from bigger particles present sharp edges. Individual particles feature $\Sigma = 3\{111\}$ twins indicating their CVD origin [96]. The cleavage occurs preferentially along low surface energy planes, notably along the $\{111\}$ planes [133]. As can be seen from the HRTEM images [134], the resulting material after milling and purification process still exhibits some degree of faceting. The surface of the particles is covered by a nondiamond carbon shell of 3 to 5 nm thickness. The TEM electron beam was accelerated by 120 kV in

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Figure 8.6: (a) Colloid BC2 contains nanoparticles of approx. 100 nm. Its blue color is attributed to the high boron content. (b) Particle size distributions obtained by fractionated centrifugation of the diamond suspension after purification.

order to avoid graphitization. Accordingly, the observed graphitic shell around the nanoparticles resulted from the mechanical impact of milling. Electron energy loss spectroscopy (EELS) was not only able to prove boron incorporation through the presence of the boron K-edge in the spectrum, but also to quantify its concentration using the scanning TEM mode. The boron content was determined to be (1.3 ± 0.2) at.% which corresponds to 2.3×10^{21} atoms cm⁻³. The tetrahedral coordination of the boron dopants in the nanoparticles was evidenced by comparing the energy-loss near-edge structure (ELNES) fine structure with the data of a boron doped reference sample [96]. In comparison to the doping level of a solid film grown under similar conditions this is lower than the concentration in the solid film prior to milling [26]. The breaking up of the grain boundaries and defective regions where boron incorporation is enhanced [27] combined with the extensive treatment with strong acids are the origin for the lower net concentration.

8.3 Applications of doped nanoparticles

8.3.1 B-doped particles as nucleation seeds

One of the most technologically relevant applications of the synthesized borondoped nanodiamonds is the use as seeds for the growth of B:NCD films. In many applications, it is of great importance that the film is conductive throughout its entire thickness and, therefore, doped with boron. When undoped seeds are used, nonconductive regions at the substrate interface are present, which is particularly unfavorable for B:NCD films of a few tens to hundreds of nanometers in thickness.

The adhesion of diamond seeds to a surface is a primarily electrostatic process [135]. Uniform seed distributions are obtained when particles and substrate present opposite surface charges. In case of equally signed surface charges, the density

of nucleation seeds is extremely low as diamond particles are repelled from the substrate.

Due to the negative zeta-potential of the colloid *BC3*, we predicted poor seeding on Si and fused silica with the standard procedure and therefore tested different strategies as listed in Tab. 8.1. For a homogeneous dispersion of the new diamond seeds, a positively charged substrate surface is expected to yield better results. The limited amount of boron doped nanoparticles, suggested a modification of the substrate surface rather than to modify the termination of the particles. Polyethylenimine (PEI) coatings yield a layer of the cationic polymer molecules and are successfully used for cell-culturing in biotechnology [136]. PEI decomposes at typical CVD temperatures and will hence not remain as interface contamination.

The colloid BC3 was sonicated by a horn sonotrode for 1.5 h prior to seeding. The sample *BC3s-A* was meant to prove the general suitability of doped particles as seeds for CVD. Gentle manual blow-drying does not spill the drop over the substrate edge. So, all particles present in the drop will spread on the substrate and contribute as seed. The influence of the PEI interlayer on the seeding density was studied on an experimental series of four samples, *PEI-I* to *PEI-IV* (Tab. 8.1). Clean and oxidized substrates were coated with PEI. The substrates were immersed for 8 h in the 0.1% concentrated PEI solution, thoroughly rinsed and blow-dried in order to obtain a monolayer of PEI. The colloid was drop-cast onto the freshly prepared substrates, and spin-dried (4000 rpm). After all, diamond was deposited in 1% C:H, 5000 ppm (B:C)gas at 3500 W and 30 Torr.

5	,		
Sample	Substrate	Interlayer	Drying
BC3s-A	Si		Man. ^a
PEI-I	Si	PEI	no seeding
PEI-II	Si	PEI	Std. ^b
PEI-III	FS	PEI	Std.
PEI-IV	Si		Std.

Table 8.1: Overview of the experimental series for the evaluation of the influence of a PEIinterlayer on the seeding density:

^aManual blow-drying

^bStandard spin-drying (4000 rpm)

Seeding of *BC3s-A* could prove the principle of using boron doped particles as seeding crystallites for CVD of NCD. However, the unfavorable surface chemistry between particles and surface leads a non uniform distribution. Particles on *BC3s-A* agglomerate in drying rings and appear only scarcely in the center (Fig. 8.7(b) and (c)). A growth during 4 h in 1% C:H with 5000 ppm B:C in the gas phase, yielded a closed film, only in regions where the seeds were dense enough. (Fig. 8.7(a)) On Si without PEI interlayer (*PEI-IV*), few randomly distributed particles lead to the growth of individual isolated crystallites indicating poor seeding. Freshly deposited PEI provides a surface with positive net charge that attract negatively charged particles. The result is dense seeding and hence a closed layer (Fig. 8.7(a)) after CVD despite the extremely low particle concentration in *BC3*-colloid. A control



Figure 8.7: (a) Closed NCD film (*PEI-I*) grown on a BC3-seeded Si substrate with a PEI interlayer, (b) Manual blow-drying leads to an inhomogeneous seed distribution. (c) Without PEI interlayer (*PEI-IV*), the poor seeding density only develops individual grains during CVD.

sample, with PEI only, did not develop any grains which confirms the importance of nucleation centers for diamond CVD.

8.3.2 Doped nanoparticles and NCD toward thermoelectrics

Thermoelectrics research focuses on finding materials with an enhanced thermoelectric figure of merit (Eq. 4.13), i.e. materials that provide a low thermal conductivity and at the same time high electrical conductivity. MATCON workpackage D 'Nanocomposite Materials for Thermoelectric and Thermionic Heat Conversion' aimed at investigating the applicability of composite thin films made from nanosize diamond and other group-IV semiconductors, such as Si and Ge. Phonon scattering processes at the increased number of grain interfaces are expected to significantly impact the thermal conductivity. Through the combination of differently doped nanoparticles, the charge carrier transfer from highly to low doped regions could boost the carrier mobility. All experiments presented in this section result from a secondment stay at WSI. This part is meant as a technological proof of concept and deals with the question whether diamond nanoparticles could generally be integrated in the existing process.

We primarily worked with the largest particles (equivalent to BC1) as the high doping level and the large particles were best suited for the experiments. Their size range permitted to visualize the particles easily by SEM in mixed films and the high concentration of BC1 facilitated deposition. The process established at WSI to fabricate thin films from Si/Ge nanoparticles consists of three steps:

 Spin-coating of an ethanol based suspension containing nanoparticles on a suitable, insulating substrate, *e.g.* Kapton[®], glass or sapphire;



Figure 8.8: (a) Drop-casting yields a continuous particle film on glass. (b) The film consists of accumulated diamond particles. The surface morphology is owed to the deposition by drop-casting.

- 2. Wet-etch of the native oxide layer of the nanoparticles;
- 3. Laser-sintering to create conductive paths.

Closed films of diamond particles form by multiple drop-casting or sedimentation. SEM shows a dense accumulation of particles and debris (Fig. 8.8(a)). Both deposition methods are not ideal as the films partially reveal inhomogeneities and drying fringes, however they yield sufficiently satisfying films for preliminary experiments. The resistance of as-deposited particle films was in the order of 200 M Ω being too high for meaningful thermopower measurements. Hydrogen plasma treatment (25 min) let the resistance drop to 60 to 70 k Ω rendering Seebeck measurements possible. A color change of the film from black to gray was noticeable by eye, though no microscopical morphology change was identified by SEM. The improved conductivity is most probably a combination of H-induced surface conductivity and etching of sp²-residuals and other impurities left over from milling.

By directly measuring the thermovoltage $V_{\rm th}$ on each silver paint contact, Seebeck measurements were conducted in the temperature range from 320 K to 670 K in a home-built vacuum system (10^{-6} mbar). Fig 8.9 outlines the measurement system in which the sample rests on two heated blocks with a temperature difference $\Delta T < 10$ K. Heat conductive paste (HCP) provides a good thermal contact. $V_{\rm th}$ was read between the alumel legs of two tiny type K thermocouples. Further details of the experimental setup are reported in [91]. We deduced the Seebeck coefficient *S* for a defined temperature from the linear regression fit of the measured thermovoltage $V_{\rm th}$ vs. ΔT (Fig. 8.10) while the mean temperature of the heater cartridges was kept constant. The fit parameter for *S* was corrected by the voltage contribution of alumel.

One particle film (PF-BC1) as well as two as-grown highly boron doped NCD films on fused silica (BNCD-5000, BNCD2-5000) for comparison were measured. Figure 8.10 plots the Seebeck coefficient as a function of temperature for the three samples. All films exhibit a linear increase of *S* with rising temperature which proves p-type conductivity at a metallic doping level. Moreover, the linear rise over



Figure 8.9: Scheme of the experimental setup for thermoelectric measurements.



Figure 8.10: Seebeck coefficient as function of temperature for the as-grown B-doped NCD films BNCD-5000, BNCD2-5000 and the particle film PF-BC1. The linear increase indicates p-type conduction and a high doping level.

a large temperature range indicates one principle transport mechanism. Assuming a hole density of states effective mass of 0.8 $m_{\rm e}$ and applying the model of degenerately doped semiconductors, allows to deduce the charge carrier density from equation 4.14 [92]. Charge carrier densities of 9 × 10¹⁹ cm⁻³ and 4 × 10²⁰ cm⁻³ respectively are in good agreement with results from Hall measurements on similar samples [26]. The NCD films present higher Seebeck coefficients than the deposited and hydrogen treated particle film. Despite similar doping level of the as-grown films and the particles, the thermopower of the particle film is far lower. This implies a correlation of the Seebeck coefficient with the film morphology. The hydrogen treatment and some graphitic residuals lead to a higher overall film conductivity and the resulting lowering of *S*.

An important issue for the integration of diamond into Si or Ge matrices is the interaction with the laser during sintering. Nanostructuring is proven to reduce thermal conductivity [137] and is one promising approach for increasing the figure of merit ZT. Laser-sintering locally melts Si and Ge nanoparticles and forms meander-like conductive paths [91, 138]. At WSI as a standard, the pulsed laser (5 to 7 ns) is



Figure 8.11: (a) SEM top view of a laser-sintered diamond-Si film. The diamond particles are embedded in the meander structure of the Si matrix. (b) Enlarged detail of the laser-sintered diamond-Si composite.

operated at $\lambda = 532$ nm with a maximum energy fluence of 520 mJ cm⁻² at a repetition rate of 10 Hz. Although irradiated with the highest possible fluence, the morphology of the diamond particles is not significantly affected, as evaluated by SEM imaging. However, sintering is expected to graphitize the surface near atomic layers [139, 140].

In order to fabricate composites, nanoparticles of undoped Si or Ge respectively were blended with hydrogen plasma treated B-doped particles. The resulting mixture was sintered in vacuum ($\leq 5 \times 10^{-5}$ mbar). The localization of the diamond particles in the sintered composite is not straightforward. (Fig. 8.11(a)) presents the Si meander-like structure with few embedded diamond particles. SEM imaging suggests a good fusion of the two materials, the molten Si meander structure embeds the much larger diamond particles (Fig. 8.11(b)). However, no electrical in-plane conductivity could be established by blend mixing, therefore no Seebeck coefficient was measurable. Possibly the concentration ratio between Si and diamond particles need to be carefully adjusted to have enough charge carriers present. Moreover, the particle size ratios are expected to be crucial for a good intermixing of the two materials and their contribution to the electrical as well as thermal conductivity.

Despite the high doping level in the diamond particles, surface traps or the diamond-Si transition are possible obstacles for the charge transport. Due to the limited amount diamond particles, no further studies were possible at this stage.

8.4 Conclusion and outlook

UNCD films grown under a continuous bias are of noncrystalline, granular material under high compressive stress with an average roughness of 3 to 4 nm. The characterization of the film has shown that a considerable amount of amorphous and graphitic carbon is present the films. The films consist of diamond grains less than 10 nm in a nondiamond carbon matrix, which would be a suitable size for diamond nanoparticle. Boron dopants have been detected, however, the preferential incorporation in the nondiamond phase, signalizes that the presented material is not appropriate for doped diamond particle production. Most of the dopants would be removed during the milling process. This study is a contribution to the fundamental analysis of UNCD material, however it evidences at the same time that the approach to obtain doped nanoparticles from UNCD has to be reconsidered. Nevertheless, UNCD remains a versatile material for electrodes and hard coatings.

Boron doped nanoparticles have been successfully created by milling a heavily doped thick polycrystalline CVD diamond film. In a multistep chemical work-up, metal contaminants and most of the disordered and graphitic carbon was removed. The result were blue coloured colloids with the smallest crystallites ranging between 30 and 70 nm in diameter. High resolution spectroscopy techniques were able to prove substitutional incorporation as well as tetrahedral coordination of the dopants. EELS quantification detected a boron content of 2.3×10^{21} atoms cm⁻³ inside selected individual grains. Despite the harsh preparation method, the diamond lattice did not suffer substantial damage. The scale-up to larger fabrication volumes seems feasible and will certainly intensify the activities on B-doped nanoparticles. We demonstrated the use of these particles as seeding for the growth of boron doped CVD diamond that does not have an insulating interface layer between the substrate and the film. Moreover, first preliminary experiments on the technology of integrating diamond nanoparticles in Si and Ge thin films for thermoelectric applications were executed. Measurements determining the Seebeck coefficient on boron doped NCD were successful, viable and reliable. Further studies should investigate the influence of the doping level, surface termination or film thickness on the thermopower of solid diamond films.

As for the diamond-group-IV semiconductor composites, (nano)particles are challenging to be used as starting material at this stage. This certainly innovative field of research requires still a lot of technological work. To the present understanding the quality of the diamond and handling of the nanoparticles needs to be fully controllable in order to obtain efficient material. For further experiments, large quantities of diamond particles in a sufficient purity and ideally narrow size distribution would be needed. More studies on diamond-Si/Ge blends would have to evaluate the role of the interface as well as the optimum concentration and particle size ratios for the thermoelectric performance. A technological alternative to overcome the challenging film preparation could *e.g.* be the growth of 'porous' doped diamond films [141], and to fill the void volume with Si or Ge nanoparticles.

9 General conclusion and outlook

The main work in context with this thesis addressed two independent aspects within the MATCON project, (1) the deposition and characterization of P-NCD for thermionic emission and (2) the manufacturing of B-doped nanoparticles.

The focus lay on the former which is a contribution to the emerging field of electron emission from n-type doped diamond. Uniform NCD thin films were deposited in a CVD plasma using high concentrations of phosphine as dopant source. As a result of the thorough characterization which has provided a better understanding of the material under investigation the first successful proven incorporation of P in NCD has been reported.

Equally important is the evidence that advanced electron microscopy techniques can be used to localize dopants at relatively low concentrations, opening up routes for the use of these techniques on other materials. With high resolution spectroscopy techniques, such as STEM-EDX, SIMS and cathodoluminescence, it was not only possible to prove and visualize phosphorus incorporation in the films but also to quantify its content.

Attempts to assess the role of dopants in the emission process have been made, however further work is needed to engineer efficient films for thermionic converters. Due to its poor electrical characteristics, P-NCD will not be a competitive semiconductor however it could to find its application in dedicated devices based on the given NEA-diamond properties. In respect to the higher P-incorporation into (111)-oriented surfaces, known from single crystal research, the latest developments are a promising step for enhanced emission characteristics. In this context, the presented results raise several ideas for follow-up experiments. The electrical characterization, the role of the surface NEA and the incorporated H needs to be assessed in further investigations. At the present state, understanding the work function variation is the greatest challenge. Additional X-ray photoelectron spectroscopy measurements will be helpful to clarify the doubts of the surface termination and contamination and its role on the work function. Further insight on the surface physics is mandatory to identify whether the Richardson-Dushman equation remains unrestrictedly valid for emission processes from doped polycrystalline semiconductors.

By depositing P-NCD on different metal substrates, the significance of the P-NCDsubstrate interface for emission could be determined. To date, the best emitters are carefully engineered N-doped NCD films, so notable improvements are expected from optimized interfaces. Cross-plane electrical characterization will help to assess the impact of carbide layers and grain boundaries. Such measurements are now easily realizable in the new set-up. Electrically sensitive atomic probing techniques have been presented useful tools to map the electrical characteristics locally on differently oriented NCD grains and grain boundaries. As a result, adapted CVD parameters with respect to doping level, orientation and sp²-content could be established. At a later state, in order to combine the properties of P-and N-doped emitters, co-doping could be tested. Moreover, one could imagine experiments to nanostructure the surface which leads to an enhancement of the active area. The emission characteristics are expected to be boosted by purposely structuring the doped film with anisotropic etching techniques.

The new experimental set-up will help the future research of thermionic emission from diamond surfaces. The design of the UHV equipment allows potential upgrades *e.g.* to address solutions to mitigate space charges between the electrodes.

In the second project B-doped nanoparticles have been produced by a top-down procedure. Bead-assisted milling of B-doped polycrystalline followed by an elaborate chemical work-up resulted in nanoparticles of a few tens of nm in diameter. The potential of such particles is huge, spanning from mere research purposes on *e.g.* superconductor properties to applied studies in the field of chemical functionalization. The aim to integrate diamond into thermoelectrics was very explorative and would need more technological efforts to optimize the handling. The obtained nanoparticles were successfully used as nucleation seeds for the deposition of NCD.

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Publications

Peer-reviewed articles

- W. Janssen, S. Turner, G. Sakr, F. Jomard, J. Barjon, G. Degutis, Y.-G. Lu, J. D'Haen, A. Hardy, M. Van Bael, J. Verbeeck, G. Van Tendeloo, and K. Haenen, *Substitutional phosphorus incorporation in nanocrystalline CVD diamond thin films*, Physica Status Solidi RRL, 8 (2014), 705 709.
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Abstracts

Oral presentations

- Z. Vlčková Živcová, O. Frank, V. Petrák, H. Tarábková, W. Janssen, P. Pobedinskas, K. Haenen, M. Nesládek, and L. Kavan, *Electrochemistry and insitu Raman spectroelectrochemistry of low and high quality boron doped diamond layers in aqueous electrolyte solutions*, Hasselt Diamond Workshop (SBDD XVII), Hasselt, Belgium, March 14–16, 2012.
- W. Janssen, F. M. Koeck, T. Sun, Y.-G. Lu, S. Turner, J. Verbeeck, H.-G. Boyen, G. Van Tendeloo, R. J. Nemanich, and K. Haenen, *Thermionic emission from P-doped CVD diamond surfaces*, MRS 2013 Spring Meeting Symposium ZZ: Carbon Functional Interfaces II, San Francisco, USA, April 1–5, 2013.
- R. J. Nemanich , M. D. Brown, F. A. Koeck, T. Sun, W. Janssen, J. Sharp, *Energy Conversion Approaches Based on Doped Nanocrystalline Diamond Films*, MRS 2013 Spring Meeting Symposium ZZ: Carbon Functional Inter-faces II, San Francisco, USA, April 1–5, 2013.
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- <u>P. Pobedinskas</u>, B. Ruttens, **W. Janssen**, G. Degutis, W. Dexters, B. B. Ferraro, B. Conings, A. Hardy, J. D'Haen, H.-G. Boyen, M. K. Van Bael, and K. Haenen, *Selective diamond growth on confined plasma treated AIN surfaces*, International Conference on Diamond and Carbon Materials, Riva del Garda, Italy, September 2–5, 2013.
- <u>A. F. Sartori</u>, M. Fischer, S. Gsell, M. Schreck, **W. Janssen**, K. Haenen, *Heteroepitaxial diamond p-n diodes on Ir/YSZ/Si(001): growth and characterization*, International Conference on Diamond and Carbon Materials, Riva del Garda, Italy, September 2–5, 2013.
- W. Janssen, F. A. M. Koeck, T. Sun, Y.-G. Lu, S. Turner, J. Verbeeck, H.-G. Boyen, G. Van Tendeloo, R. J. Nemanich, and <u>K. Haenen</u>, *Phosphorus Doped Nanocrystalline CVD Diamond Films for Thermionic Emitter Applications*, 2013 JSAP-MRS Joint Symposia Symposium M: Diamond Technology: New Developments in Electronic, Photonics and Quantum Devices, Kyoto, Japan, September 16–20, 2013.
- T. Sun, W. Janssen, F. A. M. Koeck, K. Haenen, R. J. Nemanich, *Photo induced electron emission from phosphorus doped diamond films*, MRS 2013 Fall Meeting Symposium S: Diamond Electronics and Biotechnology-Fundamentals to Applications VII, Boston, USA, December 1–6, 2013.

- <u>B. van Grinsven</u>, K. Bers, T. Vandenryt, **W. Janssen**, B. Geerets, M. Ameloot, K. Haenen, W. De Ceuninck, and P. Wagner, *Implementing Heat Transfer Resistivity as a Key Element in a Nanocrystalline Diamond Based Single Nucleotide Polymorphism Detection Array*, MRS 2013 Fall Meeting Symposium S: Diamond Electronics and Biotechnology-Fundamentals to Applications VII, Boston, USA, December 1–6, 2013.
- W. Janssen, S. Turner, G. Sakr, F. Jomard, J. Barjon, F. A. M. Koeck, G. Degutis, H.-G. Boyen, A. Hardy, M. K. Van Bael, J. Verbeeck, R. J. Nemanich, G. Van Tendeloo, K. Haenen, *Phosphorus incorporation in nanocrystalline CVD diamond films for thermionic emitter applications*, Hasselt Diamond Workshop (SBDD XIX), Hasselt, Belgium, February 19–21, 2014.

Poster presentations

- W. Janssen, B. Ruttens, G. Degutis, Y.-G. Lu, S. Turner, W. Dexters, J. Verbeeck, G. Van Tendeloo, M.K. Van Bael, A. Hardy, and K. Haenen, *Characterization of B-doped ultra-nanocrystalline diamond films grown by plasma enhanced CVD under a continuous DC bias*, Hasselt Diamond Workshop (SBDD XVII), Hasselt, Belgium, March 14– 16, 2012.
- G. Degutis, P. Pobedinskas, W. Dexters, C. De Dobbelaere, W. Janssen, S. Al-Riyami, T. Yoshitake, J. D'Haen, A. Hardy, K. Haenen, and M. K. Van Bael, *The nucleation and growth of nanocrystalline diamond on metal interlayers*, Hasselt Diamond Workshop (SBDD XVII), Hasselt, Belgium, March 14–16, 2012.
- <u>E. Ukraintsev</u>, A. Kromka, **W. Janssen**, K. Haenen, and B. Rezek, *Electro-chemical growth of polypyrrole on boron doped diamond with various sur-face termination*, Hasselt Diamond Workshop (SBDD XVIII), Hasselt, Belgium, February 27–March 1, 2013.
- W. Janssen, F. A. M. Koeck, T. Sun, Y.-G. Lu, S. Turner, J. Verbeeck, H.-G. Boyen, G. Van Tendeloo, R.J. Nemanich, and K. Haenen, *Thermionic emission from P-doped CVD diamond surfaces*, Engineering of Functional Interfaces - EnFI 2013, Hasselt, Belgium, July 8–9, 2013.
- W. Janssen, F. A. M. Koeck, T. Sun, Y.-G. Lu, S. Turner, J. Verbeeck, H.-G. Boyen, G. Van Tendeloo, R.J. Nemanich, and <u>K. Haenen</u>, *Thermionic emission from P-doped CVD diamond surfaces*, International Conference on Diamond and Carbon Materials, Riva del Garda, Italy, September 2–5, 2013.