Nanocrystalline Diamond Growth and Device Applications

DISSERTATION

zur Erlangung des akademischen Grades eines

DOKTOR-INGENIEURS

(DR.-ING.)

der Fakultät für Ingenieurwissenschaften

und Informatik der Universität Ulm

von

Michele Dipalo

AUS TORINO

Betreuer: Prof. Dr.-Ing. Erhard Kohn

Amtierender Dekan: Prof. Dr.-Ing. Michael Weber

Ulm, 02.10.2008
Contents

List of symbols

List of figures

Summary

1. Introduction
   1. Introduction 1
   2. Structure and properties of diamond 4
   3. Structure and properties of poly-crystalline (PCD) and nano-crystalline (NCD) diamond 6

2. CVD diamond
   1. CVD diamond growth 10
      1. Substrates for CVD diamond growth 12
      2. Diamond nucleation 14
   2. Plasma CVD 16
   3. Hot Filament CVD 17
   4. CVD diamond doping 20
      1. P-type Doping 21
      2. N-type Doping 23
      3. Grain boundaries Doping 24

3. Nano-crystalline Diamond (NCD):
   Growth and characterization 25
   1. Intrinsic NCD growth: the role of methane concentration 28
   2. Boron doped NCD: the role of grain size on electrical properties 32
   3. Boron doped NCD: the role of grain size on electrochemical properties 34
   4. Intrinsic NCD cap layer on boron doped NCD 37
   5. Boron delta doping of NCD in Hot Filament CVD 41
      1. Growth of boron delta doped NCD 42
      2. Electrochemical characterization 44
   6. Nanodiamond growth on InAlN/GaN in Hot Filament and Plasma CVD 47
      1. Diamond nucleation and growth 48
      2. The role of growth temperature 54

4. Diamond based chemical sensors 57
   1. Concept of pH sensor 57
   2. Introduction 58
   3. Boron delta-doped nanodiamond ISFET 62
      1. ISFET fabrication 62
2. ISFET characterization 64
3. Conclusion 70
4. Diamond-InAlN/GaN ISFET 72
   1. ISFET fabrication 73
   2. ISFET characterization 75
   3. Conclusion 80

5. Diamond for power devices 83
   1. HEMT on InAlN/GaN after NCD overgrowth and complete removal 83
   2. HEMT on InAlN/GaN with NCD overgrowth 86
      1. Ohmic contacts optimization 86
      2. HEMT fabrication and diamond growth 88
   3. Conclusion 90

6. Conclusion 91

Appendixes 95
   A. Diamond Electrochemistry 103
   B. Electrochemical cell setup and measurements 105
   C. Schematic growth method for boron delta doped NCD 107

References 107

Tables 119

List of publications 121

Patents 125
## List of symbols

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>a</td>
<td>Lattice constant</td>
</tr>
<tr>
<td>$\alpha$</td>
<td>Ratio between the growth speed of [100] and [111] orientations</td>
</tr>
<tr>
<td>$\beta$</td>
<td>Ratio between the growth speed of [100] and [110] orientations</td>
</tr>
<tr>
<td>C$_{xH_y}$</td>
<td>Radical containing carbon and hydrogen</td>
</tr>
<tr>
<td>C$_{DL}$</td>
<td>Double layer capacitance</td>
</tr>
<tr>
<td>C$_{SC}$</td>
<td>Space charge capacitance</td>
</tr>
<tr>
<td>d</td>
<td>Thickness</td>
</tr>
<tr>
<td>E$_C$</td>
<td>Conduction band energy</td>
</tr>
<tr>
<td>E$_V$</td>
<td>Valence band energy</td>
</tr>
<tr>
<td>E$_F$</td>
<td>Fermi level energy</td>
</tr>
<tr>
<td>E$_A$</td>
<td>Activation energy</td>
</tr>
<tr>
<td>E$_{GAP}$</td>
<td>Band gap energy</td>
</tr>
<tr>
<td>$\varepsilon_d$</td>
<td>Diamond dielectric constant</td>
</tr>
<tr>
<td>$\gamma$</td>
<td>Ratio between the growth speed of [100] and [113] orientations</td>
</tr>
<tr>
<td>HFCVD undoped</td>
<td>Hot Filament CVD for undoped NCD growth</td>
</tr>
<tr>
<td>HFCVD doped</td>
<td>Hot Filament CVD for boron doped NCD growth</td>
</tr>
<tr>
<td>J</td>
<td>Electrode current density</td>
</tr>
<tr>
<td>I$_D$</td>
<td>Drain source current density</td>
</tr>
<tr>
<td>L$_G$</td>
<td>Gate length</td>
</tr>
<tr>
<td>L$_{channel}$</td>
<td>Channel length</td>
</tr>
<tr>
<td>m$_{le}$</td>
<td>Electron longitudinal carrier mass</td>
</tr>
<tr>
<td>m$_{te}$</td>
<td>Electron transversal carrier mass</td>
</tr>
<tr>
<td>m$_{hh}$</td>
<td>Heavy holes carrier mass</td>
</tr>
<tr>
<td>m$_{lh}$</td>
<td>Light holes carrier mass</td>
</tr>
<tr>
<td>m$_{so}$</td>
<td>Split-off holes carrier mass</td>
</tr>
<tr>
<td>N$_A$</td>
<td>Acceptor concentration in diamond</td>
</tr>
<tr>
<td>n$_s$</td>
<td>Channel sheet charge density</td>
</tr>
<tr>
<td>p</td>
<td>Holes concentration</td>
</tr>
<tr>
<td>q</td>
<td>Elementary charge</td>
</tr>
<tr>
<td>Q</td>
<td>Constant phase element</td>
</tr>
<tr>
<td>R</td>
<td>Electrical resistance</td>
</tr>
<tr>
<td>RIE</td>
<td>Reactive Ion Etching</td>
</tr>
<tr>
<td>R.T.</td>
<td>Room temperature</td>
</tr>
<tr>
<td>RMS</td>
<td>Root mean square</td>
</tr>
<tr>
<td>R$_{DL}$</td>
<td>Double layer resistance</td>
</tr>
<tr>
<td>R$_{SC}$</td>
<td>Space charge capacitance</td>
</tr>
<tr>
<td>V$_{DS}$</td>
<td>Drain source voltage</td>
</tr>
<tr>
<td>V$_E$ vs. SCE</td>
<td>Potential between sample surface and platinum electrode</td>
</tr>
<tr>
<td>Symbol</td>
<td>Definition</td>
</tr>
<tr>
<td>--------</td>
<td>------------</td>
</tr>
<tr>
<td>$V_G$ vs. SCE</td>
<td>Potential between platinum electrode and source contact versus the reference electrode</td>
</tr>
<tr>
<td>$V_P$</td>
<td>Pinch-off voltage</td>
</tr>
<tr>
<td>$V_{FB}$</td>
<td>Flat band potential</td>
</tr>
<tr>
<td>$W_G$</td>
<td>Gate width</td>
</tr>
<tr>
<td>$W_{channel}$</td>
<td>Channel width</td>
</tr>
<tr>
<td>$\mu$</td>
<td>Carrier mobility</td>
</tr>
<tr>
<td>$\mu_p$</td>
<td>Holes mobility</td>
</tr>
<tr>
<td>$Z$</td>
<td>Impedance</td>
</tr>
<tr>
<td>$Z_i$</td>
<td>Imaginary part of impedance</td>
</tr>
</tbody>
</table>
List of figures

Fig. 1.1: Face centred cubic diamond lattice. a = 0.356 nm [2]................................................................. 4
Fig. 1.2: Diamond band diagram [3]........................................................................................................ 4

Fig. 2.1: Phase diagram of carbon [3]....................................................................................................... 9
Fig. 2.2: Schematic CVD diamond process; the main chemical species are shown................................. 10
Fig. 2.3: Bachmann triangle diagram [24]................................................................................................. 11
Fig. 2.4: Atomic hydrogen and radicals densities in respect of filaments temperature [46]............... 18
Fig. 2.5: Sketch of the “HFCVD undoped” equipped with BEN capability.......................... 19
Fig. 2.6: Sketch of the “HFCVD doped”, equipped for boron doping. No BEN capability........... 19
Fig. 2.7: Band diagram of diamond with most common dopants........................................................... 20
Fig. 2.8: Activation energy of boron in diamond as function of the effective doping conc. [50]........... 21
Fig. 2.9: Photograph and sketch of the ASTeX plasma CVD.................................................................. 24
Fig. 2.10: 2D structure NCD. B: 3D structure NCD................................................................................ 26
Fig. 2.11: Atomic hydrogen and radicals densities in respect of filaments temperature [78]............ 27
Fig. 2.12: Cyclic voltammetry of samples Ref1 and Cap2 decorated with gold particles................. 41
Fig. 2.13: Cyclic voltammetry in pH 1 in semi-log. scale of sample Cap2, compared with Ref1........ 40
Fig. 2.14: Cyclic voltammetry in pH 1 in semi-log. scale of sample Cap1, compared with Ref1........ 39
Fig. 2.15: A: 2D structure NCD. B: 3D structure NCD................................................................. 30
Fig. 2.16: Activation energy of boron in diamond as function of the effective doping conc. [50]...... 21
Fig. 2.17: Cyclic voltammetry of boron doped NCD. Scan rate = 20 mV/s.......................................... 36
Fig. 2.18: Holes mobility in respect of grain size....................................................................................... 34
Fig. 2.19: Cyclic voltammetry in pH 1 in semi-log. scale of samples Ref1, compared with Ref1........ 39
Fig. 2.20: Cyclic voltammetry in pH 1 in semi-log. scale of sample Cap1, compared with Ref1......... 39
Fig. 2.21: Cyclic voltammetry in pH 1 in semi-log. scale of sample Cap2, compared with Ref1.......... 40
Fig. 2.22: Cyclic voltammetry of samples Ref1 and Cap2 decorated with gold particles............... 41
Fig. 2.23: Electrical resistance vs. etching time in RIE for samples 60M and 30M......................... 44
Fig. 2.24: Cyclic voltammetry in pH 1 in semi-log. scale of samples Ref1 and Cap2, compared with Ref1 41
Fig. 2.25: Sample 30M. A: Imp. spectr.. B: equiv. circuit. C: equiv. circuit at freq. below 100 Hz. ...... 45
Fig. 2.26: Sample B. A: Mott-Schottky plot. B: extracted doping profile.............................................. 47
Fig. 2.27: Sketch of the InAlN/GaN heterostructure.............................................................................. 49
Fig. 2.28: BEN nucleation technique of insulating substrates.............................................................. 50
Fig. 2.29: Schematic CVD diamond process; the main chemical species are shown................................. 10
Fig. 2.30: BEN nucleation technique of insulating substrates.............................................................. 50
Fig. 2.31: Diamond nucleation on InAlN using amorphous silicon interlayer........................................ 50
Fig. 2.32: Diamond growth on InAlN using silicon dioxide and amorphous silicon interlayer........... 51
Fig. 2.33: SEM picture: morphology of diamond grown on InAlN/GaN.............................................. 52
Fig. 2.34: SEM picture: cross section of diamond on 30 nm barrier InAlN/GaN............................. 53
Fig. 2.35: SEM picture: cross section of diamond on 7 nm barrier InAlN/GaN............................... 53
Fig. 2.36: SEM picture: cross section of diamond on 30 nm barrier InAlN/GaN............................. 53
Fig. 2.37: SEM picture: cross section of diamond on 7 nm barrier InAlN/GaN............................... 53
Fig. 2.38: AFM picture. InAlN surface after diamond growth and removal........................................ 54
Fig. 2.39: InAlN/GaN sample with diamond overgrown after MESA and ohmic contacts dep. ........ 54
Fig. 2.40: I-V charact. and TLM measurements of InAlN/GaN......................................................... 55
Fig. 2.41: A: Low temperature diamond growth B: high temperature diamond growth.............. 56
Fig. 2.42: Cyclic volt. of sample A (low growth temp.) and of sample B (high growth temp.)......... 57

Fig. 3.1: I-V charact. and TLM measurements of InAlN/GaN............................................................. 55
Fig. 3.2: I-V charact. and TLM measurements of InAlN/GaN............................................................. 55
Fig. 3.3: SEM picture: morphology of diamond grown on InAlN/GaN.............................................. 52
Fig. 3.4: SEM picture: cross section of diamond on 30 nm barrier InAlN/GaN............................. 53
Fig. 3.5: SEM picture: cross section of diamond on 7 nm barrier InAlN/GaN............................... 53
Fig. 3.6: SEM picture: cross section of diamond on 30 nm barrier InAlN/GaN............................. 53
Fig. 3.7: SEM picture: cross section of diamond on 7 nm barrier InAlN/GaN............................... 53
Fig. 3.8: AFM picture. InAlN surface after diamond growth and removal........................................ 54
Fig. 3.9: InAlN/GaN sample with diamond overgrown after MESA and ohmic contacts dep. ........ 54
Fig. 3.10: I-V charact. and TLM measurements of InAlN/GaN......................................................... 55
Fig. 3.11: A: Low temperature diamond growth B: high temperature diamond growth.............. 56
Fig. 3.12: Cyclic volt. of sample A (low growth temp.) and of sample B (high growth temp.)......... 57

Fig. 4.1: Ion Sensitive FET (ISFET) concept....................................................................................... 59
Fig. 4.2: Ion Sensitive FET (ISFET) concept....................................................................................... 59
Fig. 4.3: A: output charact. of the SGFET [126]. B: Transfer charact. of the pH sensor [128]........ 62
Fig. 4.4: Concept of the boron delta doped ISFET......................................................................... 64
Fig. 4.5:  A: Boron delta doped NCD ISFET fabr. B: photo of the encapsulated ISFET device .......... 65
Fig. 4.6:  Sample Thick_δ. A: cyclic volt in pH 1 and pH 13. B: cyclic volt in pH 1 in semi-log scale... 66
Fig. 4.7:  Sample Thick_δ. Output characteristic in pH 1 ................................................................. 67
Fig. 4.8:  Sample Thick_δ. Transfer-characteristic in pH 1 and pH 13 ................................................... 68
Fig. 4.9:  Sample Thick_δ. Transfer-characteristic after NaOH 3% treatment at 50° C ..................... 69
Fig. 4.10:  Sample Thin_δ. A: cyclic volt in pH 1 and pH 13. B: cyclic volt in pH 1 in semi-log scale 70
Fig. 4.11:  Sample Thin_δ. Output characteristic in pH 1 ................................................................. 71
Fig. 4.12:  Sample Thin_δ. Transfer characteristic in pH 1 and pH 13 .................................................. 71
Fig. 4.13:  Sample Thin_δ. I_D current at V_DS = - 0.5 V and V_G = - 0.4 V (vs. SCE) in pH 1 and pH 13.. 72
Fig. 4.14:  NCD-InAlN/GaN ISFET: concept structure ................................................................. 74
Fig. 4.15:  NCD-InAlN/GaN ISFET sketches .................................................................................. 75
Fig. 4.16:  NCD-InAlN/GaN ISFET photograph ................................................................................ 76
Fig. 4.17:  Electrochemical setup for characterization of the NCD-InAlN/GaN ISFET. ............... 77
Fig. 4.18:  NCD-InAlN/GaN ISFET. A: cyclic volt. in pH 1 and pH 13. .................................78
Fig. 4.19:  NCD-InAlN/GaN ISFET. A: I-V characteristic of the Schottky diode of the HEMT. ...78
Fig. 4.20:  NCD-InAlN/GaN ISFET. Output characteristic in pH 1 .............................................79
Fig. 4.21:  NCD-InAlN/GaN ISFET: transfer characteristic in pH 1 and pH 13 at V_DS = 1.5 V ....80
Fig. 4.22:  NCD-InAlN/GaN ISFET. Transfer charact. in pH 1 in the semi-log. scale at V_DS = 1.5 V. ..80
Fig. 4.23:  NCD-InAlN/GaN ISFET: pH cycling at V_DS = 1.5 V and V_GS = 0.6 V vs. SCE........78
Fig. 4.24:  Comparison of trans. charact. in pH 1 of NCD-InAlN/GaN and boron delta doped NCD ISFETs. ......................................................................................................................... 82

Fig. 5.1:  Morphology of intrinsic NCD overgrowth on InAlN/GaN ...................................................... 86
Fig. 5.2:  Micrograph of the finished InAlN/GaN HEMT ................................................................. 86
Fig. 5.3:  Output characteristic of the InAlN/GaN HEMT after NCD overgrowth and removal .......... 87
Fig. 5.4:  Surface of InAlN MESA (a) and GaN buffer (b) after NCD nucleation on InAlN/GaN ....87
Fig. 5.5:  Effect of NCD growth on the gold ohmic contacts ............................................................ 88
Fig. 5.6:  Effect of NCD growth on ohmic contacts with tantalum top metal .................................. 89
Fig. 5.7:  Conformal NCD growth on InAlN/GaN device ............................................................... 90
Fig. 5.8:  NCD overgrowth InAlN/GaN HEMT with gate recess (b) and contacts openings (a) ....... 91
Fig. 5.9:  Output characteristic of NCD overgrown InAlN/GaN HEMT (red). .................................. 91
Diamond possesses such outstanding properties that its exploitation in many fields is desired and sought for several years now. Mechanical, thermal, electrical and chemical features of diamond render it the ideal material for power electronics, MEMS (Micro Electrical Mechanical Systems), chemical and bio sensors, tool coating, thermal dissipation and high temperature devices such as sensors and heaters. The very inadequate size of available diamond substrates, limited to few millimetres, made necessary the development of poly-crystalline (PCD) and nano-crystalline (NCD) diamond; these heterogeneous materials are today available on large area wafers and would be therefore suitable for practical applications. Unfortunately the same heterogeneous nature that allows large area is also the main obstacle to large distribution of PCD and NCD; the mixture of the different carbon phases present in PCD and NCD make it indeed difficult to reproduce the ideal diamond properties. Use of PCD and NCD is also limited by other barriers, which are shared by single crystal diamond as well. In particular the lack of shallow p-doping and the almost total absence of n-doping do not permit the fabrication of many device structures for electronics and electrochemistry. Furthermore the severe requirements of PCD and NCD growth in terms of thermal budget do not allow growing on many materials that would benefit from diamond features such as thermal conductivity and chemical stability.

In this work several issues related to NCD growth are addressed and handled, regarding especially the growth of boron doped NCD for electrochemical applications and of intrinsic NCD on III-nitrides for heat sink applications. Two new NCD growth techniques are introduced and developed. The first concerns the growth of boron delta doped NCD on silicon with suitable electrochemical properties by means of Hot Filament CVD; NCD layers with high boron concentration and nanometer range thickness are described. The second technique concerns the growth of intrinsic NCD on InAlN/GaN at high temperature by means of Hot Filament and plasma CVD; the NCD quality is verified by Raman spectroscopy and SEM microscopy, while the electronic characteristics of InAlN/GaN are completely preserved after NCD growth. The experiments related to NCD growth on InAlN/GaN include also the study of diamond nucleation on the heterostructure by means of BEN (Bias Enhanced Nucleation).

Two novel diamond based ISFET concepts are furthermore introduced. The first ISFET concept is based on oxygen terminated boron delta doped NCD and provides chemical stability and sensitivity of diamond on large area for the first time; additionally it also gives the possibility to operate in the amperometric and potentiometric mode. The second ISFET concept is based on the combination of a boron doped NCD electrode with an InAlN/GaN HEMT; this device possesses all the advantages of the boron delta doped NCD ISFET, but provides much higher sensitivity thanks to the outstanding electrical properties of the nitride heterostructure. Such a device has the performances to compete with commercialized ISFETs and circumvents some of their major restrictions.
The use of NCD as heat sink on power devices is explored by growing intrinsic NCD on InAlN/GaN HEMTs at high temperature. The HEMT characteristics are shown to be preserved after NCD growth, with minor degradations due to a still immature process; this result unlocks the chance to improve power devices performances by heat extraction with diamond overlayers.

The developments in growth and in device fabrication push NCD toward practical and functional applications, moving towards the moment in which diamond properties will be exploited to fabricate various ultimate devices in power electronics, electrochemistry and biochemistry.
Chapter 1

1.1 Introduction

During the first half of the 20th century, when semiconductors were investigated and the first electronic devices were developed, nobody could expect electronics to have the crucial role it has today in human life. We are literally surrounded by all kind of electronic devices; medical and biological devices for our health, power and logic devices for communications, electrochemical devices for environmental monitoring and control, electronic devices for work, entertainment and safety.

Such an important position of electronics contributed to push semiconductor research to the limit in a relatively short period. While in certain applications current materials still accomplish their tasks well, like silicon in digital electronics, in others the material limits have already been reached and new breakthroughs are needed, like in power electronics or bio-chemistry. For this reason special consideration is given today seeking for new materials, which would open novel possibilities and would model new standards; among new materials diamond is certainly one of the most exotic and hopeful resources, and not only because it is generally considered as the most valuable material.

Diamond possesses unique properties, which have attracted the interested of a large scientific community in the last decades. Research in diamond spread from mechanics (with tools coating) through electronics (with MEMS and electronic devices) to biochemistry (with electrochemical and biochemical sensors). The interest in diamond stems from its outstanding properties like highest thermal conductivity, highest hardness, low friction coefficient, high breakdown voltage and high chemical inertness and robustness.

Unfortunately natural diamond is a rare and therefore expensive material, available furthermore only in relatively small stones. Several techniques have hence been developed for producing artificial diamond with comparable or better characteristics than pure diamond.

For some application synthetic diamond is already a well known and common material, as in the case of tools coating, where diamond is used in its polycrystalline form and
quality requirements are not strict. In other fields, like electronics and electrochemistry, synthetic diamond does not yet meet the necessary requirements to become the reference material; improvements are therefore needed in respect of artificial diamond substrates size, purity and doping availability.

In this direction the Chemical Vapor Deposition (CVD) method is the most promising diamond growth process, allowing large area deposition (polycrystalline diamond) and high purity. Nevertheless the CVD diamond process still lacks a fully comprehensive theoretical and experimental understanding, having thus strong limitations in devices applications. Two of the most critical CVD aspects today are diamond doping, for device fabrication, and diamond heteroepitaxy, for large area accessibility. Doping of diamond has today serious restrictions in the variety of doping elements as well as in their incorporation in the diamond lattice. Due to this fact diamond devices showed only partially the advantages of the promising excellent diamond properties and basically only proof-of-concept devices have been fabricated.

Large area availability is a fundamental requisite for the spreading of a new material. Single crystal diamond is practically still limited to the millimeter size due to the lack of single crystal substrates. On the other hand single crystal diamond heteroepitaxy on large area has been strongly improved but still shows clear problems concerning lattice defects, mechanical stress, delamination and substrate availability.

Toward solving the large area problem, in the last decades a very promising path has been the development of many forms of polycrystalline diamond (PCD), which can already be grown on large area wafers up to 8 inches (Seki, p-BeSt) [1]. PCD is generally grown on silicon wafers due to the high temperature and mechanical stability of silicon, which allows growing thick diamond layers. With this technique PCD has already found applications as electrochemical electrode for heavy duty and as UV transparent window for lasers. More recently the interest in PCD of several communities moved toward nano-crystalline diamond (NCD), which is a polycrystalline material with grain size in the sub micron range. As will be discussed later NCD has many advantages in terms of homogeneity, substrate availability and patterning to micrometer or nanometer size features.

Regarding PCD and NCD the major efforts today are directed to improve their qualities and thus to transfer the ideal diamond properties to large area applications. The heterogeneity of such materials still limits their use as active or passive elements in device fabrication. As active elements PCD and NCD still lacks full doping management and adequate electrical properties, especially concerning FETs purposes. As passive elements, PCD and NCD employ is limited by strict growth conditions, such as nucleation and thermal budget.

Solving the above mentioned problems of PCD and NCD would allow circumventing current technology limits in several fields and would open new possibilities for novel device concepts. The outstanding thermal stability and thermal conductivity will be exploited for thermal dissipation of power devices, increasing power availability for long range communications. The diamond high chemical stability and biocompatibility will instead be used to realize new biocompatible sensors, allowing in vivo observation of cells and tissues.
This thesis attempts to address the issues related to NCD growth for several applications, where NCD acts as active or passive element. Such a work is performed through the improvement of the NCD growth process, the characterization of the NCD layers and the design and the fabrication of new NCD-based devices.
1.2 Structure and properties of diamond

Diamond is an allotropic configuration of carbon where atoms are placed in a face centered cubic lattice (figure 1.1) with bond length of 0.154 nm and lattice constant \( a = 0.356 \) nm [2]. The carbon atoms have \( 1s^2 2s^2 2p^2 \) electron configuration, forming in diamond a hybridized \( sp^3 \) with the valence electrons; in graphite configuration the valence electrons form \( sp^2 \) hybridization.

In the diamond lattice each carbon atom is bonded to other four by \( \sigma \) bonds set at an angle of 109° to each other. The \( \sigma \) bond is highly energetic and is responsible, with the tight tetrahedral structure, for the outstanding diamond properties.

Fig. 1.1: Face centred cubic diamond lattice. \( a = 0.356 \) nm [2].

Diamond has a wide indirect energy band gap of 5.45 eV and is therefore a highly insulating material when not doped with impurities, showing resistivity up to \( 10^{15} \) \( \Omega \) cm.

Diamond possesses also exceptional electronic properties like high breakdown electric field of 10 MV/cm, high carrier mobility of 4500 cm\(^2\)/Vs and 3800 cm\(^2\)/Vs respectively for electrons and for holes and a low dielectric constant of 5.7.

Fig. 1.2: Diamond band diagram [3]

The band diagram of diamond is shown in figure 1.2; it is similar to that of silicon with six equivalent electron minima located along the [100] k-axes, the valence band
maximum at Γ-point (k = 0) and conductance band minimum at approx. 80% of X-point position.

Effective carrier masses are:
- \( m_{le} = 1.4 \, m_0 \) and \( m_{te} = 0.36 \, m_0 \) for electrons (respectively longitudinal and transversal) [4].
- \( m_{hh} = 0.57 \, m_0 \), \( m_{lh} = 0.32 \, m_0 \) and \( m_{so} = 0.39 \, m_0 \) for holes (respectively heavy holes, light holes and split-off holes) [5].

Compared to other semiconductors diamond possesses unique properties suitable for several applications. In table 1.1 the main properties of diamond are shown in comparison to other important present semiconductors. High Young modulus, high thermal conductivity and high hardness are interesting for mechanical applications; the wide bandgap, high carrier mobility and high breakdown voltage are useful in electronics applications. Furthermore chemical inertness and biocompatibility are suitable for electrochemical and biological applications.

The wide bandgap of 5.45 eV results also in high transparency in a wide wavelength range; diamond is indeed transparent from UV to IR and shows high transmittance in the whole visible range.

<table>
<thead>
<tr>
<th></th>
<th>Diamond</th>
<th>Silicon</th>
<th>GaN</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bandgap (eV)</td>
<td>5.45</td>
<td>1.12</td>
<td>3.4</td>
</tr>
<tr>
<td>Type</td>
<td>indirect</td>
<td>indirect</td>
<td>direct</td>
</tr>
<tr>
<td>Lattice constant (nm)</td>
<td>0.36</td>
<td>0.543</td>
<td>( a: 0.319 ) ( c: 0.519 )</td>
</tr>
<tr>
<td>Dielectric constant</td>
<td>5.7</td>
<td>11.9</td>
<td>9</td>
</tr>
<tr>
<td>Thermal conductivity (W/cmK)</td>
<td>22</td>
<td>1.45</td>
<td>1.3</td>
</tr>
<tr>
<td>Holes mobility (cm²/Vs)</td>
<td>3800</td>
<td>450 - 600</td>
<td>1200</td>
</tr>
<tr>
<td>Electrons mobility (cm²/Vs)</td>
<td>4500</td>
<td>1500</td>
<td>30</td>
</tr>
<tr>
<td>Electron saturation vel. (10⁷ cm/s)</td>
<td>1.6</td>
<td>1.0</td>
<td>2.5</td>
</tr>
<tr>
<td>Hole saturation vel. (10⁷ cm/s)</td>
<td>1.1</td>
<td>0.6</td>
<td>2</td>
</tr>
<tr>
<td>Breakdown strength (10⁶ V/cm)</td>
<td>10</td>
<td>0.3</td>
<td>2.5</td>
</tr>
<tr>
<td>Young Modulus (GPa)</td>
<td>1143</td>
<td>112</td>
<td>200 - 400</td>
</tr>
<tr>
<td>Biocompatibility</td>
<td>Yes</td>
<td>No</td>
<td>Yes</td>
</tr>
</tbody>
</table>

Table 1.1: Diamond and other semiconductors properties, after [8][9][10][11][12][13][14]
The most typical diamond surface terminations are fluorine, hydrogen, oxygen and nitrogen; some of diamond’s properties depend upon the different surface termination. Hydrogen terminated surface presents negative electron affinity, high hydrophobic behavior and surface electrical conductivity [9]; oxygen terminated surface presents positive electron affinity, hydrophilic behavior and high surface electrical insulation [6]. Fluorine termination is known to show the strongest hydrophobic behavior [7].

1.3 Structure and properties of poly-crystalline (PCD) and nano-crystalline (NCD) diamond

PCD and NCD are heterogeneous materials constituted by diamond crystals (or grains) merged together within a grain boundary matrix; the grain boundaries may contain non-diamond carbon phases such as sp² bonds and amorphous carbon.

In respect of single crystal diamond, PCD and NCD may present different properties since these are the combination of the diamond grains properties and of the grain boundaries ones. The PCD or NCD properties can diverge from single crystal diamond ones according to the size, shape and disposition of diamond crystals, and to the size and composition of grain boundaries.

Concerning diamond thermal properties, the grain boundaries are known to reduce the overall thermal conductivity of PCD and NCD layers due to their lower thermal conductivity in respect of diamond crystals. H. Verhoeven et al. [15] have shown that the thermal conductivity of PCD or NCD can vary considerably when grain size and grain arrangement are changed; in particular they demonstrated that thermal conductivity presents anisotropic behavior in columnar PCD, with higher values along the grains growth direction, and that smaller grain size leads to inferior thermal conductivity.

From an electrical standpoint, the properties of undoped PCD and NCD can be very different according to the nature and the size of grain boundaries, ranging from highly insulating to conductive. In general, electrical conductivity in undoped PCD and NCD is generated by the grain boundary network [16]; according to the size of diamond grains and of grain boundaries, the insulating diamond behavior may dominate on the conductive grain boundaries or vice versa.

In ultra nano-crystalline diamond (UNCD), which will be discussed in details in sections 2.1 and 2.4, diamond grains with a size of approx. 3 – 5 nm are surrounded by a network of wide grain boundaries containing graphitic phase. Even though the small diamond grains are undoped, UNCD presents low resistivity because the wide grain boundaries form a path for metallic (graphitic) conduction through the layer. However, when grain boundaries are surrounded by larger diamond grains (larger than for UNCD) and are not widened by growth conditions, they may not affect the overall PCD or NCD electrical properties. M. Kubovic et al. [17] have for example demonstrated working MESFETs fabricated on surface conductive hydrogenated NCD; here it is shown that the grain boundaries, which surrounded 300 nm large diamond grains, did not degrade the FET gate diode by short circuiting it despite their amorphous and graphitic content.
In boron doped PCD and NCD the grain boundaries lead generally to inferior electrical performance in respect of single crystal diamond \[17\][18]; in such materials the grain boundaries may act as barriers for holes motion, reducing the carrier mobility, or as charge trapping centers, reducing the carrier concentration.

The mechanical properties of PCD and NCD are also influenced by the grain boundaries and may thus deviate from single crystal diamond ones. Typically the fracture strength of NCD is for example approximately the half of that of single crystal diamond \[21\], namely in the range of 2 – 5 GPa in respect of approx. 10 GPa \[19\]. On the other hand the Young Modulus of NCD may have values very close to that of single crystal diamond (1143 GPa \[20\]). F.H. Guillen et al. \[21\] and J. Philip et al. \[22\] reported Young Modulus of respectively 1020 GPa and 1120 GPa for NCD, both obtained by optimization of the nucleation method for high nucleation density.
Chapter 2

CVD diamond

Diamond is the stable configuration of carbon at high temperature and high pressure as shown in the phase diagram (fig. 2.1); at room temperature and atmospheric pressure the stable configuration is graphite. For decades therefore the only technique used to grow synthetic diamond has been the HPHT method (High Pressure High Temperature) [23] where diamond is grown in its natural environment, with a temperature in the range of 1000-2000 °C and a pressure in the range of GPa (fig. 2.1). In the HPHT method carbon is heated and compressed to reach the diamond region; the process is performed in the presence of metal particles which act as catalyst for the diamond crystal. The HPHT has essentially two drawbacks which limit the use of diamond grown with this technique only to industrial applications, like tool coating. Firstly the maximum obtainable crystal size is limited to few millimeters, which is too little for electronic applications; secondly the diamond crystals contain always impurities from the growth environment, especially nitrogen, and a full doping control is not possible.

A second diamond growth technique has been established during the 1950s by J. C. Angus [25] and W. Eversole [26] in U.S.A. and by B. Derjaguin [27] in USSR, with later developments in the 1980s in Japan; the chemical vapor deposition (CVD). The CVD
method works at low pressure and high temperature (Fig. 2.1), where carbon is in a metastable regime and both diamond and graphite are produced; growth conditions can be adjusted in order to reduce graphite formation and favor diamond growth.

The CVD technique has several advantages in respect of the HPHT method. Firstly a CVD system is more adjustable to growth requirements like for example substrate size or gas mixture. Moreover with CVD the purity of diamond crystal is higher and doping elements can be added to the process in order to grow doped diamond for electronics.

2.1 CVD diamond growth

The CVD method comprises of a carbon containing gas, molecular hydrogen (in most cases) and a form of activation energy. Carbon containing gas and molecular hydrogen are dissociated by the activation energy, forming carbon radicals and atomic hydrogen, which drift toward the substrate surface by a gradient in temperature and concentration (fig. 2.2). The diamond growth process is based on gas phase chemical reactions which happen on the substrate surface, on which carbon is deposited in the form of diamond and graphite. Diamond growth takes place due to the different reaction rate between hydrogen-graphite and hydrogen-diamond; in the right conditions atomic hydrogen removes graphite much faster than diamond, leading therefore to diamond layer formation.

![Schematic CVD diamond process; the main chemical species are shown.](image)

In more detail, the reactant gases break and form $\text{C}_x\text{H}_y$ radicals and atomic hydrogen; at the substrate surface these compounds undergo a series of reactions that lead carbon to form $\text{sp}^2$ (graphite) and $\text{sp}^3$ (diamond) bonds on the surface. The $\text{sp}^2$ bonds are removed by atomic hydrogen, which additionally terminates and stabilizes the $\text{sp}^3$ bonds.

The chemical reactions happening in the gas phase are complex and a comprehensive understanding of the growth mechanism is still needed. An important contribution came in 1994 from Bachmann [24] who drew the diagram illustrated in figure 2.3, which is now known as the “Bachmann triangle diagram”.
The Bachmann diagram collects data from more than 70 experiments using different process gases and different growth techniques. The diagram shows that, independently of the reactor and of the used gases, diamond grows only in the region around the CO line. This result led Bachmann to conclude that diamond growth is independent of process gases because these are rapidly broken and converted to reactive components which are the responsible elements of the growth mechanism, as also stated by P. May in 2000 [28]. Of particular interest is the bottom left region, which represents a few percents of methane in hydrogen atmosphere; this is indeed the most common gas mixture used in CVD diamond growth, with methane concentration usually between 0.3% and 5% according to the activation energy type and to the desired diamond quality.

In the past 20 years many other studies have been carried on the diamond CVD gas chemistry [29]; the fundamental reactions are accredited to involve acetylene \( \text{C}_2\text{H}_2 \) and methyl radical \( \text{CH}_3 \) [30][31][32], which are produced in the activation area by the following reactions:

\[
\text{CH}_4 + \text{H} \leftrightarrow \text{CH}_3 + \text{H}_2 \quad (2.1.1) \\
2\text{CH}_3 \leftrightarrow \text{C}_2\text{H}_6 \quad (2.1.2) \\
\text{C}_2\text{H}_6 + 2\text{H} \leftrightarrow \text{C}_2\text{H}_4 + 2\text{H}_2 \quad (2.1.3) \\
\text{C}_2\text{H}_4 + 2\text{H} \leftrightarrow \text{C}_2\text{H}_2 + 2\text{H}_2 \quad (2.1.4)
\]

Other methyl groups \( \text{CH}_X \) and \( \text{C}_X\text{H}_Y \) are also found to have a role in diamond growth [33]. The reactions 2.1.1, 2.1.2, 2.1.3 and 2.1.4 are promoted from left to right in the proximity of the activation energy and from right to left on the substrate surface; the left to right reaction is however faster and thus a non equilibrium is created in the proximity of the substrate surface, where \( \text{C}_2\text{H}_2 \) and \( \text{CH}_3 \) are not completely converted and tend to precipitate on the substrate.
In figure 2.4 the schematic diamond growth process due to CH₃ is shown as proposed by P. May [28]. Here diamond growth is represented as a stepwise process where two carbon atoms are added to the lattice and locked in diamond bonds by double CH₃ absorption.

In another diamond growth chemistry hydrogen is almost completely replaced by argon for growing poly-crystalline diamond with grain size below 5 nm; such material is called ultra nano-crystalline diamond UNCD [34].

2.1.1 Substrates for CVD diamond growth

CVD diamond can be grown on HPHT diamond stones or on foreign substrates like silicon, quartz and metals; on HPHT stones CVD diamond can be grown single crystalline, whereas on foreign substrate CVD diamond results generally in polycrystalline layers. In case of CVD growth on foreign substrates, a nucleation pretreatment of the substrate is necessary; this process will be described in the next section.
HPHT diamond stones are cut with a thickness of approx. 0.5 mm and polished (fig 2.5); they do not require further treatments before growth and are the most suitable solution to grow single crystal CVD diamond with high purity and low defect density. The drawback of these CVD diamonds is that the maximum available size is limited to the size of the HPHT stones, namely ca. 5x5 mm.

The growth of single crystal CVD diamond can also be achieved on large area substrates; in this case the most significant results have been obtained using iridium layers on foreign substrates [35] due to the small lattice constant difference between diamond and iridium (7%). MESFETs devices have been already demonstrated on diamond grown on iridium [36]; however further developments are still needed to solve the problem of thermal mismatch between diamond, iridium and the substrate during diamond growth.

Substrates for polycrystalline CVD diamond growth are various and have usually larger area than substrates for single crystal diamond growth. The most common substrate material is silicon, where diamond can be grown on wafers up to 8 inches (Seki-ASTeX) [1]; other common substrate materials are silicon dioxide, silicon nitride and metals like titanium or tungsten.

Foreign substrates for CVD diamond growth must satisfy the following requirements:
- High temperature stability (600° – 900° C).
- Stability in atomic hydrogen environment.
- Formation of carbide.
- Thermal expansion coefficient in the range of diamond.
Diamond growth on substrates which do not form carbide can be performed using a thin carbide forming interlayer, like silicon for example. Figure 2.6 depicts a 4” silicon wafer coated with 3 µm NCD grown by Hot Filament CVD at the Institute of Electron Devices and Circuits of the Ulm University.

2.1.2 Diamond nucleation

Diamond growth on foreign substrates requires a nucleation process in order to form a carbide layer interface between the substrate and the diamond, like for instance SiC in case of a silicon substrate or TiC in case of a titanium substrate. This carbide layer is essential for the formation of the first diamond nuclei, from which diamond growth starts. Nucleation can be achieved mainly in two ways, with hard particle powder or with Bias Enhanced Nucleation (BEN).

The powder method is a mechanical process where nucleation is achieved by scratching or seeding the substrate surface with hard particles; in the past SiC particles were commonly use, while today diamond particles from detonation are preferred because they allow higher nucleation densities [37].

The mechanical polishing of the substrate surface with SiC or diamond particles leads usually to a high nucleation density as the particles scratch the substrate leaving diamond or SiC fragments; on the other hand this method damages the substrate surface by creating defects and therefore is not functional for applications where the substrate surface should be preserved.

Diamond particles can also be used in seeding processes, in which the substrate is exposed to colloids where nanodiamond particles are dispersed. Critical parameters of this technique are the crystallinity and the size of the nanodiamond particles used in the colloid; indeed nanodiamond particles from detonation, which have size of few nanometers, tend to aggregate in large particles with size of 100 – 200 nm, with which high nucleation density is not obtainable. O. Williams et Al. have shown that high nucleation density can be achieved using monodispersed aqueous colloid of primary nanodiamond particles with size of less than 10 nm [37].

![Bias Enhanced Nucleation](image)

The Bias Enhanced Nucleation method was introduced by X. Jiang in 1993 [38]; here the formation of a carbide layer and diamond nuclei stems from carbon ions bombardment of the substrate surface in the CVD reactor. This bombardment is obtained by applying a negative potential to the substrate which attracts ions from the plasma. At high
temperature the substrate, being negatively biased, acts also as source of electrons which accelerate toward the plasma or the filaments and enhance gas ionization (fig. 2.7).

In the case of HFCVD, the ion concentration in the plasma is much lower than in MWCVD, therefore ion bombardment of the substrate during BEN is usually less effective in HFCVD; to avoid this problem a second bias voltage is commonly used for BEN in HFCVD. This second bias is positive and is applied to a metal grid placed behind the hot filaments (respect of the substrate); the positive bias attracts and accelerates electrons thermally emitted from the filaments, increasing largely gas ionization.

![Graph showing ion current versus time](image)

**Fig. 2.8:** Ion current to 4” silicon wafer during BEN

Fig. 2.8 shows the ions current on the substrate versus time. The current remains constant until the first diamond nuclei appears on the substrate surface; subsequently it increases due to the fact that diamond nuclei have higher electron emission than the substrate and thus gas ionization is increased [39]. The substrate and grid biases are then turned off and the current drops down to zero, the process continuing with standard diamond growth. The ion current value for stopping the nucleation biases is chosen according to the desired nucleation density; for BEN nucleation with the HFCVD used in this thesis the optimum final ion current value has been calibrated by K. Janischowsky [39].

Compared to diamond powder nucleation the BEN method has the disadvantage that the substrate must be conductive in order to be biased, however insulating substrates can also be nucleated with BEN using a thin conductive interlayer. The advantage of the BEN nucleation technique is that it can be performed directly in the diamond CVD reactor without interruptions before growth.

A further diamond nucleation method has been established by S. Rotter in the 1997 [40]; this technique is based on a two step process. Firstly, a very thin (~ 10 nm) carbon film is formed on the substrate; secondly the substrate is treated with ultra-sonic seeding which deposits nanometer size diamond particles on the thin carbon layer. During the CVD process, a diamond layer then grows on the diamond seeds consuming the carbon film formed during the pre-treatment [40].
2.2 Plasma CVD

Microwave plasma CVD (MWCVD) uses electric discharge to produce the radicals necessary for diamond growth. In MWCVD, the microwave power is coupled into the growth chamber via a quartz window in order to generate a discharge. According to the design and the size of the chamber cavity, only one microwave mode is permitted in order to create one plasma ball directly above the substrate surface. The microwave energy is transferred to electrons which oscillate and accelerate ionizing the gases.

In respect of HFCVD, MWCVD is a much cleaner technique since there is no metal contamination. Furthermore HFCVD is less reproducible than MWCVD because the filaments age from one growth to one other changing their properties, and moreover a set of filaments is not always perfectly reproducible. On the other hand the maximum substrate size is smaller in MWCVD, since it is limited to the plasma ball size; additionally MWCVD is generally more expensive than HFCVD and has the disadvantage that the plasma has higher etching power of the substrate, limiting the availability of materials which can be used with this technique (i.e. SiO$_2$ or Si$_3$N$_4$ masks for selective growth are fast etched in plasma CVD).

Fig 2.9 shows the ASTeX plasma CVD system which has been used for part of the experiments described in this manuscript. The system is equipped with a 2.45 GHz microwave generator and a heater to control the substrate temperature. Single crystal (on HPHT) and polycrystalline diamond can be grown on areas up to approx. 1 cm$^2$. The used RF power is generally in the range of approx. 700 W, while the sample heater uses a power in the range of 3 kW.

A movable boron rod can be inserted into the plasma for boron doping and delta doping [41]; the rod is made out of tungsten and coated with boron. The boron doping level may be adjusted by varying the insertion length of the rod in the plasma (approx. 4 – 5 cm) and by using one or more rods simultaneously.

The used chemistry includes hydrogen, methane and nitrogen; hydrogen flux is generally set at 200 sccm, whereas methane and nitrogen fluxes vary in the range of 1 to 10 sccm, the process pressure being in the range of 2 – 3 kPa. The substrate holder can be negatively biased up to -200 V for diamond nucleation of foreign substrates such as silicon, quartz and sapphire.
2.3 Hot Filament CVD

The Hot Filament CVD technique (HFCVD) is based on heating of metal filaments up to 2000°-2200°C in order to break molecular hydrogen and carbon compounds and to form the C,H_x free radicals necessary to diamond growth. The basic structure of a HFCVD reactor includes a set of filaments, the number depending on the size of the substrate, which face the substrate at a distance between few millimetres to some centimetres, which is in the range of the diffusion length of the radicals. The filaments material has to satisfy certain requirements: it has to be carburized during growth, it must have a melting point higher than 2200° – 2300° C, must not react with atomic hydrogen and must have a low evaporation coefficient. The inertness of filaments to atomic hydrogen is needed to avoid hydrogen recombination, while the low evaporation coefficient of the carburized alloy is necessary to reduce metal contamination during diamond growth. The two most used materials for filaments are Tungsten and Tantalum; the latter has a lower evaporation coefficient and is easier to be manipulated in respect of Tungsten, which is however cheaper than Tantalum.

The mechanism of atomic hydrogen formation in the proximity of the filaments can be described as follows:

\[ \text{H}_2 + S^* \leftrightarrow H + SH \]  \hspace{1cm} (2.3.1)

\[ SH \leftrightarrow H + S^* \]  \hspace{1cm} (2.3.2)

where H_2 is the molecular hydrogen, H the atomic hydrogen, S* an active site on the filament surface and S a saturated site. From left to right equation 2.3.1 represents the adsorption of one hydrogen atom by the active site and the formation of atomic hydrogen, while from right to left it represents the desorption of one hydrogen atom by the saturated site and the formation of molecular hydrogen. Equation 2.3.2 represents from left to right the formation of atomic hydrogen by the desorption of the saturated site, while from right to left represents the saturation of the active site on the filament. The two reactions 2.3.1 and 2.3.2 are promoted from left to right only when the filaments temperature is high enough to break molecular hydrogen (reaction 2.3.1) and to release hydrogen from the saturated site (reaction 2.3.2). In Hot Filament CVD the temperature of the filaments is therefore fundamental to obtain the atomic hydrogen necessary for diamond growth.

Figure 2.10 shows the radical concentration in a HFCVD environment in respect of the filament temperature as numerically simulated [46]. Atomic hydrogen concentration begins to overtake the carbon radical’s concentrations only for filaments temperatures above 1900°C; higher temperatures in the range of 2000° – 2100° C are hence needed for atomic hydrogen concentration to be much higher than the carbon radical one.

An important aspect of the filaments is the fact that they undergo carburization during the CVD process at high temperature in presence of carbon. During carburization the filament metal combines with carbon forming carbide from which diamond can start to grow around the filament; such process may induce cracks and stress in the filaments and may hence shorten their lifetime. The carburization is indeed the main effect responsible for the filaments aging and is present for both tungsten and tantalum. The only filament material which satisfies all the requirements for HFCVD diamond growth and do not
form carbide is rhenium, which indeed has usually longer lifetime; however this material is expensive and therefore rarely used for filaments in HFCVD.

In contrast to microwave plasma CVD methods, the ionizing rate and power in HFCVD chambers are much lower and lower are thus the ions/molecules ratio and the ions energy in proximity of the substrate surface. On the one hand this fact leads usually to lower growth rates in HFCVD chambers; however on the other hand the lower ions energy allows growing diamond on a larger variety of substrates, including the ones which are etched or degraded by the stronger hydrogen microwave plasma.

Diamond or foreign substrates may be heated by a separate heating element or directly by the filaments; in the second case the substrate is heated by radiative and convective heat transfer due to light emission from filaments and to drifting of atomic hydrogen toward the substrate.

Two Hot Filament CVD (HFCVD) systems are available for diamond growth in the Institute of Electron Devices and Circuits; the systems have been designed and realized by Klemens Janischowsky [39]. These systems are home-produced and share a similar structure, one is used for intrinsic and nitrogen doped diamond growth and the other for boron doped diamond growth; both CVD systems are capable of growing diamond on silicon wafers up to 4 inches. In the following experiments in this manuscript, the two Hot Filament CVD systems will be referred as “HFCVD undoped” for the intrinsic machine and as “HFCVD doped” for the boron doping machine.

Fig. 2.11 shows the chamber sketch of “HFCVD undoped”. The silicon wafer is held vertically by a pressure difference to avoid dust particle depositing on it; in front of the silicon wafer, at a distance of approx. 15mm, 20 tungsten filaments are vertically placed in order to cover the complete 4 inches surface.

At the filaments back, at a distance of approx 10 mm, a tungsten grid is located; the grid covers the entire 4 inches surface and is used to perform Bias Enhanced Nucleation (BEN) on foreign substrates. During BEN process the substrate is biased at -200V and the grid at + 45V.
The “HFCVD doped” is depicted in fig. 2.12; the system has the same structure of “HFCVD undoped” with a vertical substrate holder for 4” wafers and a set of tungsten filaments in front of it. “HFCVD undoped” has no BEN capability but allows diamond boron doping.

Boron doping is performed using a liquid boron source, Trimethyl Borate (B(OCH$_3$)$_3$), and a bubbler system. With this method Trimethyl Borate (TMB) is stored in a tank at specific pressure and temperature, hydrogen is fluxed into the tank at the bottom of the solution and acts as carrier for TMB molecules to the CVD chamber. The amount of TMB carried from the hydrogen flux depends on the vapour pressure above the liquid TMB surface, which subsequently depend on the pressure and the temperature of the TMB solution. Boron doping can therefore be adjusted by varying the hydrogen flux in the bubbler and the temperature and the pressure of the TMB solution.
2.4 CVD Diamond doping

Doping is probably the most critical aspect of diamond growth; today application of diamond to electronics is certainly limited from the absence of shallow donors and acceptors in diamond.

Due to the small lattice constant of diamond, the incorporation of impurities is not facilitated and in most cases leads to stress and alterations in the diamond lattice; this fact limits seriously the variety of doping elements which can be incorporated in diamond interstitially or substitutionally without compromising the lattice structure. Furthermore the fact that all doping elements for diamond are not shallow leads to the need of high doping concentration and this also affects the diamond lattice.

The three most common doping elements for diamond are shown in the band diagram in fig. 2.13. Boron is p-type doping element and has 0.37 eV activation energy; phosphorous and nitrogen are n-type doping elements and have respectively activation energy of 0.6 eV and 1.7 eV. With such high activation energies none of these elements is fully activated at room temperature.

The n-type doping with donor level at 0.23 eV corresponds to double deuterated boron complexes and has been proposed by Z. Teukam [42] in 2003. This n-type doping is achieved by deuterium diffusion in homo-epitaxially grown (100) boron doped diamond; diffusing through the layer, deuterium passivates the boron and converts the p-type conductivity to n-type. With such doping technique electrical conductivities up to $2 \times 10^4$ cm$^{-1}$ and electron mobilities of the order of a few hundred cm$^2$ V$^{-1}$ s$^{-1}$ have been obtained [42]; however this doping method resulted to be unstable at high temperatures since the deuterium diffuses out of the diamond layer at temperatures higher than 520° C [43], reducing thus the electron concentration and therefore the n-type conductivity.

In diamond there are also two additionally doping methods; the hydrogen induced surface doping for single crystal, PCD and NCD diamond, and the nitrogen doping of grain boundaries in UNCD (Ultra Nano-Crystalline Diamond). The first one is a p-type doping method which stems from the hydrogen termination of the diamond surface. The second
one is an n-type doping technique which involves conductive grain boundaries between the diamond crystals.

### 2.4.1 P-type Doping

P-type conductivity in diamond can be achieved with boron doping or with hydrogen termination. These doping methods are of particular importance since n-type doping is still not completely established and therefore p-type doping is the current way to produce electronic diamond devices.

Boron is the shallowest and basically the only effective acceptor in diamond. Its activation energy is 0.37 eV, therefore boron is not fully activated at R.T., which means that conductivity of boron doped diamond depends on temperature. This feature might be useful in certain devices like for example the boron doped diamond thermal sensor [47], where temperature is measured from the variation of conductivity. However, for most types of devices, full activation at R.T. is needed in order to achieve high and constant (over temperature) conductivity.

Since CVD diamond is typically grown in hydrogen rich atmosphere, an important aspect has to be taken into account; the formation of boron-hydrogen complexes, where one hydrogen forms a pair with one boron atom, induces a passivation of the boron acceptors [44]. In such case the hole concentration in the boron doped diamond layer drops down after the formation of the neutral B-H complexes. This boron-hydrogen compensation effect has been predominantly observed with boron doped diamond treated in deuterium plasma at temperatures below 600° C [43][44][45]. During CVD diamond growth in hydrogen atmosphere at higher temperatures (~700° - 800° C) the boron-hydrogen complexes formation is not favorable and boron doping is thus not compensated.

![Activation energy of boron in diamond as function of the effective doping conc.](image)

Fig. 2.14: Activation energy of boron in diamond as function of the effective doping conc. [50].

The fit uses $\alpha = 4.5 \times 10^{-8}$ eVcm.

The activation energy ($E_A$) of boron is not constant but depends on the boron concentration ($N_A$) [48]; more correctly $E_A$ decreases when $N_A$ increases and becomes
negligible for \( N_A > 10^{20} \text{ cm}^{-3} \) [48]. Experimental behaviour of \( E_A \) versus \( N_A \) for boron in diamond is fitted in fig. 2.14 with the formula from [49], valid also for silicon and germanium; from the fit the following rule can be extracted [50]:

\[
E_A = 0.37 - 4.5 \cdot 10^{-8} (N_A - N_D)^{1/3}
\]

(2.4.1)

where \( N_A - N_D \) represents the effective acceptor concentration.

With high boron concentration full activation in diamond is obtained at room temperature, taking also into account the hopping conduction effects observed by several groups [51][52]. The achievement of low sheet resistance in boron doped diamond requires however also high holes mobility. This is an important aspect of diamond growth today, since high boron incorporation in diamond leads to degradation of the lattice and hence to loss of mobility; qualitatively, mobility is in fact inverse proportional to the boron concentration \( \mu \sim 1/N_A \).

Degradation of diamond lattice and boron cluster formation for high boron concentration stem mainly from two effects. Firstly interstitial and substitution boron generates defects and induces stress in the lattice causing mismatch problems; secondly the incorporation of high amount of boron requires a fast diamond growth rate, which in turn increases defects density and lowers diamond quality. These effects are more significant in single crystal diamond than in poly and nano-crystalline diamond, where the defect density is already high and hence the lattice is less affected by the boron concentration or by the growth rate.

A disadvantage of boron doping is that boron is easily incorporated in diamond during growth processes in boron contaminated CVD chambers; boron contamination in the growth chamber is indeed sufficient to result in a boron concentration of \( 10^{17} \) – \( 10^{18} \) \text{ cm}^{-3}. This fact stems mainly from the high volatility of BH complexes, created by the hydrogen rich atmosphere in combination with boron deposited on the CVD chamber walls, and from the wide growth parameters window in which boron is incorporated in diamond. This results in a boron background contamination whenever diamond is grown in CVD chambers, where boron has been previously used. In electronic applications, where multilayers of intrinsic and doped diamond are often needed, this represents one of the most critical issues today. In order to avoid this problem two CVD systems are commonly used to grow intrinsic and boron doped diamond; alternatively one CVD system can be periodically cleaned and used for intrinsic and boron doped growth.

Boron doping in diamond can be achieved using solid, liquid and gas sources. Common boron sources are diborane \( \text{B}_2\text{H}_6 \) (gas), trimethyl borate \( \text{B(OCH}_3)_3 \) and trimethyl borane \( \text{B(CH}_3)_3 \) (liquid), and boron coated metal rods (solid); the liquid sources are used in combination with a bubbler and a gas carrier, as discussed in section 2.3, while boron rods are directly inserted in the CVD plasma, as described in section 2.2. Gas and liquid sources are more commonly used in CVD diamond growth because they allow more reproducibility from one growth to another or during long time growth, where boron rods get consumed after a certain time and boron concentration may vary. On the other hand boron rods are the standard source for delta doping since they allow fast insertion of boron in the process.
P-type conductivity at the diamond surface may also be achieved by hydrogen termination of undoped diamond. When the diamond surface is terminated with hydrogen a p-type channel is produced just below the surface with sheet carrier density of approx. $10^{13}$ cm$^{-2}$. Such surface conductivity by hydrogen termination has already been used to fabricate various FETs structures for electronics [53][54][55] and for chemical sensing [56]. On the other hand all these devices share the same disadvantage stemming from the instability of the hydrogen termination; when hydrogen is replaced by oxygen on the diamond surface the conductivity disappears and diamond becomes very resistive. Since the diamond surface is easily oxidized either at high temperature in air or at anodic overpotentials in electrolyte, the above mentioned devices are not stable under these conditions.

Several theories try to explain the nature of this surface doping effect but a comprehensive description is still missing. The two most recognized models relate the shallow acceptors in one case to hydrogen incorporated in the diamond surface and in the other case to surface adsorbates.

The first model comprises shallow acceptors produced by diffusion of hydrogen in the diamond surface during the hydrogen plasma [57]; however this model is in contradiction with the fact that surface conductivity depends upon the chemical environment.

In the second model the shallow acceptors stem from surface adsorbates with electron affinity large enough to induce charge transfer and thus creation of holes in the valence band [58]. The problem of this second model is that the positive charges are situated directly at the diamond surface excluding thus the possibility of metal/diamond Schottky contacts, which are on the other hand experimentally observed [59]. A solution of this contradiction has been proposed by A. Denisenko et al. [60], who suggested the presence of a thin insulating layer between diamond surface and holes channel.

2.4.2 N-type Doping

Today n-type doping of diamond is restricted to two doping elements, phosphorous and nitrogen. They have respectively 0.6 eV and 1.7 eV activation energy and therefore are not activated at room temperature. Research in diamond n-type doping is however very active because bipolar devices such as DUV LEDs need n-doped diamond layers. Even though its activation energy is too high and nitrogen doped diamond is not conductive at room temperature, nitrogen is however useful as doping element in certain cases, i.e. n-doped diamond field emitter with reduced work function [61] or for acceptor compensation of p-doped diamond [62].

Phosphorous has a lower activation energy in diamond in respect of nitrogen and thus is a better candidate for n-type doping of diamond. Unfortunately phosphorous incorporation in diamond is not easy and the growth conditions window to grow phosphorous doped diamond is very narrow. On single crystal diamond phosphorous can be better incorporated on 111 surfaces [67], which are however rare, more expensive and more difficult to process; recent publications reported nevertheless about successful phosphorous doping of 100 single crystal diamond [68].
Efforts are also directed toward the growth of phosphorous doped polycrystalline diamond, which in combination with boron doped polycrystalline diamond would permit the fabrication of blue and UV diodes on large area. Recently A. Lazea et al. reported the growth and the characterization of phosphorous doped polycrystalline diamond with suitable features for diodes fabrication [69]. However such technology is not suitable for electronics since the low phosphorous activation leads to low current levels.

### 2.4.3 Grain boundaries doping

A further use of nitrogen has been found at the Argonne National Laboratory in 2001; they have reported the growth of nitrogen doped ultra nano-crystalline diamond (UNCD) [63] with shallow donor lever and activation energy of approx. 0.05 eV [63] (fig. 2.15). As already discussed in section 2.1, UNCD presents a grain size of approx. 2 – 5 nm and is grown in argon rich atmosphere. Nitrogen doped UNCD presents in addition a “large grain boundaries” network; the low activation energy of such doped layers stems from the fact that nitrogen is not substitutional in the diamond grains but is largely incorporated within the grain boundaries [64]. With nitrogen incorporation the grain boundaries are widened and give rise to graphitic (metallic) conduction; the electrical conductivity is thus heterogeneous since it flows only through the grain boundary network and not through the diamond grains.

![Fig. 2.15: HRTEM morphology of nitrogen doped UNCD [63].](image)

Nitrogen doped UNCD has already been used to fabricate high temperature stable all-diamond pn junctions in combination with boron doped diamond [65][66]. On the other hand the extended grain boundaries network and thus the high concentration of non-diamond phases make this material less attractive for other purposes, like electrochemical devices or heat sink.
Nano-crystalline Diamond (NCD):
Growth and Characterization

Nano-crystalline diamond is by definition a heterogeneous material with a mixture of diamond, graphite and amorphous carbon phases. The diverse arrangement and different concentration of these phases may change NCD properties drastically, producing a more or less appropriate material according to the application. Besides the contained phases in the NCD layer, the crystal orientation of diamond grains and their shape also strongly affect its properties; in this sense an important NCD feature is the so called 2D (2 dimensional) or 3D (3 dimensional) grains arrangement.

In the 2D type, diamond crystals have an elongated shape along the growth direction and form a columnar grain structure (fig. 3.1A) where some of the initial crystals, from the nucleation process, prevail and continue to grow uninterruptedly. These crystals also tend to become larger during the growth and thus the final grain size of 2D NCD depends on the layer thickness.

In the 3D type, diamond grains have isotropic shape and the resulting structure has no preferential directions (fig. 3.1B). In this configuration the grain size remains constant during growth and is therefore independent of the layer thickness.
The development of 2D or 3D NCD depends largely on the renucleation rate. The renucleation process involves the formation of a new diamond grain and the consequently growth interruption of the grain on which the new one is produced. According to the renucleation rate, each grain will have a certain time to grow bigger before a new grain is formed. For 2D NCD the renucleation rate is negligible and the crystals formed during the nucleation process continue to grow; instead for 3D NCD renucleation happens with a rate depending on the growth parameters, leading then to a specific grain size.

Some of the diamond properties vary drastically from one structure to the other. Thermal conductivity for example has an anisotropic behavior in the 2D structure and an isotropic behavior in the 3D structure [70], showing the highest values for the vertical direction of the 2D structure. Mechanical stress may depend upon the grain structure as well; in 2D NCD it is relatively easy to induce a high stress gradient along the growth direction because of the lateral expansion of diamond crystals during their growth.

Due to these property variations it is important to gain a comprehensive knowledge about the growth conditions, which lead to different grains structures, having thus the opportunity to grow the most suitable NCD film for the designed application. For heat sink applications it is for instance desirable to grow 2D NCD for taking advantage of the higher thermal conductivity, while for MEMS (Micro-Electrical-Mechanical-Systems) it is desirable to have a more homogeneous stress distribution and hence 3D NCD.
An example of different grain configurations is illustrated in figure 3.2, which depicts the SEM cross section of 2D NCD grown on top of 3D NCD by mean of Hot Filament CVD; the bottom layer is intrinsic NCD grown by ρ-Best Coatings GmbH (Innsbruck, Austria), while the upper layer is boron doped NCD grown in the “HFCVD doped” system (see chapter 2). The columnar structure is clearly visible in the upper part of the image, where the size of the big crystals increases along the growth direction; the bottom part results to have isotropic morphology with smaller crystals that do not change in size with the thickness.

A further diamond crystal arrangement, which has been extensively studied, is the Highly Oriented Diamond (HOD) configuration, which was realized initially by S.D. Walter [71] and X. Jiang [72] in 1994; A. Flöter in 1998 [73] optimized the HOD growth technique by using a modified bias nucleation method. In the HOD configuration diamond grains develop in the 2D structure and possess moreover the same crystal orientation, resulting in a highly textured surface of oriented diamond; typical HOD films may have grain size of several tens of microns. In the past 10 years HOD diamond has been proposed as suitable material for mechanical applications [74], for sensing applications [75] and as substrate material for silicon electronics [76]; however the lateral diamond outgrowth occurring in HOD produces generally stress gradients, further developments are therefore still needed.

The diamond crystal arrangement has been investigated firstly by C. Wild et al. in 1993 [77] when they first introduced the α parameter, which is the ratio between the growth speed of [100] and [111] orientations:

\[ \alpha = \frac{V_{100}}{V_{111}} \]  

Fig. 3.3: \( \alpha \) parameter trend for PCD and NCD [78]

The \( \alpha \) parameter defines the shape of one diamond grain, which results to be cubic for \( \alpha = 1 \), octahedral for \( \alpha = 3 \) and a combination of these shapes for \( \alpha \) between 1 and 3.

C. Wild et al. have also correlated the \( \alpha \) parameter with the substrate temperature and the CH₄/H₂ ratio [78] (figure 3.3), defining suitable growth conditions for different NCD
configurations. In particular, the regions for $\alpha < 1.5$ and $\alpha > 3$ result in 2D and 3D NCD structures respectively.

In the past years the investigation into crystal arrangements has been further extended and two more parameters have been introduced, $\beta$ and $\gamma$, which are the growth speed ratios respectively of [110] and [113] in respect of [100]; a description of these parameters has been provided by F. Silva [79][80].

Besides bulk properties, diamond crystal orientation strongly affects also NCD surface features. Boron concentration in boron doped diamond for instance is found to be largely dependent on crystal orientation [79]; NCD surfaces with diverse crystal orientations will thus present different electrical and electrochemical properties.

In this chapter NCD growth is explored in terms of growth parameters and substrate conditions in order to study and understand the most suitable configuration for each particular application. The results of these experiments will be then exploited for fabrication of novel devices or for new uses of NCD, as will be described in the following chapters.

Most of the experiments are performed using the two HFCVD systems of the Institute of Electron Devices and Circuits, whereas plasma CVD is used in some cases. The choice of HFCVD is not only due to higher availability of the systems in the institute, but mainly due to the fact that experiments have been carried out in the perspective of large area applications of diamond, where HFCVD offers easier and cheaper up-scaling.

### 3.1 Intrinsic NCD growth: the role of methane concentration

As already discussed in chapter 2, CVD diamond properties are completely determined by the growth parameters. In case of Hot Filament CVD the most important growth parameters are gas pressure, filament temperature, substrate temperature, filament-substrate distance and CH$_4$/H$_2$ ratio.

Among them the CH$_4$/H$_2$ ratio is of fundamental importance. On the one hand the CH$_4$/H$_2$ ratio affects in fact significantly diamond properties such as the crystal size and configuration or the sp$^2$ content; on the other hand however the variations of the CH$_4$/H$_2$ ratio do not influence appreciably the other growth parameters like for instance the substrate temperature. The adjustment of methane concentration is therefore a simple and important method for tuning the diamond growth process.

In this section the relationship between methane concentration and NCD properties is investigated in terms of grain size, sp$^2$ content and optical transparency. Methane concentration in hydrogen atmosphere affects primarily the amount of carbon radicals above the substrate surface and affects therefore the carbon deposition rate on the substrate [84]. However, as shown in fig 3.4, the methane concentration affects also the amount of atomic hydrogen at a given filament temperature [85]; more specifically, higher methane concentrations cause a decrease of atomic hydrogen because of the higher recombination rate between hydrogen and carbon radicals. The decrease of atomic
hydrogen with the use of higher methane concentration leads to a lower efficiency of graphite etching and affects therefore the defect density in the diamond layer. Defects and graphitic clusters can in turn promote diamond renucleation interrupting thus the growth of big crystals; the methane concentration affects therefore not only the diamond growth rate but also the maximum size of diamond crystals and consequently the amount of grain boundaries in the NCD layer.

As will be discussed later, the size of diamond grains and the features of the grain boundaries strongly affect almost all of the final NCD properties; it is hence of prime importance to achieve full control of these characteristics through the adjustment of the CH₄/H₂ ratio during the growth process.

The influence of the CH₄/H₂ ratio on the NCD layer is investigated here using a set of four NCD samples grown in “HFCVD undoped” (see chapter 2) with different methane concentrations in hydrogen atmosphere; the samples share all the remaining growth parameters (listed in table 3.1) but growth time, which is set in order to result in the same layer thickness of approx 3 µm. Three samples are grown with respectively 0.3% (sample BIG), 0.6% (sample MEDIUM) and 1.5% (sample SMALL1) methane in hydrogen, while the last one with 1.5% methane and 1.5% nitrogen in hydrogen (sample SMALL2). The presence of nitrogen in the growth chemistry enhances diamond renucleation and thus contributes to decrease the grain size and to widen the grain boundaries [86].

The SEM images of figure 3.5 show the surface morphology of the four NCD layers. From the pictures the trend of the grain size is observed to decrease with the increasing of methane concentration; the average grain size values are 1 µm, 500 nm, 150 nm and 15 nm, respectively for samples BIG, MEDIUM, SMALL1 and SMALL2. The grain size of sample SMALL2 was too small to be evaluated by SEM microscopy; therefore XRD (X-Ray diffraction) measurements have been used [87].

It is interesting to notice that, even though the grains are randomly oriented, samples BIG and MEDIUM show a preferential growth orientation, respectively [110] and [100]; this orientation transition was also reported by K. Janischowsky [89]. Sample SMALL1 morphology presents a mixture of larger grains in the range of 250 – 300 nm and of
smaller grains in the range of 50 – 100 nm. Sample SMALL2 presents again a homogeneous grain size as samples BIG and MEDIUM.

The quality of the four NCD samples is evaluated by Raman spectroscopy; the spectra of samples BIG, MEDIUM, SMALL1 and SMALL2 are shown in figure 3.6, where the characteristic diamond shift peak at 1332 cm\(^{-1}\) is highlighted. The light source used for the Raman experiment is green laser with 514 nm wavelength. Samples BIG and MEDIUM show a similar spectrum with a pronounced diamond peak and the presence of the G-band at 1580 cm\(^{-1}\), which is characteristic of graphite content [93]; the additional shoulder at 1480 cm\(^{-1}\) is related to transpolyacetylene [92]. The diamond peak of sample BIG is sharper and more intense than the one of sample MEDIUM because of the lower grain boundaries density due to bigger grains. Samples SMALL1 and SMALL2 share also a comparable spectrum; in this case the diamond peak is only slightly appreciable for sample SMALL1, while almost invisible for sample SMALL2. The reason of this phenomenon is the pronounced rising of the D-band at 1355 cm\(^{-1}\) due to the decrease of grain size. The D-band is in fact shown to be related to small size graphite clusters [93] which in turn are found to be present in NCD with small grain size [94]; the higher intensity of the D-band peak is therefore an
indication of higher content of graphitic phases in the grain boundaries of the NCD layer. Samples SMALL1 and SMALL2 also show sharper G-band and transpolyacetylene peaks.

Samples MEDIUM and SMALL2 are also investigated in terms of their optical properties. For transmittance measurements, 5 x 5 mm² NCD membranes are fabricated by silicon etching from the backside of these two samples; the silicon etching is performed with SF6 plasma in ICP (Inductive Coupled Plasma).

Figure 3.7 shows the transmittance of the two samples from UV to IR light. For UV and visible light below 500 nm wavelength sample MEDIUM presents higher transmittance than sample SMALL2; this effect stems from the fact that in this wavelength range only the diamond crystals are transparent, while other carbon phases like graphite or amorphous carbon adsorb light. Sample MEDIUM presents bigger grain size and lower grain boundaries density; it possesses therefore higher transmittance for short wavelength.

Above 500 nm wavelength the transmittance of sample MEDIUM becomes lower than that of sample SMALL2; in this case the phenomenon may be explained by higher light scattering in sample MEDIUM due to the higher roughness and to the grains with size comparable to the wavelength [87]. The roughness of the two samples was measured by AFM and resulted to be 43 nm RMS for sample MEDIUM and 9 nm RMS for sample SMALL2.
The wave behaviour of the transmittance is due to the interference between the radiation reflected by the diamond surface and the radiation reflected by the diamond backside. The oscillation depends therefore on the sample’s thickness and indeed this method may be used for measuring the thickness of transparent layers.

![Graph showing transmittance spectrum of samples MEDIUM and SMALL2.](image)

**Fig. 3.7:** Transmittance spectrum of samples MEDIUM (red) and SMALL2 (black).

### 3.2 Boron doped NCD: the role of grain size on electrical properties

As discussed above PCD and NCD can have a grain size, which varies from tens of micrometers down to few nanometers. According to the application a certain grain size will be desired due to its advantages and drawbacks related to surface roughness and surface defect density. A large grain size has a lower grain boundary density and therefore lower density of defects related to graphite and amorphous carbon; on the other hand the surface of large grain size PCD is rougher and too inhomogeneous for planar device fabrication in the sub-micron range. On the contrary NCD with very small grain size has a smoother and more homogeneous surface, but some of the outstanding diamond properties may be degraded and no longer suitable for the application, like for instance a lower Young’s modulus for mechanical applications or a lower electrical conductivity for electronic devices.

In case of conductive diamond, the fluctuation of electrical properties such as conductivity and holes mobility must be also investigated in terms of the grain size in order to be able to grow diamond in the proper conditions required by the application.

In the following experiment five boron doped NCD layers are grown in the “HFCVD doped” system with different grain size for the evaluation of electrical conductivity and holes mobility; the parameters of the five samples are listed in table 3.2. The boron doped NCD samples are all grown onto pieces of the same intrinsic NCD layer grown in the “HFCVD undoped” system for electrical insulation from the 4” silicon wafer. The average grain size of the five samples is estimated by measuring the size of the grains on the surface in SEM microscopy; the values are listed in table 3.3. These grain size values can be considered homogenous throughout the diamond bulk since the samples are grown with conditions in order to obtain 3D structure NCD; following the previous discussion
Growth and characterization

on 2D and 3D NCD, the grain size of 3D NCD is in fact constant along the growth direction.

<table>
<thead>
<tr>
<th>Sample name</th>
<th>Smallest</th>
<th>Small</th>
<th>Medium</th>
<th>Big</th>
<th>Biggest</th>
</tr>
</thead>
<tbody>
<tr>
<td>Grain size (nm)</td>
<td>100</td>
<td>200</td>
<td>300</td>
<td>400</td>
<td>800</td>
</tr>
</tbody>
</table>

Table 3.3. Sample’s average grain size. Growth parameters in table 3.2

For electrical characterization a 1 x 1 cm² piece is cut from each sample and is patterned with 4 Ti/Au contacts at the corners; the evaluated electrical properties are conductivity, acceptors concentration ($N_A$) and mobility. Conductivity is measured by Van der Pauw method while $N_A$ concentration and mobility by Hall effect measurements.

Figure 3.8A shows the sample’s conductivities expressed in mΩ cm in respect of the grain size. From the graph it can be observed that the trend is not linear but presents a clear step in the range of 200 – 400 nm of grain size; the conductivity values ranges from 24 mΩ cm for the sample with 200 nm grain size to 100 mΩ cm for the sample with 800 nm grain size. Electrical conductivity can be expressed by the equation 3.2:

$$\sigma = q p \mu_h$$  \hspace{1cm} (3.2)

where $q$ is the elementary charge, $p$ the carrier (holes) concentration and $\mu_h$ the carrier (holes) mobility.

The difference in conductivity may be therefore related to variations in carrier concentration or in carrier mobility. The carrier concentrations of the five samples are shown in figure 3.8B. The samples have all carrier concentrations between $1 \times 10^{20}$ cm$^{-3}$ and $3.5 \times 10^{20}$ cm$^{-3}$, as expected for the 2% TMB in H₂ flux used after the calibration performed by K. Janischowsky [88]; at such high values boron activation at room temperature can be considered complete and thus the carrier concentration can be in first approximation considered equal to the boron concentration in the NCD layers.

Fig. 3.8:  
A: conductivity measurements. B: Acceptor concentrations. (in respect of grain size)
The concentration fluctuations are relatively small and do not explain the strong reduction in electrical conductivity; moreover higher conductivity in figure 3.8A do not correspond to higher acceptor concentration in figure 3.8B. The conductivity step should then be related to changes in carrier mobility between samples with different grain size. The mobility values are shown in figure 3.9 in respect of the grain size. Here it can be observed that mobility drops drastically below 400 nm, reaching a minimum at approx. 1 cm²/Vs for grain size of 200 nm.

![Graph showing mobility vs grain size](image)

**Fig. 3.9:** Holes mobility in respect of grain size

Thus the observed drop in mobility for grain size less than 400 nm fits well with the strong reduction in electrical conductivity of the samples; the 400 nm grain size seems to be therefore a critical value for obtaining highly conductive NCD with the used growth conditions in Hot Filament CVD. The lower mobility of samples Smallest, Small and Medium can be related to the denser grain boundaries network which increases largely the holes scattering between diamond grains. Comparable effects of the grain boundaries on the hole mobility of NCD and PCD have been observed by M. Kubovic [17] and by T. Sugino [81], respectively for hydrogen terminated NCD and for boron doped PCD.

### 3.3 Boron doped NCD: the role of grain size on electrochemical properties

Following the previous arguments here the electrochemical properties of boron doped NCD are correlated with its grain size. The electrochemical behaviour of NCD in respect to changes in the grain size is of crucial importance to evaluate the most suitable range in which chemical sub-micron devices are permitted and ideal electrochemical properties of diamond are preserved. The electrochemical characterization techniques used for this experiment are described in appendixes A and B. The overall electrochemical properties of NCD depends on the grain boundary properties at the surface, since these generally show different chemical activity as compared to diamond; the contribution of the grain boundaries to the overall chemical behaviour depends on their composition, on their size, associated to the distance between diamond
grains, and on their density, tightly related to the NCD grain size. A relatively large grain size with low density of thin grain boundaries would be therefore desired for reproducing the ideal properties of diamond. On the other hand it is important that the density of grain boundaries in NCD electrodes is high enough to render the micro-electrode behaviour independent from the number of grain boundaries on the NCD electrode surface.

Let us consider for example a PCD layer with grain size of 2 µm used for electrodes with size of 1 µm; since the electrode size is smaller than the grains, the electrode can lie either completely on a diamond crystal, with no grain boundaries, or between 2 or more crystals, including several grain boundaries. The properties of such electrode will be highly affected by its position on the PCD surface. If the 1 µm electrode is instead placed on NCD with 50 nm grain size, the average number of grain boundaries in the electrode will be almost independent of the position.

A compromise for the grain size is thus necessary for the fabrication of small electrodes and devices with appropriate electrochemical behaviour.

Such compromise for the grain size is investigated through the following experiment, where two boron doped NCD samples are grown in the “HFCVD doped” system with different grain size for electrochemical characterization: sample SG (small grains) with approx. 15 nm grain size and sample LG (large grains) with approx. 100 nm grain size, the thickness of the NCD samples being approx. 2 µm, which ensures a pin hole free surface. The different grain sizes of the two samples are obtained by varying the methane concentration in hydrogen and adding nitrogen for sample SG, as described in section 3.1; high boron doping in the range of $10^{20}$ cm$^{-3}$ is obtained using a 2% TMB in H$_2$ flux, as also done in for the experiment of section 3.2.

Electrochemical characterization of these boron doped NCD layers is carried out according to the theoretical background discussed in appendix A and with the setup described in appendix B for electrode configuration. The preparation of the NCD samples comprises the cut of 1 cm$^2$ sample piece, the oxidation of the surface by oxygen plasma and by chemical treatment in chromium sulphuric acid and the packaging on a PCB carrier with PTFE tape passivation.

The surface of samples SG and LG is evaluated by cyclic voltammetry measurements, which provide significant information on the chemical surface activity as described in appendix A.3; the cyclic voltammetry measurements were performed by Carsten Pietzka, also at the Institute of Electron Devices and Circuits. Figure 3.10 illustrates the respective curves in pH 1 and pH 13 for sample SG (left) and sample LG (right) in linear scale. The comparison between the two samples shows clear differences in both the potential window width and the background current density. Sample SG with 15 nm grain size possesses a high background current, which suggests the presence of an activity current related to chemical activity of defects or other states on the diamond surface (See Appendix A.3). On the contrary, sample LG with 100 nm grain size shows low background current and a well defined potential window of almost 3 V, which is the typical value for diamond in water.

An adsorption peak is also observed in pH 1 at $V_E = 1.5$ V vs. SCE for samples SG and LG, even though it is clearer for sample LG due to the lower background current;
according to [82], this peak may be related to activity of non-diamond carbon phases. The hysteresis behaviour of this peak is due to adsorption and desorption.

![Graph showing cyclic voltammetry of boron doped NCD](image)

**Fig. 3.10:** Cyclic voltammetry of boron doped NCD. Scan rate = 20 mV/s. Measurements by Carsten Pietzka.

The curves for pH 1 are reproduced in semi-logarithmic scale in figure 3.11 for better evaluation of the background current level and of the hydrogen and oxygen evolution onset potentials. From the graph it can be observed that the background current is reduced of approximately one order of magnitude in the sample with larger grains, reaching density below 10 nA/mm²; such background current is comparable to the one reported for highly boron doped single crystal diamond [90][91]. Figure 3.11 shows also that the hydrogen evolution of sample SG is shifted to positive potentials and results thus in a narrower potential window. Considering an upper limit for the current of 100 nA/mm², the potential window of sample SG is approx. 2.1 V; within the same current limit the potential window of sample LG results to be in contrast approx. 2.7 – 2.8 V.

![Graph showing cyclic voltammetry in pH 1](image)

**Fig. 3.11:** Cyclic voltammetry in pH 1 in semi-logarithmic scale for samples SG (green) and LG (pink). Measurements by Carsten Pietzka.
The higher background current and the narrower potential window of sample SG can be associated to the high surface density of non-diamond phases of carbon within the grain boundaries. Sample SG presents obviously a higher grain boundary density than sample LG due to the smaller grain size; however the effect of nitrogen must be also taken into account as an additional cause for the deterioration of electrochemical diamond properties. As reported by T. D. Corrigan [95] and by J. Birrell [64], the addition of nitrogen in the growth chemistry tends indeed to enlarge the grain boundaries and to increase their sp\(^2\) content. Therefore sample SG does not only present higher grain boundaries density, but also larger and more graphitic boundaries, which contribute to an increase in background current and to a narrow potential window in electrolyte. On the other hand sample LG, with approx. 100 nm grain size, proves to be a useful material for chemical electrodes in the micron size range with suitable electrochemical properties.

3.4 Intrinsic NCD cap layer on boron doped NCD

The benefits of using doped NCD for electrochemical applications depend strongly on the possibility to reproduce as much as possible single crystal diamond properties; in case of electrochemical electrodes, the NCD background current in the potential window in electrolyte is certainly a crucial parameter that affects signal/noise ratio and thus the diamond sensitivity, especially when high doping concentration and small grain size are used.

In this section a new method is described to reduce the background current in electrolyte of highly boron doped NCD without varying neither doping concentration nor grain size. The background current reduction is obtained instead by overgrowth of the boron doped NCD with a thin intrinsic NCD cap layer.

The thickness of such intrinsic layer is the key parameter of the technique; the cap layer should in fact be thin enough not to suppress hydrogen and oxygen evolution transfer currents and thus the possibility of amperometric operation. On the other hand it should be thick enough to reduce remarkably the background current in electrolyte. With the appropriate thickness, the intrinsic NCD cap layer would reduce the background current by shielding boron related defects and by improving thus grains and grain boundary quality, and at the same time it would allow hydrogen and oxygen evolution by current flow through the grain boundary network.

To investigate the correct thickness of the intrinsic NCD cap layer, a highly boron doped NCD reference sample is grown in the “HFCVD doped” system (parameters in table 3.4), with a thickness of approx. 300 nm, grain size of approx. 100 nm and boron of approximately $2 \cdot 10^{20}$ cm\(^{-3}\) (see section 3.2); such boron concentration range has been used in order to obtain full boron activation and to avoid at the same time the formation of boron clusters or of surface defects, as already discussed in chapter 2.
Table 3.6: Samples set for intrinsic cap layer experiments

<table>
<thead>
<tr>
<th>Sample</th>
<th>Ref1</th>
<th>Cap1</th>
<th>Cap2</th>
<th>Cap3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Growth time (boron doped NCD)</td>
<td>8 h</td>
<td>8 h</td>
<td>8 h</td>
<td>8 h</td>
</tr>
<tr>
<td>Nₐ (boron doped NCD)</td>
<td>~ 2·10²⁰ cm⁻³</td>
<td>~ 2·10²⁰ cm⁻³</td>
<td>~ 2·10²⁰ cm⁻³</td>
<td>~ 2·10²⁰ cm⁻³</td>
</tr>
<tr>
<td>Growth time (NCD cap layer)</td>
<td>-</td>
<td>90 min.</td>
<td>60 min.</td>
<td>30 min.</td>
</tr>
<tr>
<td>Expected thickness (NCD cap layer)</td>
<td>-</td>
<td>100 nm</td>
<td>70 nm</td>
<td>40 nm</td>
</tr>
<tr>
<td>Curve colour in graphs</td>
<td>Red</td>
<td>Blue navy</td>
<td>Green</td>
<td>Blue</td>
</tr>
</tbody>
</table>

The reference sample is cut in four pieces, one used as reference (sample Ref1) and three for intrinsic cap layer overgrowth (samples Cap1, Cap2 and Cap3). Samples Cap1, Cap2 and Cap3 are then overgrown in the “HFCVD undoped” system with the same parameters (table 3.5) but different growth times; the resulting three cap layers present thus the same characteristics but different thickness, being the used growth parameters for 3D NCD structure. Growth times are 90, 60 and 30 minutes, respectively for sample Cap1, Cap2 and Cap3. According to the used growth parameters and to previous calibrations, a growth rate of approx 70 nm/h is expected for the cap layers in the “HFCVD undoped” system; hence the three cap layers are expected to have a thickness of approx. 100 nm (Cap1), 70 nm (Cap2) and 40 nm (Cap3). Table 3.6 summarizes the characteristics of the samples.

Before electrochemical characterization the four samples are oxygen terminated and cleaned by oxygen plasma and a chemical treatment in chromium sulphuric acid. The cyclic voltammetry of the reference sample Ref1 is displayed in figure 3.12. The current density in the potential windows results to be in the range of 1 – 10 nA/mm², while the potential window is approx. 2.8 V considering a current upper limit of 100 nA/mm²; the sample reproduces therefore the electrochemical features of the sample with the same grain size investigated in section 3.3 (sample LG).
Sample Cap1, with the thickest cap layer of 100 nm, possesses a much lower background current as can be observed in figure 3.13; background current density is in fact below 1 nA/mm², more than one order of magnitude lower than for sample Ref1 without cap layer. However hydrogen and oxygen evolutions do not occur in a wide potential range between -2 and +2.5 V vs. SCE, resulting in a flat cyclic voltammogram; this effect is due to the cap layer thickness, which results to be too large and hence suppresses completely current flow through the diamond/electrolyte interface until breakdown. Such NCD cap layer does not accomplish the task of the experiment for it prevents the amperometric mode of the NCD electrochemical electrode.
Figure 3.14 shows cyclic voltammetry measurements of sample Cap2 (70 nm) compared with the reference sample Ref1. In this case the background current in the potential window results to be suppressed of about one order of magnitude, reaching approx. 1 nA/mm\(^2\) along the complete diamond potential window in water. In contrast to sample Cap1, the new sample preserves however hydrogen and oxygen evolution branches, in addition with the same current levels and the same onset potentials of the reference sample.

The overlapping of the onset evolution potentials suggests that the intrinsic cap layer does not act as a MOS-like barrier between the boron doped diamond and the electrolyte. As discussed at the beginning of the section, the preservation of the hydrogen and oxygen evolution branches can be related to conduction through the grain boundaries, which act as electrical resistance in parallel to the cap layer capacitance at the diamond/electrolyte interface [96].

To confirm this explanation the samples Ref1 and Cap2 have been patterned by electroplating with gold particles; on sample Cap2 the electroplating technique allowed depositing the gold particles preferentially on the grain boundaries, which represented the dominant path for the current through the cap layer. Subsequently they have been characterized again by cyclic voltammetry for the detection of the peak related to the gold activity [96].

Figures 3.15 A and B show the cyclic voltammograms of samples Ref1 and Cap2 decorated with gold particles in the linear and semi-logarithmic scale. The gold activity peak is observed at approx. 1.15 V vs. SCE on sample Ref1 and at approx. 1.17 V vs. SCE on sample Cap2, resulting thus in a small potential shift of 0.02 V vs. SCE. Such small difference in the gold activity peak potential confirms that the cap layer did not introduce a significant voltage drop on sample Cap2 and that the electrical resistance to the gold particles via grain boundaries across the cap layer did not limit the activity of the particles. The shift of the hydrogen evolution potential observed in figure 3.15A is due to the intrinsic diamond cap layer on sample Cap2 and has been already seen in the measurements taken before gold particles deposition (figure 3.14).
By capacitance measurements in electrolyte, discussed in appendix A, the thickness of the cap layer on sample Cap 2 resulted to be approx. 60 nm. [96], in agreement with the expected thickness mentioned in table 3.6.

The last investigated sample of this experiment is sample Cap3, with the thinnest intrinsic NCD cap layer of 40 nm given by the shortest growth time of 30 minutes. Cyclic voltammetry of the sample is shown in figure 3.16 in comparison with the reference sample Ref1; hydrogen and oxygen evolutions are preserved but the reduction of background current is only slightly noticeable. In this case the intrinsic cap layer results to be too thin for the purpose, leading to ineffective shielding of boron related defects, like clusters, and maybe to tunnelling effects through the intrinsic grains.
3.5 Boron delta doping of NCD in Hot Filament CVD

As discussed in section 2.4.1 boron is a deep acceptor in diamond and thus is not fully activated at R.T.; the activation energy is 0.37 eV and becomes negligible only for high boron concentration above $10^{20}$ cm$^{-3}$.

In FET technologies a boron doped diamond channel needs to be depleted by the gate within the breakdown voltage of diamond, limiting so the channel sheet charge density; full carrier activation at R.T. requires however high boron concentration in the channel. Since the channel sheet charge is equal to $n_s = \text{thickness} \cdot N_A$, these conditions result in a channel thickness confined to the nm range in which a boron concentration peak of $10^{20}$ cm$^{-3}$ is restricted. Such growth technique is called delta doping and has already been applied to single crystal diamond to produce boron doped diamond FETs [97]. These boron delta doped diamond layers were grown in plasma CVD using a solid boron rod as doping source (see section 2.2); the delta doping profile could be achieved thanks to a fast growth step obtained with a methane pulse introduced in the hydrogen plasma [98].

In boron doped polycrystalline and nanocrystalline diamond, the low carrier mobility (compared to single crystal diamond) does not allow applications in power electronics. Nevertheless a delta doping technique on these materials would permit the fabrication of FETs for sensing applications, where the requirements are mainly high chemical inertness and sensitivity and not high current densities or saturation regime; in this case a diamond electrode can be implemented directly in the FET channel. The electrical requirements for a delta-doped channel for sensor devices are indeed more relaxed than for power electronics. Firstly the saturation regime is not essential since common sensing devices operate at low voltage. Secondly devices for sensing applications do not need to work at high frequencies but rather in DC.

Concerning NCD, a further important fact to consider is that typical surface roughness values are in the range of 5 – 15 nm RMS and 30 – 200 nm peak-to-peak. Such values are much larger than the expected thickness of delta doped layers of few nanometers, the growth of homogeneous thin layers being then rather difficult. Therefore delta doped NCD layers shall be considered as heterogeneous very thin layers, where only a small part has a thickness of few nanometers; used as channel in a field effect transistor, the resistance of the delta doped channel can still be considerably varied by depleting and pinching-off those areas with low thickness. In this section the growth of boron delta doped layers is transferred from single crystal diamond to NCD and to Hot Filament CVD, allowing thus large area growth; the boron delta doped NCD layers are characterized electrically and electrochemically.

3.5.1 Growth of boron delta doped NCD

The delta doping technique with Hot Filament CVD relies on different effects in respect of the plasma CVD technique developed by M. Kunze et al. [41], where the delta doped layer was grown by pulsing the methane flux as described in the previous section. Using the “HFCVD doped” system, the boron delta doped NCD growth relies on the time the
gases need to fill the CVD chamber (~ 50 dm$^3$) and on the minimum methane and TMB ($\text{H}_2 + \text{TMB}$) from the bubbler) concentrations necessary to grow NCD with high boron doping.

The growth process in the HFCVD system can be divided essentially in three phases: filaments warm up in hydrogen atmosphere, growth phase with hydrogen, methane and TMB, and at last the filament cool down in hydrogen. The second and more important phase, the growth, is however not a static process at the beginning; once the mass flow controllers are opened methane and TMB need in fact a certain time to fill the CVD chamber and to reach the required concentration in hydrogen to grow and to dope NCD, especially because their fluxes are generally very small. This means that NCD starts to grow and to be highly doped only past a certain time period after the beginning of the growth phase. Therefore, if the gases are introduced in the correct sequence and the growth phase is stopped at the right moment, very thin layers of highly boron doped NCD can be grown by Hot Filament CVD. More precisely, flux and opening time for methane have to be adjusted in order to rapidly reach the growth regime just before the end of the growth phase; similarly flux and opening time for TMB have to be adjusted to rapidly reach high boron doping at about the same moment. A schematic representation of the technique is given in appendix C.

The following experiments of boron delta doped NCD growth are all performed using a 4 µm intrinsic NCD layer as buffer, grown on a 4” of diameter silicon wafer in the “HFCVD undoped” system for electrical insulation from the silicon wafer. The buffer has a grain size of approx. 100 – 150 nm and is cut in 1 x 1 cm$^2$ pieces for the growth of the delta doped layers in the “HFCVD doped” system.

The thickness of the boron delta doped NCD layer is then roughly estimated by measuring the electrical resistance of the layer in respect to the etching time in RIE with argon and oxygen. The etching rate of NCD in RIE has been previously calibrated by step height measurements and is equal to approx. 2.2 nm/min. (parameters in table 3.7); by SEM and AFM microscopy, the etching rate calibration did not show a preferential etching of grain boundaries in respect of the diamond grains. The electrical resistance is measured with two metal needles firstly on the as-grown sample, secondly after surface oxidation in oxygen plasma and then after each etching step of 60 seconds; all measurements are performed at room temperature.

In this section are described two boron delta doped NCD samples with different growth time and gas fluxes: sample 60M grown for 60 min. and 3 sccm TMB opened after 30 min., and sample 30M grown for 30 min. and 8 sccm TMB opened after 15 min.. The growth conditions are listed in table 3.8; the remaining conditions, shared by the two samples, are filament temperature ~ 2000° C, substrate temperature ~ 700° C, pressure: 2.5 kPa, $\text{H}_2$ flux: 400 sccm.

Figure 3.17 shows the electrical resistance trend of samples 60M and 30M starting from the as-grown condition to the point at which no current could be measured. Counting from the oxidized surface, 6 minutes are necessary to obtain an electrically insulating layer at room temperature for sample 60M; the etching rate of 2.2 nm/min gives then an estimated average thickness of approx. 12 – 13 nm for this sample. 2 minutes etching are instead needed to obtain an electrically insulating layer at room temperature for sample 30M, resulting therefore in an average estimated thickness of approx. 4 nm.
From the graph in figure 3.17 it is also worth noticing that the electrical resistance increases of a factor 2 just after surface oxidation for sample 60M and of a factor 5 for sample 30M; this effect is related with surface holes depletion caused by the oxygen termination, which introduces donor-type surface states in diamond at approx. 1.7 eV above the valence band [100].

Knowing the estimated thickness of the delta doped layers, acceptor concentration and carrier mobility can be evaluated by Hall Effect measurements on other pieces of samples 60M and 30M with four metal contacts. For sample 60M mobility results to be approx. 2 cm²/Vs while acceptor concentration approx. 6·10²⁰ cm⁻³. Sample 30M presents instead mobility of approx. 1 cm²/Vs and acceptor concentration approx. 2·10²⁰ cm⁻³. The mobility values of these delta doped NCD layers are comparable to the ones obtained on hydrogen terminated NCD [99].

Here it is interesting to notice that sample 30M possesses a smaller acceptor concentration than sample 60M even though a higher TMB flux was used, 8 sccm vs. 3 sccm. This phenomenon may be explained by the shorter growth time used for sample 30M (30 min.) in respect of sample 60M (60min.); in fact the maximum boron doping efficiency may have not been reached for sample 30M despite the higher TMB flux before the stop of the growth phase. Nevertheless the two previous samples show that thin layers of highly boron doped NCD can be grown even by Hot Filament CVD with a thickness in the range of few nanometers, which is less than the NCD grain size (~ 100 – 150 nm in this case).

NCD layers with the same conditions of samples 60M and 30M have been grown using shorter growth times than 60 and 30 min. respectively for 3 and 8 sccm of TMB; these samples however did not show any electrical conductivity at room temperature after surface oxidation. This fact may be due to different reasons according to the growth phase time; for growth times close to the ones used for samples 60M and 30M, the boron doped NCD layer may have been thin enough to be completely depleted by the oxygen termination. For even shorter growth times the doping concentrations reached were not high enough to achieve boron activation at room temperature.
In the next paragraph sample 30M, with an estimated thickness of 4 nm, is electrochemically characterized by impedance spectroscopy and C-V measurements to extract the doping profile.

### 3.5.2 Electrochemical characterization

The electrochemical characterization of sample 30M is performed after sample packaging in electrode configuration (the packaging is later shown in figure 4.5B of section 4.3.1). The carrier profile is extracted from capacitance-voltage (C-V) measurements in the electrolyte as described in appendix A. Prior to the evaluation of C-V plot, the electrical equivalent circuit of the diamond-electrolyte interface is analysed using the electrochemical impedance spectroscopy technique described in appendix A; the Bode plot of the NCD electrode is shown in Fig. 3.18A.

![Fig. 3.18: Sample 30M. A: Impedance spectroscopy. B: equivalent circuit. C: equivalent circuit at frequency below 100 Hz.](image)

The measurements are performed in 0.1 M KOH at 0 V vs. SCE. The impedance data can be fitted to the equivalent circuit shown in Fig. 3.18B; it consists of two RC elements in series (details about the diamond/electrolyte interface are found in appendix A). For better fit, one capacitance is replaced by a constant-phase element $Q_2$ (CPE) as shown in Fig. 3.18B. A constant phase element $Q$ represents the behaviour of a non ideal capacitor and is equal to $Q = 1/Z = Q_0(j\omega)^n$, where $\omega = 2\pi f$ with the frequency $f$; $n$ varies between 0 (pure resistor) and 1 (ideal capacitor).

The same equivalent circuit is used also at other surface potentials in 0.1 H$_2$SO$_4$ and 0.1M KOH electrolytes. The best fit of the impedance data at 0 V and with $f = 63$ Hz in 0.1M KOH yields the following values: $C_1 = 3.3 \mu F/cm^2$ and $R_1 = 3.5 \text{ M} \Omega \text{ cm}^2$. The dispersion factor $n$ of the CPE $Q_2$ is about 0.98, which is very close to the case of an ideal capacitance ($n = 1.0$). The nominal capacitance related to the CPE $Q_2$ at $\omega = 1$ is approx. $92 \text{ nF/cm}^2$ with the parallel resistance $R_2$ of 1.5 k$\Omega$ cm$^2$.

The $C_1$ element is slightly lower than the typical capacitance values of the electrical double layer on oxygen terminated diamond in electrolyte, which is in the range between 5 and 20 $\mu F/cm^2$ (see appendix A.3); on the other hand the $C_1$ element value, 3.3 $\mu F/cm^2$, fits well with the depletion layer capacitance of highly boron-doped diamond, which
ranges between 1 and 3 \( \mu \text{F/cm}^2 \) \cite{103}, and varies with bias. Therefore one can attribute the \( R_1C_1 \) element to the depletion layer in the boron-doped diamond. The \( C_2/Q_2 \) element, with nominal capacitance of 92 nF/cm\(^2\), is much below the capacitance range of the electrical double layer on oxygen terminated diamond in electrolyte; the \( R_2 \) element in series to \( R_1C_1 \) correlates however to the sheet resistance of the delta-doped layer. So the \( R_2Q_2 \) element might be attributed to the boron-doped layer in series to the diamond-electrolyte interface.

At low frequencies below 100 Hz the elements \( R_1 \) and \( Q_2 \) can be however neglected, resulting in the simplified equivalent circuit shown in Fig. 3.19C. The depletion layer capacitance can be hence directly calculated from the imaginary part of the impedance measured below 100 Hz frequency. This procedure allows determining the doping profile from capacitance-voltage measurements in the electrolyte.

The doping profile can be extracted from the C-V plot by a standard procedure used in the analysis of metal-semiconductor junctions \cite{104}:

\[
N_A(x) = \frac{-2}{q\varepsilon_r\varepsilon_0} \left[ \frac{1}{d((1/CV^2)/dV)} \right]
\]  

where \( q = 1.602 \times 10^{-19} \text{ C} \) is the elementary charge, \( \varepsilon_0 = 8.85 \times 10^{-14} \text{ F/cm} \) the dielectric constant and \( \varepsilon_r = 5.5 \) the relative permittivity of diamond. Here, \( C(V) = 1/j\omega Z_i(V) \), where \( Z_i(V) \) is the imaginary part of the diamond-electrolyte interface impedance at different surface potentials. To avoid errors due to parasitic activity, the applied bias \( V \) is limited to the diamond potential window in water.

The C-V plots of sample 30M are shown in Fig. 3.19A for the potential scans in 0.1 M H\(_2\)SO\(_4\) and 0.1 M KOH. The measurements are taken at a frequency of 63 Hz, where the simplified equivalent circuit shown in Fig. 3.18C is valid. The two curves are nearly identical with a shift of approx. 60 mV/pH, which is close to the Nernst’s limit (59.2 mV/pH as described in appendix A). This shift represents the pH sensitivity of the flatband potential, expected for the oxygen-terminated diamond \cite{105}, and indicates the presence of high density of chemically active surface states, pinning the surface potential. These surface states are most likely caused to the carbon-oxygen functional groups induced on the surface by the oxidation treatment \cite{105}.

The carrier profiles extracted from the C-V data in 0.1 M KOH at frequencies of 38 Hz and 63 Hz according to the described procedure are shown in Fig. 3.19B. The measurements at the two frequencies yield nearly identical profiles; this verifies that the used equivalent circuit is the correct representation of the diamond/electrolyte interface.

The extracted profile shows a peak concentration of \( 3 \times 10^{20} \text{ 1/cm}^3 \), which is in good agreement with the value obtained by Hall Effect measurement. The full width at half magnitude of the peak is approx. 1 nm and the carrier sheet charge density obtained from integration of the profile approx. \( 1 \times 10^{13} \text{ 1/cm}^2 \). The profile shows a shoulder which may be caused by the inhomogeneous nature of the nanocrystalline layer.
The doping profile extracted by electrochemical characterization confirms that doping concentration peaks above full boron activation can be obtained within few nanometers on NCD grown in Hot Filament CVD. The doping profile and the electrochemical behaviour render the boron $\delta$-doped NCD layers suitable for FET devices to be used in electrolyte as chemical sensor; this application will be described in details in chapter 4.
3.6 NCD growth on InAlN/GaN in Hot Filament and Plasma CVD

The combination of diamond with other semiconductors such as silicon or III-nitride heterostructures can be very advantageous for heat sink and electrochemical applications. In the first case the high thermal conductivity of intrinsic diamond may be exploited for heat extraction on electronic devices for improving their performance; in the second case the high chemical stability and inertness of intrinsic or doped diamond may be used for fabricating stable chemical devices for harsh environment.

The use of diamond on silicon/III-nitride devices for electrochemical applications is discussed in the introduction to chapter 4.4, whereas the implementation of diamond as heat sink is described in the following paragraphs.

One of the most useful application of diamond as heat sink material would be in the field of power devices, where thermal dissipation becomes a critical issue to avoid performance loss at high current densities.

Nowadays GaN-based heterostructures allow realizing the highest power densities in microwave and switching devices due to their high channel sheet charge density, high breakdown strength and high thermal stability [106]. However extreme power densities have been demonstrated only in pulse power mode of operation to limit the thermal losses [107]. In fact from the electronic properties standpoint, GaN heterostructures are capable of managing power more than one order of magnitude higher than silicon based devices; but such advantage is not entirely exploited yet due to the lack of an efficient heat extraction technique. The major limit to the heat extraction is the relatively low thermal conductivity of GaN, which acts as bottleneck even when combined with high thermal conductive substrates like silicon carbide (SiC).

Here diamond is an ideal candidate and may be implemented underneath or on the top of the GaN-based device. Whereas diamond substrates can be implemented by several (mostly hybrid) technologies like soldering or wafer bonding, diamond overlayers need to be realized by overgrowth.

Although already proposed in 1991 [108], no such diamond overlayer with high thermal conductivity has been realized up to now on any semiconductor material system. The most important barrier, which prevented diamond growth on electronic power devices, has always been the thermal stability of the active material; in case of post-processing steps silicon based devices are not stable at temperatures above 350 °C, while GaN-based devices are degraded at high temperature by hydrogen.

In 2001 M. Seelmann-Eggbert et al. have grown polycrystalline diamond on GaN-FETs [110]. The GaN-FETs showed identical performances before and after diamond growth; however the growth temperature was below 500°C and no investigation about the quality has been published on the diamond overgrown layers.

Recently CMOS circuits have also been coated by UNCD by A. V. Sumant et al. [111], however the growth temperature was again between 400° - 500° C, and additionally the UNCD layer possessed an extended grain boundary content.

However a novel InAlN/GaN heterostructure has been developed during the last 3 years. This heterostructure not only showed the best performances in terms of current density
and transconductance [112], but also proved to be stable at very high temperature; FET characteristics have been achieved with InAlN/GaN HEMTs working at 1000 °C for a short period of time [113]. For these reasons InAlN/GaN may be a suitable candidate for diamond growth for heat sink applications.

A sketch of the InAlN/GaN heterostructure is shown in fig. 3.20; it consists of 2 µm GaN, 1 nm AlN (used to enhance carrier mobility) and 5 to 10 nm InAlN barrier. The percentage of indium in the InAlN can be chosen to have a stress free configuration, in which case the polarization of this heterostructure has no piezo component and stems only from the difference in the spontaneous polarization of the individual materials InAlN and GaN. The high thermal stability results from these characteristics, due to the fact that high temperature does not induce stress in the heterojunction. The InAlN/GaN layers used for diamond growth experiments have been deposited on 250 µm thick sapphire substrates; lattice match and stress free configurations were chosen for higher thermal stability.

![Fig. 3.20: Sketch of the InAlN/GaN heterostructure](image)

### 3.6.1 Diamond nucleation and growth

Diamond growth on InAlN/GaN requires a diamond seeding or nucleation process. The thin InAlN barrier cannot be used for nucleation because the electronic properties of the heterostructure would be compromised; the first step toward diamond growth is therefore the investigation of a suitable interlayer for diamond nucleation.

As discussed in section 2.1.1 the interlayer material must form a carbide in order to promote diamond growth; moreover the interlayer should be as thin as possible to limit bottlenecks of the heat dissipation and it should be insulating. In this case silicon is a suitable material since it can be grown amorphous on InAlN by mean of PECVD and diamond nucleation conditions on silicon are already known.

In addition to the interlayer also the nucleation process configuration has to be reconsidered; the sapphire substrate of the InAlN/GaN heterostructure is indeed insulating and prevents to apply the nucleation bias to the sample surface. This problem is solved by the nucleation configuration shown in figure 3.21. Firstly a 4” silicon wafer with a 2 mm hole in the middle is used as holder of the InAlN/GaN sample; the silicon wafer is necessary to clamp the heterostructure to the graphite holder by pressure difference (details in chapter 2). The InAlN/GaN sample is then coated with a thin amorphous silicon film in a way that also the sides and a part of the backside are coated. When the sample is clamped to the graphite holder, the nucleation bias is carried to the sample surface via the silicon wafer and the amorphous silicon on the sample backside. In this way the ions accelerated toward the substrate sees a whole 4” silicon surface, namely
the silicon wafer plus the amorphous silicon on the InAlN/GaN sample; this allows to monitor and to control the BEN nucleation process by the ion current in the same way as it is done for standard BEN nucleation of 4” silicon wafers.

In a first experiment an amorphous silicon layer with a thickness of 250 nm has been deposited on InAlN in a PECVD reactor; subsequently diamond nucleation has been performed in HFCVD with BEN at approx. 700° C (table 3.9).

Fig. 3.22 shows the amorphous silicon surface after the diamond nucleation process with optical microscope (A) and SEM (B). Nucleation density results to be approx. $2 \cdot 10^{10}$ cm$^{-2}$ from SEM, which is in the range of nucleation on silicon wafers; however the surface seems to be covered with bubbles, some of which have exploded. This phenomenon may be caused by reactions between silicon and the nitride at high temperature in hydrogen atmosphere.

To avoid reactions between amorphous silicon and InAlN a SiO$_2$ interlayer has been deposited between them by mean of PECVD; SiO$_2$ is a more stable material in respect of amorphous silicon at high temperature and is commonly used as mask for selective diamond growth. The diamond nucleation process by BEN in HFCVD has been repeated
on InAlN using a stack interlayer of 150 nm SiO$_2$ and 250 nm amorphous silicon. The BEN parameters have been the same as in the first experiment, where only amorphous silicon has been used (table 3.9). As shown in fig. 3.23, the nucleation density is again approx. $2 \cdot 10^{10}$ cm$^{-2}$ from the SEM picture (B), but in this case the optical image (A) reveals a clean and homogeneous surface, which can also be observed in the photograph 3.23C. Diamond nucleation using BEN has been successfully performed with thinner interlayer stacks down to 150 nm (50 nm SiO$_2$, 100 nm a-Si), which could still provide electrical conductivity around the sample for BEN nucleation and at the same time electrical insulation after outgrowth. BEN nucleation processes with these interlayer stacks have been completed using either HFCVD or plasma CVD.

Using BEN and silicon based interlayers, homogeneous diamond nucleation has been achieved on InAlN/GaN with nucleation density up to $2 \cdot 10^{10}$ cm$^{-2}$. If the $\alpha$, $\beta$ and $\gamma$ parameters (described in the introduction of chapter 3) are optimized for NCD lateral outgrowth, this nucleation density results to be suitable to grow intrinsic NCD, for heat sink purposes, and boron doped NCD for electrochemical applications, with pin holes free layers for a thickness above 400 – 500 nm.

Such nucleation may therefore now be used for the growth of intrinsic NCD on the heterostructure at high temperature in HFCVD and in plasma CVD. In the next NCD growth experiments the thickness of the NCD layers was limited to 300 - 400 nanometers.
in order to avoid inducing stress in the heterostructure, since growth conditions were not optimized for stress free diamond growth on sapphire.

Fig. 3.24: SEM picture: morphology of diamond on InAlN/GaN

Fig. 3.25: UV Raman spectrum of diamond grown on InAlN/GaN

In fig. 3.24 the SEM image depicts the surface of NCD grown on InAlN/GaN at 750° C. The distinctive crystalline morphology of NCD is clearly observable and is comparable with the one of NCD grown on silicon shown in section 3.1; diamond grains are approx. 100 nm in size, while the NCD thickness is approx. 400 nm. To confirm the high diamond quality, Raman spectroscopy has been performed on the NCD layer. Fig. 3.25 shows the Raman spectrum of the 400 nm NCD layer on InAlN/GaN; the picture confirms that the peak at 1332 cm⁻¹, characteristic of diamond bond sp³, is predominant and therefore that diamond is the main configuration of carbon in the layer.

After having verified the NCD quality, the morphology and the electronic properties of the InAlN/GaN heterojunction must be evaluated. The integrity of the heterostructure after diamond growth is observed by SEM in cross section and by AFM (after diamond removal) on two InAlN/GaN samples with different barrier and interlayer thicknesses.
The InAlN barriers are 30 and 7 nm thick, which allow in the first case to observe the barrier by SEM and in the second to test the stability of thin barriers.

The SEM cross sections are shown in fig. 3.26 and 3.27; in the first image (fig. 3.26) the 30 nm barrier can be easily recognized and shows no damage after the diamond growth process. The high contrast at the interface between InAlN and SiO₂ suggests that diffusion of materials has not occurred.

In the second cross section image (fig. 3.27) the whole layer stack after diamond growth is recognizable; the picture shows that even with the very thin InAlN barrier (7 nm) the heterostructure is still stable during diamond growth. All the layers present in fact well defined edges.

In order to investigate the InAlN surface after diamond growth, the NCD layer and the interlayers are removed by mean of Reactive Ion Etching (RIE), with Ar and O₂ to etch NCD and CF₄ to etch amorphous silicon and SiO₂. The SiC clusters (formed during BEN nucleation) between NCD and the interlayers are also removed by O₂ RIE plasma [109].

Fig. 3.28 shows the AFM image of the InAlN surface after diamond growth and removal; the measured roughness is 0.6 nm RMS, which is comparable with roughness values of
unprocessed InAlN. The conservation of surface roughness suggests again that no reactions took place between InAlN and the interlayer during diamond growth. The pits on the InAlN surface in figure 3.28 may have been caused by the CF$_4$ plasma etching of the interlayers.

![AFM picture. InAlN surface after diamond growth and removal. Roughness is 0.6 nm RMS.](image)

In order to use diamond effectively as heat sink on electronic devices, a very important matter is that electronic performances of the devices are not degraded; in case of the InAlN/GaN heterostructure we must first of all check that the 2DEG is not affected by diamond growth at high temperature. In order to carry this experiment two pieces of the same InAlN/GaN layer have been processed with MESA etching and ohmic contacts deposition with TLM structures; on one sample 400 nm thick diamond is grown at high temperature using standard interlayers, while the other sample is used as reference. On the InAlN/GaN layer overgrown with diamond MESA and ohmic contacts have been fabricated before diamond growth mainly for two reasons. Firstly, as will be discussed later in chapter 5, the ohmic contacts deposition after diamond growth may be problematic since the diamond layer (and the interlayers) would have to be etched away completely without degrading or affecting the InAlN surface. Secondly, and more significantly, the full coating of HEMT devices with diamond for heat sink requires that the diamond layer is grown on the completely finished electronic devices; it is therefore important to be capable to overgrow the ohmic contacts without degrading them.

Before performing electrical measurements diamond is structured by plasma etching for opening of the ohmic contacts; the structure is shown in fig. 3.29.

![InAlN/GaN sample with diamond overgrown after MESA and ohmic contacts deposition. Contacts are then open by plasma etching.](image)

I-V characteristics and TLM results of the two InAlN/GaN samples are depicted in fig. 3.30. From the I-V characteristic it is seen that the maximum current density is
completely preserved, while a slight degradation is observed for the saturation voltage. This degradation can be explained by the TLM results; the slope of the two fitting lines is very similar, meaning that the sheet resistance of the heterostructure is preserved, but the intercept at \( x = 0 \) is 3 times higher in the case of InAlN/GaN overgrown with diamond, suggesting that ohmic contacts have been degraded during the high temperature CVD process. Furthermore, measurements on the ohmic contact surface showed that the resistance of the top metal in the ohmic contact stack has increased by a factor 5 after diamond growth, probably because of carburization of the metal surface. Therefore the variation of the slope of the I-V characteristic and the different saturation point can be attributed to a change in the configuration of the top metal of the ohmic contacts.

The maximum current density shown in figure 3.30 depends on the carrier sheet charge density \( (n_s) \) of the heterostructure; as already discussed above in this section, for InAlN/GaN \( n_s \) is given only by the spontaneous polarization discontinuity. The conservation of the maximum current density after diamond growth (shown in figure 3.30) is therefore the indication that the polarization discontinuity did not change and that the 2DEG has been preserved after the CVD process at high temperature. This result is very promising, since it proves conceptually that InAlN/GaN devices can be overgrown with high quality diamond.

### 3.6.2 The role of growth temperature

As discussed in the introduction of this section, the substrate temperature during diamond growth is a critical parameter for overgrowing GaN heterostructures and silicon devices; diamond growth on such materials can be achieved normally only at temperatures below 500° C [110][111], whereas on InAlN/GaN it has been shown here that NCD can be grown at high temperatures up to 750° C.

The negative effects of low temperature growth on diamond quality and diamond growth rate have been studied widely in the past ten years, regarding both single crystal and polycrystalline diamond [114][115]. In particular T. Sharda et al. [116] and A. Heiman et
al. [117] reported about the role of high substrate temperature for reducing non-diamond carbon phases and for promoting diamond particles formation.

As reported by T. Teraji et al. the diamond growth rate is affected by substrate temperature as well; they show that high substrate temperature increases largely diamond growth rate [121].

In this section the role of substrate temperature for NCD growth on InAlN/GaN is investigated in order to evaluate the requirement of high temperature growth. Two pieces of the same InAlN/GaN layer are used for NCD growth at different substrate temperature; NCD growth is performed in plasma CVD by mean of the ASTeX system (describe in chapter 2) because such technique offers more freedom for the choice of substrate temperature without varying other parameters (i.e. filaments temperature in case of HFCVD).

Before NCD growth, the two samples are nucleated by BEN in plasma CVD with the same parameters in order to share the same nucleation conditions (table 3.9), including in this case also the same substrate temperature of 750° C. The growth process is instead performed using two different substrate temperatures, namely 400° C (sample A) and 700° C (sample B), while all other parameters (CH4/H2, pressure, time, plasma power) are the same for the two samples and are listed in table 3.10.

Fig 3.31 shows the surface morphology of NCD on sample A (left) and sample B (right) by SEM microscopy after 60 minutes growth. The first evident difference is the fact that, after the same growth time, sample A does not have an enclosed surface, while sample B does not present holes in SEM microscopy. Considering that the starting point (nucleation density) was the same and that the growth time was equal in the two processes, the fact that the layer grown at low temperature is not closed corresponds to a smaller thickness of the film and thus to lower growth rate.

This difference between the two growth processes shall be seen in respect of the used thermal budget, which is defined as the total amount of thermal energy transferred to the sample during the high temperature process. The thermal budget of sample A is in this case lower than the one of sample B. In order to obtain the same thermal budget, the growth time of the low temperature process has to be increased, leading then to the same layer thickness.

![Image A: Low temperature diamond growth](image1.png)

![Image B: high temperature diamond growth](image2.png)

Fig. 3.31: A: Low temperature diamond growth B: high temperature diamond growth
A further important observable difference between the two sample’s surfaces is that sample B grown at higher temperature shows faceted and bigger crystals, whereas crystals in sample A have no regular shape, suggesting thus that sample B is not only thicker but also possesses higher diamond crystal quality.

In order to confirm and evaluate the different crystal quality, boron doped NCD is grown on both samples using again 400° and 700° C as substrate temperature; subsequently the two layers are electrochemically characterized. Since the growth rate at lower temperature is reduced (as discussed above), boron doped NCD growth at 400°C is performed with longer growth time in order to ensure that both samples A and B possess comparable thickness and that no pin holes are present on their surfaces; the other parameters are again the same for the two samples.

After boron doped NCD growth samples A and B are oxidized by oxygen plasma and chemical treatment in chromium sulphuric acid for surface oxidation and cleaning. The two samples are then packaged in electrode configuration (packaging shown in figure 4.5B of section 4.3.1) and characterized by cyclic voltammetry as described in appendix A.

The results are shown in fig. 3.32. NCD grown at 400° C results to possess much higher background current in the potential window than NCD grown at 700° C; moreover hydrogen and oxygen evolution onsets occur at lower potentials, narrowing thus the potential window. The higher background current suggests that diamond grains and grain boundaries have higher non-diamond carbon phase density, like graphite or amorphous carbon, and a higher defects density.

The background current and the potential window width of the sample grown at 700° C are comparable to the ones obtained for NCD growth on silicon shown in previous sections of this chapter.

![Cyclic voltammetry of sample A (low growth temperature) and of sample B (high growth temperature)](image)

High substrate temperature during NCD growth results therefore to be crucial to achieve high quality diamond, which is consequently essential to obtain advantages in terms of thermal dissipation or chemical stability in power and chemical devices.
Chapter 4

Diamond based chemical sensors

4.1 Concept of pH sensor

A pH sensor, or ISFET (Ion Sensitive FET), can be defined as an electrochemical device which provides an electrical response to the pH of the electrolyte; its first introduction was made in the 70’s by P. Bergveld [122]. The pH sensor advantages in respect of traditional pH measuring techniques, like pH paper or coloured chemical reactions, are the suitability for miniaturization, system integration, cost-effectiveness and the possibility to digitally process the result.

Figure 4.1 depicts the concept structure of an ISFET device; a Si-based ISFET is taken as example. The pH difference, i.e. difference in hydrogen ions concentration, acts as change in the gate potential and modulates thus the drain-source current.

The solid/electrolyte interface and its electrochemical properties are discussed in appendix A.

![Fig. 4.1: Ion Sensitive FET (ISFET) concept](image-url)
4.2 Introduction

Chemical sensors and actuators are devices of major importance for bio-medical, biochemical and electrochemical synthesis and analysis. The main devices in these fields are the electrochemical electrode and the chemical field effect transistor (ChemFET or ISFET). The electrochemical electrode is used for stimulating chemical reactions in the electrolyte by applying a potential and by allowing current flow through it (amperometric mode); the chemical field effect transistor is used for measuring the pH of the electrolyte or to sense potential signals of reactions (potentiometric mode). A third type of device may be generated by the combination of an electrochemical electrode with an ISFET, where the electrochemical electrode is placed between the ISFET and the electrolyte; such device is very interesting, because it grants the possibility to use only one device for operation in the amperometric and in the potentiometric mode. For example this combined device would be useful for stimulating cell reactions and for measuring their response.

Sensing and actuation in chemical applications requires materials which are able to operate in harsh environment, like high anodic overpotentials, corroding or oxidizing media and in certain cases high temperature. The most common used materials are inert metals oxide for electrodes and silicon for FETs. However none of these materials satisfy completely the above mentioned requirements, since metals and silicon undergo oxidation at anodic overpotentials or deterioration with corroding substances. Furthermore the insulating gate electrodes do not allow driving current through the device/environment interface and thus do not permit bio-chemical stimulations.

In figure 4.2 an ISFET realized by Infineon Technology is depicted [125]; the device is based on a silicon MOSFET and uses a metal oxide as chemical electrode electrically connected to the MOSFET gate.

Such an ISFET presents two main disadvantages, which limit its possible applications. Firstly the MOSFET gate oxide and the metal oxide electrode prevent current flow through the device; the amperometric mode of operation is therefore not allowed and the
device can’t be used as chemical electrode. Secondly the metal oxide is not completely chemically stable, since it can be corroded for example by HF.

Apart from silicon technology, research is also active toward nitride based ISFETs, using for example the well established AlGaN/GaN or the novel InAlN/GaN which has been introduced in chapter 3.6. Such heterostructures are wide band gap materials and provide some advantages in respect of silicon based ISFETs, like for example higher thermal stability, higher chemical stability and superior electronic properties.

In 2002 M. Stutzmann et al. [118] reported on the use of an AlGaN/GaN HEMT as Ion Sensitive FET. In this device the sensitivity was provided by the response of the 2DEG to variations of the surface potential, being the AlGaN surface in contact with the electrolyte. Such structure provided sensitivity to various polar liquids like isopropanol and acetone; nevertheless the AlGaN surface was not stable in all conditions, in particular being increasingly oxidized in electrolytes with pH of about 9 or higher and with V_DS higher than 0.2 V. In 2007 C. Pietzka et al. [132] proposed a similar structure using InAlN/GaN with the InAlN surface in direct contact with the electrolyte; however the ISFET device showed severe performance degradation due to surface oxidation at high anodic overpotentials.

The ideal substitute material for the above mentioned chemical devices is diamond because of its resistance to corrosion and to hydrolysis at high over potentials; moreover diamond is biocompatible, chemically inert, can be insulating or conductive and can be functionalized (the general chemical properties of diamond are found in appendix A, while in section 3.3 and 3.4 the nano-crystalline diamond electrochemical properties are firstly introduced). Diamond is therefore a perfect candidate as active or passive material for chemical electrodes or ChemFETs. As chemical electrode diamond, used in its polycrystalline boron doped configuration, is already the standard material for heavy duty and waste water treatments [119]; however, in ISFET technology diamond has not yet been exploited and research is still in a prove of concept stage.

In ISFET devices, diamond may be implemented mainly in two ways: as chemical passivation or as active electric material. As chemical passivation diamond may be used as passive element in combination with the above mentioned devices; in such case the superior chemical stability of diamond would be exploited by protecting the silicon or the nitride based FET device with a diamond gate layer, which would face the electrolyte. This approach has been reported for example in 2004 by T. Guzdek et al. [120] which reported about a silicon based ISFET with NCD overgrown gate dielectric; however no data about the quality of the NCD layer have been published. In this case the NCD layer has to be in fact grown at low temperature due to the low thermal stability of silicon electronics; grown at low temperature, NCD would not then preserve the outstanding diamond properties due to a higher graphitic content. In the same way, the requirement of high temperature growth, necessary for achieving high quality diamond, limits the application of diamond electrodes to GaN based ISFETs.

As active part of the ISFET, many diamond based devices have been demonstrated in the past years, always using single crystal diamond in combination with surface doping by hydrogen termination [126][127] or boron delta doping [129]. These devices are based on
the modulation of the 2DEG channel by the electrolyte potential, being the electrolyte in direct contact with the diamond channel.

Hydrogen terminated diamond ISFETs have been reported by H. Kawarada [126], by A. Denisenko [127] and by J. Garrido [128]. These devices showed high pH sensitivity and suitable electronic properties, as shown from the reported graphs in figure 4.3. The pH sensitivity of these hydrogen terminated diamond ISFETs is induced by partial oxidation of the surface, which is for example obtained by ozone treatment in the case of the device from J. Garrido (figure B); such partial oxygen termination however reduces the surface conductivity of the hydrogen terminated diamond and this is reflected in low current levels of the ISFETs.

Thus hydrogen terminated diamond ISFETs present two main limitations. Firstly the sensitivity strongly depends on their hydrogenation and surface preparation. Secondly the carbon-hydrogen groups at the diamond surface are replaced by carbon-oxygen groups under high anodic overpotentials or when in contact with strongly oxidizing media, suppressing the electrical surface conductivity and thus degrading the device performance. The hydrogen terminated diamond ISFETs are therefore not stable in harsh environment and do not allow current flow through the diamond surface, preventing the amperometric mode of operation.

A diamond ISFET based on boron delta doped single crystal diamond has been proposed by A. Denisenko et al. in 2007 [129]. Such device is characterized by an oxygen terminated boron delta doped diamond layer in direct contact with the electrolyte. Thanks to the oxygen termination this new device showed much better chemical stability than the hydrogen terminated diamond ISFETs, being able to operate under anodic conditions without degradation of performance. However the sensitivity of the device resulted to be limited by the high $n_s$, which led to low transconductance and thus to a low current modulation of approximately 1% (see discussion on boron delta doping of diamond in section 3.5). On the other hand the optimization of the boron delta doped diamond channel would lead to an ISFET device with outstanding stability and performance, limited then only by the small area substrate.
The solution to the small area problem could be the use of NCD as active material for the FET channel. The realization of a boron delta doped NCD layer is described for the first time in the section 3.5.1 of this thesis; as a result the first use of boron delta doped NCD for ISFET applications is discussed in the next section (4.3).

In this chapter two novel diamond-based ISFET structures are proposed and fabricated using the growth techniques described in chapter 3. The first is an all-diamond ISFET with a boron delta doped NCD layer which acts as active channel and as interface with the electrolyte; the advantages of such devices in terms of stability and sensitivity will be illustrated.

The second device is an InAlN/GaN ISFET with boron doped NCD overgrowth as chemical gate electrode; the outstanding electronic properties of InAlN/GaN will be here exploited for producing a highly sensitive and stable device.

All the experiments in electrolyte are performed with the setups and the techniques described in appendix B and according to the concepts described in appendix A.
4.3 Boron delta-doped NCD ISFET

In this section a novel diamond ISFET structure is described, which comprises a boron delta doped NCD layer, grown according to the technique described in section 3.5, and oxygen termination. Such structure represents the transposition of the delta doped single crystal diamond ISFET [129] (mentioned in the introduction of this chapter) to NCD.

The concept of this new device is shown in figure 4.4. The boron delta doped NCD channel is oxygen terminated and in direct contact with the electrolyte; its thickness, limited to the nm range, allows modulation of the channel current by the potential at the electrolyte/NCD interface within the diamond potential window in water. The device is therefore conceptually sensitive to ion concentrations (pH sensitivity) as well as to potential signals (bio-sensing).

The oxygen termination provides stability over a wide potential range, making the device suitable for operation above the onsets of hydrogen and oxygen evolution, especially at high anodic overpotentials. Such characteristic, in combination with the fact that the NCD channel is in direct contact with the electrolyte, allows driving current through the gate interface without degrading the performance. The device is therefore capable of operating both in amperometric and in potentiometric mode. This last feature renders the device unique, since it enables reaction stimulation and signal recording with the same device.

![Fig. 4.4: Concept of the boron delta doped ISFET](image)

4.3.1 ISFET fabrication

The NCD layers are grown on silicon substrates by HFCVD in a three step process. The first step is the nucleation on a 4” silicon wafer performed by bias enhanced nucleation (BEN) in the “HFCVD undoped” system (chapter 2). Next a pinhole free intrinsic NCD buffer of high electrical resistivity is grown for electrical insulation from the silicon substrate (growth parameters in table 4.1). The film thickness is approx. 4 μm and the grain size about 100 nm, following the experiments in chapter 3.3 about electrochemical
properties of NCD. Finally, the 4” wafer containing the buffer layer is then cut into 5 x 10 mm samples and used for delta doped NCD growth with various delta thicknesses. The boron delta-doped channels of the FETs are grown in the “HFCVD doped” reactor as described in chapter 3.5 using a trimethyl borate liquid doping source. The as-grown samples are hydrogen terminated and must therefore be oxidized; oxidation is performed firstly by oxygen plasma and subsequently by chemical treatments in H₂SO₄+H₂O₂ (2:1) and in chromium sulphuric acid, which also cleans the diamond surface from sp² bonds.

The ISFET device fabrication process consists of 4 steps as illustrated in Fig. 4.5A: ohmic contact deposition, MESA etching, SU8 passivation and PTFE encapsulation. Ohmic contacts consist of 2 x 2 mm Ti and Au pads with various drain-source distances, ranging from 100 µm to 3 mm on different samples. MESA etching is performed by Reactive Ion Etching (RIE) with argon and oxygen plasma. Subsequently the sample surface is coated with SU8, a photosensitive epoxy which is chemically stable and inert; the SU8 is patterned with two openings for the ohmic contacts and an opening for direct contact between electrolyte and the NCD channel. The size of this last opening defines the gate area of the ISFET device; gate lengths from 50 to 500 µm are used on different samples.

The last steps of the fabrication process include the packaging of the device onto a PCB carrier and the complete encapsulation of the ISFET device structure using a PTFE foil with a window for the electrochemical gate electrode. Fig. 4.5B shows the resulting device configuration.

Fig. 4.5: A: Boron delta doped NCD ISFET fabrication. B: photograph of the encapsulated ISFET device
4.3.2 ISFET characterization

In this section two different $\delta$-boron doped NCD ISFETs are electrochemically characterized. The ISFETs are realized using two $\delta$-doped layers of different thickness and doping in order to evaluate the different device performances in terms of current levels and pH sensitivity. The two samples are named Thick_$\delta$ and Thin_$\delta$, the first one having a thicker delta doped NCD layer than the second.

Sample Thick_$\delta$

The ISFET named “sample Thick_$\delta$” is fabricated on a boron delta doped NCD layer with an average thickness of approx. 10 nm and boron doping of $6 \cdot 10^{20}$ cm$^{-3}$, calculated from Capacitance-Voltage (C-V) measurements in electrolyte. The device dimensions are $L_G = 500 \mu$m and $W_G = 2$ mm.

The device is firstly configured as electrode, short-circuiting drain and source as described in appendix B, for characterization of the diamond/electrolyte interface; cyclic voltammetry is performed in pH 1 and pH 13, the results are shown in figure 4.6A. This measurement is important for the characterization of the ISFET device since the diamond potential window in cyclic voltammetry represents the operating range of the gate in ISFET configuration. A wide potential window allows a larger gate voltage range and therefore higher current modulation in the ISFET mode. Furthermore the background current within the potential window is an indicator of the leakage current through the gate diode of the ISFET.

![Sample Thick_$\delta$](image)

Fig. 4.6: Sample Thick_$\delta$. A: cyclic voltammetry in pH 1 and pH 13. B: cyclic voltammetry in pH 1 in semi-log scale

Figure 4.6A shows that the diamond potential window of sample Thick_$\delta$ reaches approx. 3V in pH 1 and approx. 2.5 V in pH 13, resulting to be close to the ideal case for diamond. In order to have a better evaluation of the diamond surface, the cyclic voltammetry is plotted in semi-logarithmic scale in figure 4.6B for pH 1; here one can see that hydrogen and oxygen evolution onsets are respectively at approx. -1 V and 1.75 V, with background current below 50 - 100 nA/mm$^2$. 
After electrode characterization the device Thick_δ is mounted in ISFET configuration, where an additional voltage can be applied between source and drain. In figure 4.7 the output characteristic is depicted for \( V_{DS} = 1 \text{ V} \) and \( V_G \) from 0.5 to -1.5 V vs. SCE. Before discussing the results it is worth to remark that the gate potentials used in ISFET mode are opposite in sign of the potentials used in electrode configuration; therefore the gate range \( V_G = 0.5 \) to -1.5 V (vs. SCE) corresponds to \( V_E = -0.5 \) to 1.5 V (vs. SCE) in cyclic voltammetry measurements.

![Figure 4.7: Sample Thick_δ. Output characteristic in pH 1](image_url)

The output characteristic of sample Thick_δ shows that the drain-source current \( I_D \) is modulated by the voltage applied at the diamond/electrolyte interface; the device behaves therefore as a ChemFET where \( I_D \) modulation can be expected with gate potentials restricted to the diamond potential window in water. The total current modulation is however low and reaches only approx. 10 % of the maximum current density. Such low modulation stems from the high carrier sheet charge density in the boron delta doped NCD channel; for sample Thick_δ, in fact, an average boron concentration of \( 6 \cdot 10^{20} \text{ cm}^{-3} \) in combination with a thickness of 10 nm gives a carrier sheet charge density \( (n_S) \) of approx. \( 6 \cdot 10^{14} \text{ cm}^{-2} \), which is one order of magnitude higher than the desired value for complete modulation within the diamond potential window [129].

Moreover the maximum gate bias range \( \Delta V_G \) of the device can be defined by the equation 4.3 as in the case of a MESFET, where \( N_A \) is the acceptor concentration, \( \varepsilon_d \) the dielectric constant of diamond and \( d \) the maximum channel thickness which can be depleted. Such an analogy has been already used by A. Denisenko [129] to evaluate the maximum gate bias range \( \Delta V_G \) of a boron delta doped single crystal diamond layer.

\[
\Delta V_G = qN_A \frac{d^2}{\varepsilon_d \varepsilon_0}
\] (4.3)
If we consider an acceptor concentration of $6 \cdot 10^{20}$ cm$^{-3}$ and that the maximum gate bias range $\Delta V_G$ should fall within the 3 V of the diamond potential window in water, the resulting thickness which can be depleted results to be approx. 1.2 nm. In contrast the channel thickness of sample Thick$\_\delta$ is approx. 10 nm and this fits well with a drain source current modulation of about 10% in the output characteristic in figure 4.7.

The transfer characteristic of the ISFET Thick$\_\delta$ is shown in figure 4.8; the measurement is performed at $V_{DS} = -1$ V in pH 1 and pH 13. From the graph it is noticeable that there is a constant shift in the pinch-off voltage between the two electrolytes. This shift is related to the pH sensitivity of the NCD layer surface and results to be $\sim 480$ mV, which corresponds to a pH sensitivity of approx. 40 mV/pH. Before comparing such value with the theoretical Nernst limit (59 mV/pH) one shall consider that the potential at the diamond/electrolyte interface is not constant along the channel direction in ISFET mode, since it must be combined with the drain-source voltage at each point. The relatively large gate length (500 µm) and the drain-source bias (-1 V) used for sample Thick$\_\delta$ make such difference not negligible.

The transconductance of the ISFET device can be calculated from the derivative of the transfer characteristic from figure 4.8; the maximum transconductance can be found at $V_G = -0.6$ V vs. SCE and results to be 0.27 µS/mm. A major contribution to this low transconductance is certainly the low mobility of the boron delta doped NCD channel.

As discussed in the introduction, a major target of designing a diamond ISFET is to obtain a stable device in harsh environments where other ISFETs would fail, like corroding liquids. The device Thick$\_\delta$ is therefore immersed in a solution containing 3% NaOH and heated at 50° C for several minutes. Such aggressive solution can easily damage permanently silicon or GaN based ChemFETs [130] and is thus a significant stability test for diamond ISFETs.

Figure 4.9 illustrates the transfer characteristics of sample Thick$\_\delta$ in pH 1 and pH 13 with the same bias conditions used for figure 4.8 after exposure to NaOH for 45 minutes. After the exposure to the aggressive media sample Thick$\_\delta$ still shows FET behavior; the
diamond-based chemical sensors  69
drain-source current is in fact still modulated by the gate potential. The current density is
moreover essentially preserved after the harsh treatment; this means that the carrier sheet
charge density of the δ-doped channel layer has been preserved. Furthermore the voltage
shift between the curves in pH 1 and pH 13 is comparable with the one observed in figure
4.8, meaning that also the pH sensitivity of the device did not change significantly after
the treatment.
Minor changes in the transconductance, in the current density and in the pH sensitivity of
the device may also be caused by degradation of the SU8 passivation or of the PTFE
encapsulation.
This result shows that the boron doped NCD diamond may be capable to withstand harsh
environments without important degradation of electronic and electrochemical properties
despite its poly-crystalline nature; however further studies on the stability are needed to
determine the effects of the packaging and to investigate the diamond surface
configuration after harsh treatments.

Fig. 4.9: Sample Thick δ. Transfer-characteristic after NaOH 3% treatment at 50° C
Sample Thin$_{\delta}$

The ISFET Thin$_{\delta}$ is fabricated using a boron delta doped NCD layer grown with the same routine used for the sample described in section 3.5.2 (sample 30M); the average thickness is thus approx. 2 – 3 nm and the doping concentration approx. $2 \cdot 10^{20}$ cm$^{-3}$ (from C-V in electrolyte). The device dimensions are $L_G = 200 \ \mu$m and $W_G = 2 \ \text{mm}$.

Cyclic voltammetry measurements in electrode configuration are shown in figure 4.10A for pH 1 and pH 13; cyclic voltammetry in semi-logarithmic scale is shown in figure 4.10B for pH 1. The sample’s features reflect the ones of sample Thick$_{\delta}$, with a potential window of approx. 2.7 V and a background current in the range of 50 – 100 nA/mm$^2$.

![Graphs A and B](image)

**Fig. 4.10:** Sample Thin$_{\delta}$. A: cyclic voltammetry in pH 1 and pH 13. B: cyclic voltammetry in pH 1 in semi-logarithmic scale

The output characteristic of sample Thin$_{\delta}$ in ISFET mode is depicted in figure 4.11; the total current modulation reaches in this case approx. 50% within the diamond potential window. The higher modulation in respect of sample Thick$_{\delta}$ stems from the lower $n_S$ of the boron delta doped NCD channel, which results to be $4 – 6 \cdot 10^{13}$ cm$^{-2}$ for a boron concentration of $2 \cdot 10^{20}$ cm$^{-3}$ and a thickness of 2 – 3 nm.

Using equations 4.3 and 4.4 and considering the 3 V gate bias range of the diamond potential window, the thickness which should be modulated results to be approx. 2.2 nm; therefore sample Thin$_{\delta}$ is theoretically capable of being pinched off within the diamond potential window in electrolyte. The diamond/electrolyte leakage limits however the gate bias range to 2.1 V which corresponds to approx. 1.7 nm channel depletion and prevents higher current modulation of the device.

The lower carrier sheet charge density also leads to lower current density; for sample Thick$_{\delta}$ the maximum current density was in fact approx. 5 µA/mm, whereas is only approx. 0.25 µA/mm for sample Thin$_{\delta}$. With such low current density the gate leakage current through the diamond/electrolyte interface becomes noticeable and can be observed for $V_{DS} \approx 0$ V in graph 4.11.
For evaluation of the pH sensitivity of sample Thin_δ the transfer characteristic is illustrated in figure 4.12 for $V_{DS} = -0.5$ V; sample Thin_δ shows a pH sensitivity of approx. 50 mV/pH and thus higher than sample Thick_δ. This difference may be related to the different boron concentration peak of the NCD delta layer, which is 3 times higher in sample Thick_δ; the higher boron concentration may lead to higher density of non-diamond phases at the diamond/electrolyte surface and hence to a variation of the pH sensitivity.

The highest $I_D$ variation between pH 1 and pH 13 is located at $V_G = 0.1$ V vs. SCE and results to be 50 nA/mm, which results in a current sensitivity of 4 nA/mm per pH for $L_G = 200$ μm. The maximum transconductance of ISFET Thin_δ results to be 0.09 μS/mm at $V_G = 0.05$ V vs. SCE from the derivative of the transfer characteristic in figure 4.12.
The chemical stability of the ISFET Thin_δ is tested by stressing the device at high anodic overpotentials (Vₑ = 1.5 V vs. SCE) in pH 13 electrolyte for 3 minutes and for a total charge transfer of approx. 50 mC/cm². This harsh process is repeated three times over a period of three months in which the device is periodically tested in pH 1 and pH 13. The results of this stability test are shown in figure 4.13, where I_D is measured at V_DS = - 0.5 V and V_G = - 0.4 V (vs. SCE) for 8 pH cycles; one can notice that the current levels remained completely stable after the three strong anodic treatments and after the pH cycling. The maxima current variations are approx. 3 % for pH 1 and 4 % for pH 13.

![Figure 4.13: Sample Thin_δ. I_D current at V_DS = - 0.5 V and V_G = - 0.4 V (vs. SCE) in pH 1 and pH 13. The measurements are taken cycling between the 2 electrolytes.](image)

**4.3.3 Conclusion**

The concept of the oxygen terminated boron delta doped diamond ISFET, introduced for the first time by A. Denisenko on single crystal diamond [129], has been successfully transferred to nano-crystalline diamond (NCD), circumventing thus the problem of large area substrates availability. The realization of such devices took advantage from the novel technique for growing boron delta doped layers on NCD described in chapter 3. Two ISFET devices have been characterized in this chapter, sample Thick_δ and sample Thin_δ with delta doped channels of respectively 10 nm and 3 nm. Sample Thick_δ showed maximum current density of approx. 5.5 µA/mm, 10% current modulation and pH sensitivity of approx. 40 mV/pH. The low current modulation was due to the excessive thickness of the delta doped layer.

Sample Thin_δ showed maximum current density of approx. 0.25 µA/mm, 50% current modulation and pH sensitivity of approx. 50 mV/pH. In this case the current modulation was limited by the narrower gate bias range due to current leakage through the diamond/electrolyte interface.

The electronic and electrochemical performances of the two ISFET devices did not degrade significantly after exposure to aggressive media (NaOH for sample Thick_δ) and
to anodic overpotentials for various cycles (sample Thin_δ); such chemical stability also indicated that the boron delta doped NCD surface does not contain large amount of non-diamond phases, which would have been otherwise etched or altered by the harsh environment to which the samples have been exposed. These new diamond-based ISFETs can be said to be therefore chemically high stable and suitable for electrochemical or biosensing applications.

Further improvements of the boron delta doped NCD ISFET may come from the use of the intrinsic NCD cap layer described in chapter 3, which would strongly reduce the background current in the potential window and thus increase the signal/background ratio.
4.4 Diamond-InAlN/GaN ISFET

The boron delta-doped NCD ISFET described in section 4.1 possesses high chemical stability and suitable electrochemical properties; however the low carrier mobility of the boron delta doped channel results in very low current density and thus in low signal/noise ratio. In fact, although the current modulation reaches approx. 50% within the diamond potential window, the current sensitivity to pH is only approx 4 nA/mm per pH for $L_G = 200 \, \mu m$. Furthermore the boron delta doping technique proved to be feasible but complicated and not perfectly reproducible over large area substrates.

In this section a new device concept is described, which tries to circumvent the problems of the boron delta doped NCD ISFET and at the same time to preserve the advantage of using a diamond electrode. The new device consists of a boron doped NCD layer overgrown onto a lattice-matched InAlN/GaN HEMT; here the doped NCD layer acts as chemical gate electrode and is the only part of the device in direct contact with the electrolyte. The InAlN/GaN is therefore protected by corroding substances or by oxidation at anodic overpotentials.

Such a concept can be realized on the base of the experiments of diamond overgrowth at high temperature on InAlN/GaN described in chapter 3. As already shown in section 3.6, diamond nucleation and growth at high temperature can be indeed successfully achieved on InAlN/GaN without degrading its electrical properties, which are in this specific case necessary to realize the ISFET. Furthermore in section 3.6 it has also been shown that pin-hole free and high quality boron doped NCD can be grown on InAlN/GaN.

The InAlN/GaN heterostructure provides high current densities and high transconductance which translates into a high sensitivity of the device. Such characteristics have been already exploited for fabricating an ISFET device [132]; here the InAlN surface was however in direct contact with the electrolyte. This device showed high current sensitivity to pH up to 16 µA/mm per pH for $L_G = 500 \, \mu m$; On the other hand the InAlN surface proved to be unstable when in direct contact with the electrolyte and was oxidized at anodic overpotentials, leading to degradation of device performances. The combination of InAlN/GaN FET performance with diamond chemical stability would therefore be an ideal solution to achieve highly stable and highly sensitive ISFETs.

![Fig. 4.14: NCD-InAlN/GaN ISFET: conceptual structure](image-url)
The basic concept of this novel structure is shown in fig. 4.14 and 4.15. The new structure includes a boron doped nanodiamond layer overgrown onto InAlN/GaN according to the technique described in chapter 3. The boron doped nanodiamond is electrically connected to the gate of the InAlN/GaN transistor and acts as interface between the electrolyte solution and the active channel of the device.

### 4.4.1 ISFET fabrication

The above described concept has to be slightly modified to meet the requirements of NCD growth on InAlN/GaN as discussed in chapter 3. The new structure, as shown in figure 4.14, requires in fact that the conductive NCD electrode is electrically connected to the metal gate. Such requirement is however not compatible with the technique developed in chapter 3, where a SiO₂ interlayer is needed for stability during diamond growth; the SiO₂ interlayer is highly insulating and would act as gate oxide forbidding amperometric mode of operation and decreasing the sensitivity of the device in the potentiometric mode. The solution to this problem is the modification of the conceptual structure as illustrated in the sketches from figures 4.15A, B and C, respectively side view with passivation, top view without passivation and top view with passivation. In the new structure the diamond electrode is placed beside the active device and is electrically connected to the gate by a metal extension of the gate pad. Such configuration allows using any suitable interlayer for diamond growth, either insulating or conductive, and does not prevent the operation in amperometric mode.

![Fig. 4.15: NCD-InAlN/GaN ISFET sketches. A: side view with SU8 passivation, B: top view without SU8 passivation, C: top view with SU8 passivation](image-url)
The deposition of the boron doped NCD electrode is carried out following the experiments described in chapter 3.6. Before diamond growth the InAlN/GaN heterostructure is patterned with MESA etching and ohmic contact deposition; details about ohmic contacts are found in chapter 5.2.1.

The first step of diamond growth is the deposition of the silicon based interlayer for diamond nucleation by PECVD, which is then performed by BEN in Hot Filament CVD (HFCVD undoped) at high temperature (680°C); the interlayer thickness is approx. 300 nm and the resulting nucleation density approx. $2 \times 10^{10}$ cm$^{-2}$. Subsequently a pin-hole free intrinsic NCD layer is grown at approx. 700°C by Hot Filament CVD (HFCVD undoped) in CH$_4$/H$_2$ chemistry; the thickness of the intrinsic NCD layer is approx. 200 nm and is used for electrical insulation from the silicon based interlayer. The last diamond growth process is the growth of a highly boron doped NCD layer by plasma CVD with the ASTeX microwave plasma CVD; this layer is grown at 700°C in CH$_4$/H$_2$ chemistry with a thickness of about 400 nm.

The boron doped NCD layer, including the interlayers beneath, is then etched by Reactive Ion Etching (RIE) plasma from most part of the InAlN/GaN sample, leaving a 300 x 500 µm electrode in the proximity of the FET channel. Consequently a 2µm Ni/Au gate is deposited on the FET channel, with the pad overlapping partially the NCD electrode in order to have electrical connection between the gate and the NCD film.

At last the ISFET device is passivated with 5 µm thick SU8 epoxy, which is patterned with three openings; two apertures for the ohmic contacts and one for the NCD electrode. The aperture onto the NCD electrode has a size of 200 x 300 µm and defines the contact area between electrolyte and diamond. The final structure is shown in the photograph of figure 4.16. Before the measurements the ISFET device is packaged with PTFE tape on a PCB carrier as in the case of the boron delta doped NCD ISFET described in the previous section.

![NCD-InAlN/GaN ISFET photograph.](image-url)
4.4.2 ISFET characterization

For clarity, the electrochemical setup described in general in appendix A is here reproduced in figure 4.17 in the case of the Diamond-InAlN/GaN ISFET; as discussed in appendix A the characterization in electrode mode is performed by short-circuiting source and drain.

![Electrochemical setup for characterization of the NCD-InAlN/GaN ISFET in ISFET configuration.](image)

The boron doped NCD electrode of the ISFET device is firstly characterized in electrode configuration by cyclic voltammetry in pH 1 and pH 13, depicted in figures 4.18A and B in linear and semi-logarithmic scale.

The two curves in figure 4.18A represent typical potential windows in electrolyte for NCD, with hydrogen and oxygen evolution onsets in the same potential range of the boron delta doped NCD ISFETs in section 4.1; the semi-logarithmic representation in figure 4.18B shows that the background current is approx. 1 nA/mm² for a potential range of ca. 2.3 V. Considering a limit of 100 nA/mm² for defining the diamond potential window (as done in the case of previously described NCD electrodes), the width results to be approx. 3 V. The boron doped NCD electrode preserves therefore the electrochemical properties of NCD with similar grain size grown on silicon or other conventional substrates.

Figure 4.18A shows also an unexpected current saturation in the oxygen evolution in pH 13; the phenomenon is also observed after several potential cycles in the electrolyte. Considering that positive $V_E$ potentials correspond to negative $V_G$ voltages, the observed current saturation occurs in reverse polarization of the Schottky diode where the HEMT channel is depleted; hence the saturation in the voltammogram may be attributed to depletion of the 2 DEG channel.

For the particular structure of this ISFET it is important to consider that the measured current $J$ does not flow only through the diamond/electrolyte interface but also through the nickel-InAlN Schottky diode; the series resistance of the Schottky diode must be therefore evaluated and taken in account for the correct electrochemical characterization.
of the diamond surface. The nickel gate Schottky diode of the InAlN/GaN FET is characterized by measuring the device in air contacting the nickel gate pad directly with a metal needle and not through the diamond electrode, so that only the leakage current through the nickel diode is measured.

Figure 4.18: NCD-InAlN/GaN ISFET. A: cyclic voltammetry in pH 1 and pH 13. B: cyclic voltammetry in pH 1 in semi-logarithmic scale

Figure 4.19A depicts the I-V characteristic of the nickel Schottky diode in linear scale. This curve is compared with the cyclic voltammogram of the ISFET in pH1 in the semi-logarithmic scale in figure 4.19B. It is observable that the diode leakage current is 4 orders of magnitude higher than the diamond/electrolyte background current even with the smaller contact surface area of the gate strip as compared to the electrode area (10^-6 vs. 10^-4 cm²). This means that the current J of the cyclic voltammetry measurement in electrolyte can be attributed mostly correlated to the diamond/electrolyte impedance and thus to the quality of the NCD electrode.

Figure 4.19: NCD-InAlN/GaN ISFET. A: I-V characteristic of the Schottky diode of the HEMT. B: Cyclic voltammetry in pH 1 in semi-logarithmic scale compared with the Schottky diode characteristic. The V_E scale on graph B corresponds to –V in graph A
The large difference between the diode leakage current and the diamond/electrolyte background current results also advantageous in terms of device design possibilities. The gate length may in fact be reduced by factor 10 for improving the device performance without limiting the current through the diamond electrode and thus the amperometric mode of operation.

The diamond-InAlN/GaN device is then measured in ISFET configuration to evaluate drain-source current modulation and pH sensitivity in electrolyte. The output characteristic of the device is illustrated in figure 4.20 in pH 1. The graph shows that the drain current of the InAlN/GaN HEMT can be effectively modulated via the diamond electrolyte by applying a potential to the electrolyte; the device behaves therefore like a ChemFET.

The graph in figure 4.20 illustrates that the device can be pinched off by a gate voltage within the potential window of the NCD electrode in water; moreover the maximum current density results to be approx. 40 mA/mm. These two features makes the device very sensitive for small potential signals detection for example in bio applications like cells activity monitoring. Another important feature of the output characteristic is that the device can be operated in the saturation regime, which contributes to an increase of the transconductance and thus of the sensitivity of the device.

![Fig. 4.20: NCD-InAlN/GaN ISFET: Output characteristic in pH 1](image)

The pH sensitivity of the diamond-InAlN/GaN ISFET is tested by transfer characteristic in pH 1 and pH 13. The measurements are depicted in figure 4.21 for $V_{DS} = 1.5$ V; the two curves have a constant shift in the pinch-off voltage of approx. 580 mV, which corresponds to a pH sensitivity of 48 mV/pH. This value is comparable with the pH sensitivity obtained for the boron delta doped NCD ISFETs described in the previous section, namely ~ 50 mV/pH.
The derivative of the transfer characteristic gives a maximum transconductance of 72 mS/mm at $V_G = 0.65$ V vs. SCE. This value correlates well with transconductances obtained with 7 nm barrier InAlN/GaN in standard HEMT configuration [134], where 500 mS/mm were reported for 0.25 µm gate length. At $V_G = 1$ V vs. SCE the maximum $I_D$ variation between pH 1 and pH 13 is calculated to be 35 mA/mm, which gives a current sensitivity to pH of 3 mA/mm per pH for $L_G = 2$ µm.

Because of the extremely low gate leakage current, limited by the diamond electrode as shown in figure 4.19, the ISFET works also in the sub-threshold regime, where the sheet charge density is modulated exponentially by the gate voltage. This is shown in figure 4.22, which depicts the transfer characteristic at $V_{DS} = 1.5$ V in pH 1 in the semi-logarithmic scale. Here it can be observed that the drain current is modulated with gate
bias down to -1.7 V vs. SCE, where the substrate leakage level is reached. Considering the FET regime together with the sub-threshold regime, the device possesses thus an on/off current ratio of 5 orders of magnitudes, which is in the range of MOSFET devices. As in the case of the boron delta doped NCD ISFET, the chemical stability of the diamond-InAlN/GaN ISFET is tested by exposing the device to anodic overpotentials and by cycling between pH 1 and pH 13. Anodic treatment is performed at $V_E = 1.5$ V vs. SCE in pH 13 electrolyte for 2 minutes for total charge transfer higher than $5 \times 10^{16}$ electrons/cm$^2$.

Figure 4.23 illustrates the 8 pH cycles at $V_{DS} = 1.5$ V and $V_{GS} = 0.6$ V vs. SCE. The maximum current variations is 4 % for pH 1 and 9 % for pH 13, however decreasing trends are not observed for the two curves. The diamond-InAlN/GaN ISFET shows therefore higher chemical stability than the InAlN/GaN ISFET proposed by C. Pietzka et al. [10], which reported 1 orders of magnitude reduction of the $I_D$ current after anodic oxidation with total charge transfer of approx. $1 \times 10^{16}$ electrons/cm$^2$.

![Fig. 4.23: NCD-InAlN/GaN ISFET: pH cycling at $V_{DS} = 1.5$ V and $V_{GS} = 0.6$ V vs. SCE](image-url)
4.4.3 Conclusion

The combination of boron doped NCD and InAlN/GaN resulted in a novel ISFET structure with high sensitivity and high chemical stability. The NCD electrode reproduces features of boron doped NCD grown on silicon used for electrochemical electrodes in chapter 3.3 and for boron delta doped NCD ISFETs in section 4.1; potential window width, background current and pH sensitivity are comparable with the values from the boron delta doped NCD ISFETs. The electronic properties of the InAlN/GaN heterostructure lead however to exceptional advantages of the new device in terms of drain-source current density, transconductance and current sensitivity to pH. A clear overview of these advantages is given in the graph in figure 4.24, which shows the transfer characteristics in pH 1 of the three ISFETs described in this chapter; for clearness of the comparison, \( I_D \) current is inverted in sign for the two boron delta doped NCD ISFETs (because their channel is p-type).

The higher sensitivity of the NCD-InAlN/GaN ISFET is given by the high current density and by the current modulation of more than 2 orders of magnitudes in the linear FET regime; the high sensitivity of the FET regime can furthermore be extended to higher negative gate potentials by varying the InAlN barrier thickness of the heterostructure, which would shift indeed the pinch-off voltage of the HEMT. Doing so, the NCD-InAlN/GaN ISFET would be able to operate in FET regime, where the sensitivity is higher, with the gate bias covering the complete diamond potential window from the cathodic to the anodic region, where H-terminated diamond ISFETs cannot operate.

On the other hand the advantages of the boron delta doped NCD ISFETs are the cheapness of the substrates (silicon vs. InAlN/GaN) and the larger area availability (8” vs. 2”) once the delta doping technique is optimized in terms of homogeneity on large substrates.

![Graph showing transfer characteristics in pH 1 between NCD-InAlN/GaN and boron delta doped NCD ISFETs](image)

Fig. 4.24: Comparison of transfer characteristics in pH 1 between NCD-InAlN/GaN and boron delta doped NCD ISFETs (samples Thick_δ and Thin_δ). The transfer characteristic of samples Thick_δ and Thin_δ appear to be flat due to the small current modulation; clearer graphs may be observed in figure 4.10 and 4.13.
The NCD-InAlN/GaN ISFET is also suitable for integration in MEAs (Multi Electrode Array) due to the large area availability of InAlN/GaN and to the easier reproducibility of NCD overgrown electrodes in respect of boron delta doped NCD layers. Another important advantage of the NCD-InAlN/GaN ISFET is that its performances can be easily and largely improved by optimization of the device design; the use of e-beam lithography for sub-micron gate length and larger $W_G$ will indeed allow increasing the sensitivity of the device.

Among the ISFET structures with diamond/electrolyte interface which have been proposed to date by many groups, the new NCD-InAlN/GaN ISFET represents the first device that can compete with standard silicon based ISFETs in terms of electronic performance and can offer, at the same time, the chemical stability and bio-compatibility of diamond. Moreover it is also the first device which can merge such features with the possibility to measure in both amperometric and potentiometric modes, unifying thus the functions of chemical electrodes and ISFETs.
Chapter 5

Diamond for power devices
(Initial experiments)

In this chapter the first experiments and results on diamond as heat sink are described. The NCD growth on InAlN/GaN technique developed in chapter 3 is applied to HEMT technology in order to evaluate the effects of the high temperature CVD process to the electronic properties of the devices; particular attention is given to maximum current density, transconductance and pinch-off voltage. The following preliminary tests are performed with the perspective of applying NCD heat sink to InAlN/GaN HEMT for power applications. The aim of this work is therefore to prove conceptually that such application is feasible, even though many further optimizations will be required.

In a first experiment NCD is grown on unprocessed InAlN/GaN and then completely removed by plasma etching; subsequently an HEMT structure is fabricated on the heterostructure and electrically tested. In a second experiment NCD is grown on InAlN/GaN after the patterning of the latter with MESA etching and ohmic contact deposition; the NCD layer is then removed only from the necessary regions to complete the HEMT structure and to characterize it.

The experiments have been carried out using InAlN/GaN materials provided by EPFL (Ecole Polytechnique Fédérale de Lausanne, Switzerland) and by Thales (Alcatel Thales III-V lab, Marcoussis, France), which kindly provided samples with different features for this investigation.

5.1 HEMT on InAlN/GaN after NCD overgrowth and complete removal

For this experiment an InAlN/GaN heterostructure with 15 nm thick barrier is used; the heterostructure is deposited on sapphire. On this heterostructure a 500 nm thick intrinsic NCD layer is grown at high temperature by Hot filament CVD (HFCVD undoped) using the interlayers and the growth conditions described in chapter 3 (table 5.1). The morphology of the NCD layer is shown in figure 5.1.

The diamond layer and the Si-based interlayers are then removed by plasma etching for fabrication of the HEMT structure. The removal of the interlayers is a critical step due to the fact that the plasma etching can damage the underlying InAlN barrier and can have thus negative effects on the ohmic behaviour of the contacts, which are deposited next. Silicon dioxide and amorphous silicon are in fact removed by reactive ion etching (RIE).
with CF$_4$; F. Medjdoub et al. [135] have however demonstrated that such plasma process implants fluorine into InAlN/GaN and depletes the 2DEG (2 dimensional electron gas). The depletion of the heterostructure beneath the ohmic contacts would therefore degrade dramatically the ohmic behaviour. On the other hand the problem cannot be solved by avoiding the over-etching of the interlayers; a remaining SiO$_2$ film on InAlN would in fact degrade the ohmic contacts as well.

In order to solve this problem the interlayers here are not etched by RIE but by RF CF$_4$ plasma without external DC component; such etching process is essentially slower than RIE but allows etching the interlayers completely without affecting the InAlN/GaN heterostructure.

Fig. 5.1: Morphology of intrinsic NCD overgrowth on InAlN/GaN

Fig. 5.2: Micrograph of the finished InAlN/GaN HEMT

After the complete removal of diamond and interlayers, the InAlN/GaN is patterned by MESA etching by Ar plasma. Subsequently ohmic contacts are deposited using a standard metal layers stack, comprising Ti/Ni/Al/Au, which is then annealed at 900º C with a rapid thermal annealing system (RTA); the channel dimensions are $L_{\text{channel}} = 3 \, \mu m$
and $W_{\text{channel}} = 50 \, \mu\text{m}$. At last a 0.5 $\mu\text{m}$ Ni/Au gate is deposited using e-beam lithography. A photograph of the finished device is depicted in figure 5.2.

![Graph showing output characteristic](image)

**Fig. 5.3:** Output characteristic of the InAlN/GaN HEMT after NCD overgrowth and removal

The output characteristic of the InAlN/GaN HEMT is shown in figure 5.3; the graph shows clearly that the device behaves as a transistor even after the heterostructure has been exposed to diamond growth at high temperature. The maximum current density results to be approx. 1.2 A/mm while the transconductance is approx. 136 mS/mm at $V_{GS} = -1 \, \text{V}$. These features are comparable to the ones obtained with standard HEMT fabricated on InAlN/GaN heterostructures with the same barrier thickness [136].

The output characteristic shows however that the device cannot be pinched off most likely because of buffer leakage after diamond growth at high temperature. The degradation of the GaN buffer after diamond growth at high temperature was in fact also observed in other experiments. Figure 5.4 depicts the SEM image of InAlN MESA and GaN buffer after diamond nucleation; here the MESA etching was performed before the diamond growth CVD process. The standard SiO$_2$ + amorphous silicon interlayer was used.

![SEM image of InAlN MESA and GaN buffer](image)

**Fig. 5.4:** Surface of InAlN MESA (a) and GaN buffer (b) after NCD nucleation on a InAlN/GaN heterostructure
While the InAlN MESAs appear to be clean after the diamond nucleation process, the GaN buffer shows heavy surface degradation with the appearance of bubbles on the surface; this suggests that the GaN buffer used in this case is not stable in hydrogen atmosphere at temperatures above 600° C.

On the sample used for the experiment described in this section (figure 5.1, 5.2 and 5.3) bubbles did not appear on the GaN buffer because diamond nucleation and growth have been performed on the bare InAlN/GaN heterostructure, while the MESA etching was performed after the complete removal of the diamond/interlayer stack; thus the GaN buffer was protected by the InAlN barrier during the diamond nucleation/growth process. Even though bubbles did not appear because of the above mentioned reason, the diamond nucleation/growth process at high temperature may have degraded the GaN lattice reducing drastically its resistivity, resulting then in the high buffer leakage observed in the output characteristic in figure 5.3.

### 5.2 HEMT on InAlN/GaN with NCD overgrowth

In this section an InAlN/GaN HEMT is fabricated including an intrinsic NCD layer onto the active part of the device, i.e. the channel. In contrast to the experiment described in section 5.1, here the InAlN/GaN HEMT is partially fabricated before diamond growth; more specifically MESA etching and ohmic contacts deposition and annealing are performed before the deposition of the Si-based interlayers.

#### 5.2.1 Ohmic contacts optimization

In a first test NCD is grown according to the technique described in chapter 3 on InAlN/GaN with MESA etching and Ti/Ni/Al/Au ohmic contacts. As shown in figure 5.5 the ohmic contacts results to be damaged after the CVD process at high temperature; in particular the ohmic contacts edges facing the channel are no longer straight and in most cases are short-circuited.

![Effect of NCD growth on the gold ohmic contacts](image-url)
This problem can be related to the low melting point of gold, which is approx. 1064°C. If the layer is thin, as in the case of electric contacts, gold may start to become soft and to drift at temperatures below the melting point; this effect can be observed even after rapid thermal annealing (RTA) in figure 5.2, where the gold contacts show deformation and bubbling even though the annealing temperature of 900°C was much lower than the melting point. The RTA process lasts usually only approx. 3 minutes and the contacts can thus maintain their sharp edges; in a diamond growth process however, the contacts are exposed to a temperature of about 700°C – 750°C for several hours and therefore gold may have time to flow over the contact edges producing short-circuit between source and drain.

In a second NCD growth test the gold on the ohmic contacts is thus replaced by tantalum, which possess very high melting point (~ 3000°C) and is commonly used as diffusion barrier in high temperature processes; the ohmic contact layers stack is then Ti/Al/Ni/Ta (6% Ti/Al ratio) with approx. 30 nm of tantalum. In figure 5.6 the new ohmic contacts are shown after NCD growth at high temperature. In this case the ohmic contacts present still sharp edges on the channel and no short-circuit occurs; moreover the ohmic contacts surface does not show bubbling effects as in the case of gold contacts. On such devices HEMT fabrication is therefore not prevented.

Apart the ohmic contacts, figures 5.5 and 5.6 present also a clean GaN surface without bubbles after diamond growth at high temperature, in contrast thus with the experiment performed on the GaN buffer layer shown in figure 5.4. Taking into account that both nucleation and growth processes have been performed in the same conditions on the two samples (using also the same interlayers), the different stability during the high temperature CVD process may be attributed to different quality of the two GaN buffer layers in terms of purity and crystallinity.
5.2.2 HEMT fabrication and diamond growth

An InAlN/GaN heterostructure deposited on sapphire and with 7 nm thick barrier is used in this experiment. After MESA etching and ohmic contacts (with tantalum barrier) deposition, the device dimensions are $L_{\text{channel}} = 5 \, \mu\text{m}$ and $W_{\text{channel}} = 50 \, \mu\text{m}$. In contrast to the device described in section 5.1, the channel length is higher in order to have more relaxed conditions for the device fabrication; in this case in fact the NCD layer will cover completely the channel and will have to be selectively etched to open the region for gate deposition.

Intrinsic NCD is grown at approx. 750° C for a total thickness of 400 nm and grain size of approx. 100 nm, details of the growth are listed in table 5.2. The surface morphology of the InAlN/GaN device after NCD growth is illustrated in the SEM image of figure 5.7; the picture shows that the InAlN barrier, the GaN buffer and the ohmic contacts are homogeneously covered by a conformal diamond layer, preserving the sharpness of the edges and showing neither cracks or bubbling.

By means of plasma etching the NCD and the Si-based interlayers are removed selectively with a $\text{Si}_3\text{N}_4$ mask; the layers are removed from above the ohmic contacts, to allow electrical measuring, and from the gate area where Ni/Au will be deposited. In this way the diamond layer lays on the most critical parts of the device, namely between source and gate and between drain and gate, where the heat is primarily produced. The device at this stage is shown in the SEM images of figure 5.8; for clearness the NCD layer is framed within dashed red lines, the NCD gate opening is 2 $\mu$m wide. At last a 2$\mu$m wide Ni/Au gate is deposited overlapping the opening in the NCD layer.
Before the electrical characterization gold is deposited on the HEMT ohmic contacts in order to reduce their surface resistance, which was increased during the diamond growth process as already observed in chapter 3.6. The output characteristic of the finished HEMT is depicted in figure 5.9 in comparison with a reference HEMT fabricated on the same InAlN/GaN layer with standard process. From the graph it can be observed that the two devices present similar behaviour, with comparable maximum current density and transconductance; thus the NCD growth did not change dramatically the HEMT features.

A discrepancy between the output characteristics of the two devices is found in the gate bias; the maximum current density is reached at $V_G = 3$ V for the NCD overgrown HEMT, while at $V_G = 2$ V for the reference HEMT. This shift is also reflected in a change of the pinch-off voltage $V_P$ of the two devices, namely approximately -3 V for the reference and approximately -2 V for the NCD overgrown HEMT. The gate bias shift between the two samples may be related with partial depletion of the 2DEG by the CF$_4$.
plasma treatment used for etching the interlayers in the recess area, as already mentioned in section 5.1.

The NCD overgrown HEMT shows also an increase of the source resistance $R_S$, which may be attributed to a degradation of the source contact during the NCD growth process. The increase of the source resistance $R_S$ is reflected in the higher knee voltage $V_K$ of the NCD overgrown device.

5.3 Conclusion

In this chapter two working InAlN/GaN HEMTs have been demonstrated after NCD growth at high temperature above 650°C. NCD growth has been carried out following the experiments described in chapter 3, using SiO$_2$ and amorphous silicon interlayers and Hot Filament CVD.

A first HEMT was entirely fabricated on an InAlN/GaN heterostructure after growth and removal of 500 nm thick intrinsic NCD. This InAlN/GaN device showed transistor behaviour with 1.2 A/mm maximum current density and 136 mS/mm maximum transconductance. However the device could not be pinched off because of leakage current through the GaN buffer, which was degraded by diamond growth.

The second HEMT was fabricated on InAlN/GaN provided by Thales (France). The major stability of the GaN buffer allowed growing the NCD layer after MESA etching and ohmic contacts deposition. The Ni/Au gate was deposited after the opening of the NCD layer (by etching), allowing thus to measure the HEMT device with NCD covering the channel and partially the ohmic contacts. The NCD overgrown HEMT features were comparable to those of the reference sample without NCD overgrowth; the device showed the same maximum current density, a comparable transconductance and could be pinched off. A shift in the pinch-off voltage was observed, likely due to fluorine implantation in InAlN during the interlayer etching in the recess.

These results are very promising in the perspective of using NCD as top heat sink layer in power devices. In this direction there are however still important steps to take. Firstly the NCD layer must be grown thicker in order to increase the heat sink efficiency. Thicknesses of approx. 20 µm are predicted to be suitable for this task [137] but in this range the stress management must be optimized for avoiding degradation of the HEMT performance. The diamond crystal arrangement must also be optimized in order to achieve the highest possible thermal conductivity; in this case the 2D structure described in chapter 3 will be preferred because the vertical columnar crystals are ideal heat extractors from the underlying device.

At last, the SiO$_2$ interlayer shall be replaced by a material with higher thermal conductivity in order to avoid bottlenecks in the heat conduction; a suitable candidate may be silicon nitride.
Conclusions

Among semiconductors, diamond is certainly the most promising material. Its properties, when conveniently exploited, would allow overcoming some of the current limits of modern semiconductor devices and in some case would permit new device concepts. In the last years poly and nano-crystalline diamond (PCD and NCD) have especially gained not only the interest of the scientific community but also of industries which see in these materials new possibilities and new applications. PCD and NCD are however heterogeneous materials and therefore require comprehensive study of their configuration in order to be suitable for practical applications. Apart surface termination and other minor features, all characteristics of PCD and NCD are determined by the growth techniques and conditions; hence the understanding of the growth process is essential for developing these materials.

Although CVD diamond growth has been established for many years and large improvements have been made in terms of purity and doping, PCD and NCD are still immature for being a standard material in large scale production of devices. In some specific case it is not only the quality of the material that is insufficient, but it is also the lack of particular features like n-type conductivity or low temperature growth that prevents from taking advantage from PCD and NCD in device fabrication. It is exactly in this perspective that the work described in this thesis is addressed; it attempts to bring improvements to NCD growth in terms of quality and to circumvent some of the most critical barriers for future implementation of NCD in devices for various applications.

The work concerning NCD growth is grouped in chapter 3. Firstly NCD growth is investigated in terms of methane concentration and of the effects that this parameter has on NCD properties such as grain size, grain orientation, quality and transparency. Then the investigation moves on to the electrical and electrochemical properties of boron doped NCD correlated to growth parameters and grain size; in particular the most suitable grain size is explored for getting NCD with high electrical conductivity and superior electrochemical qualities such as large potential window in water and low background current.

A new growth technique is also developed in chapter 3 for the growth of boron delta doped NCD layers by mean of HFCVD. Very thin layers of boron doped NCD have been grown in a standard Hot Filament CVD with boron concentration above full activation (> $10^{20}$ cm$^{-3}$) and thickness of few nanometers. The boron δ-doped NCD layers have been characterized electrically by mean of Hall Effect and electrochemically by mean of impedance spectroscopy and capacitance voltage measurements. The reference boron δ-doped NCD layer reached doping concentration peak of $3 \times 10^{20}$ cm$^{-3}$ within a thickness of less than 3 nm, resulting in a sheet charge density of approx $1 \times 10^{13}$ cm$^{-2}$. The growth of such boron delta doped layers was performed on NCD by Hot Filament CVD for the first time.
At last in chapter 3 the growth of NCD on InAlN/GaN is developed by mean of Hot Filament and Plasma CVD. In contrast to previous NCD growth on GaN works, which were performed at low temperature, the NCD growth on InAlN/GaN was performed in standard conditions at high temperatures above 650°C and up to 750°C; this condition permitted to grow high quality NCD on a nitride heterostructure for the first time. The NCD quality was investigated by SEM microscopy, with which typical diamond grains could be observed, and by Raman spectroscopy, which showed a predominant diamond peak (sp³) at 1332 cm⁻¹. Boron doped NCD has been also grown onto InAlN/GaN at low and high temperature in order to investigate the quality of diamond layers grown at different temperatures; these layers were characterized electrochemically by cyclic voltammetry to observe the benefits of high temperature on diamond quality.

Morphology and electrical properties of InAlN/GaN were also explored after NCD growth to evaluate the effects of the high temperature CVD process on the heterostructure. AFM microscopy revealed that InAlN/GaN roughness was completely preserved after NCD growth and removal, while SEM microscopy of the samples cross section confirmed that the heterostructure did not break down. TLM and I-V measurements proved also that the electrical properties of InAlN/GaN were maintained after NCD growth; the conservation of maximum current density and of current saturation verified that the 2DEG was not degraded by the high temperature CVD process.

Two novel diamond based ISFETs are developed in chapter 4: the oxygen terminated boron δ-doped NCD ISFET and the boron doped NCD-InAlN/GaN ISFET.

The O-terminated boron δ-doped NCD ISFET relied on the boron delta doping technique developed and described in chapter 3. The device comprised the direct contact between the diamond channel and the electrolyte and thus gave the possibility to operate in amperometric and potentiometric mode. The oxygen termination circumvented the problems of instability at anodic overpotentials and at exposure to aggressive (oxidizing) media of the hydrogen terminated diamond ISFET; the novel boron δ-doped NCD ISFET proved to be indeed stable after treatments at high anodic overpotentials and in hostile media such as hot KOH and NaOH. This device represents moreover the first ISFET based on boron doped NCD, which allow large area growth for integration in MEAs or other micro-electrode systems.

The boron doped NCD-InAlN/GaN ISFET took advantage of the NCD growth technique on InAlN/GaN described in chapter 3. This structure used an oxygen terminated boron doped NCD as electrochemical electrode overgrown on an InAlN/GaN HEMT and electrically connected to its gate. As for the boron δ-doped NCD ISFET, the direct and exclusive contact between the NCD electrode and the electrolyte assured operation in amperometric and potentiometric mode, while the oxygen termination provided stability at anodic overpotentials. The superior electrical properties of InAlN/GaN permitted however to achieve far better performance than that obtained with other diamond based ISFETs. The high transconductance and the high current density of InAlN/GaN FETs, in combination with diamond pH sensitivity, resulted in very high current sensitivity to pH up to almost 3 mA/mm per pH, which can be still improved by downscaling of the device dimensions.
NCD growth on InAlN/GaN is also explored in chapter 5 as heat sink overlayer on top of InAlN/GaN HEMT. Here NCD has been grown directly on the active part of the FET device where the heat is produced, namely the channel. Working InAlN/GaN HEMTs have been demonstrated after complete removal of the overgrown NCD as well as keeping the NCD layer on the device channel. Electrical features such as current density, transconductance and pinch-off voltage were preserved after growth at high temperature of 400 – 500 nm intrinsic NCD, showing for the first time that InAlN/GaN HEMTs for power devices can be overgrown by high quality diamond. It has not been possible to observe improvements in device performance due to better thermal management because of the thickness of the NCD layer, which was thin to avoid mechanical stress in the device. The stress management optimization may allow growing thicker NCD layers in the range of tens of microns for efficient heat extraction from the device.

The improvements in NCD growth and the advancements in NCD based device fabrication are very promising in the perspective of NCD use for various industrial applications.
Appendix A

Diamond Electrochemistry

A.1 Introduction

Electrochemistry studies the electrochemical reactions in an electrolyte when this is in contact with a solid electrode, being the latter a metal or a semiconductor. The electrolyte can be any solution containing free ions that can move and thus can give rise to electrical conductivity.

The studied electrochemical reactions can be driven by an external applied voltage, as in electrolysis, or by a voltage created by a chemical reaction, as in a battery. These reactions involve charge transfer across the electrode/electrolyte interface, being the charged ions or electrons.

The ions of the electrolyte are produced by dissociation of salts, acids or bases in a polar solvent; therefore in the electrolyte there are always positively and negatively charged ions and both these types contribute to electric current. In an electrochemical reaction these ions can undergo two types of reactions; reduction or oxidation (redox), where charge transfer occurs, and adsorption or desorption, where charge transfer may or may not occur.

In redox reactions electrons are transferred from a donor (the reducing agent) to an acceptor molecule (the oxidizing agent). A redox reaction may be a simple redox process, where only one transfer of electrons occurs, or a complex redox process in which various successive transfers of electrons take place. When a redox reaction involves oxygen, oxidation means that oxygen is added to the ion; in this case the oxygen is reduced.

In an adsorption reaction the dissolved ions accumulate on the electrode surface forming a film of molecules or atoms (adsorbates). Desorption is the reverse process, namely the removal of the excess concentration of the adsorbates from the electrode surface. Adsorption reactions are generally divided in physisorptions and chemisorptions according to the nature of the bonding between adsorbates and the atoms on the electrode surface; physisorption involves weak van der Waals forces, while chemisorption is used in case of covalent bonding.

According to the type of dissociated molecules, electrolytes may present different hydrogen ion concentrations; the hydrogen ions in solution occur as a number of cations including hydronium ions (H$_3$O$^+$). The concentration of these hydrogen ions defines the pH of the electrolyte.
For the experiments described in this thesis two electrolytes with different pH are used. The first one is 0.1M KOH (potassium hydroxide) in water; here the salt is dissociated in K⁺ and OH⁻ and the electrolyte is therefore basic with pH = 13. The second electrolyte is 0.1M H₂SO₄ (sulphuric acid) in water; here the sulphuric acid is dissociated in SO₄²⁻ and H₃O⁺ and the electrolyte is thus acid with pH = 1.

Electrochemistry is then a science where solid electrodes (or FETs) are used for studying chemical reactions in electrolyte, either by detecting the produced voltage/current signals or by stimulating the reactions. If however the reactions in the electrolyte are known, the same techniques can be used for studying the properties of the solid electrode material in terms of responses to potentials applied to the electrolyte in which is immersed. As will be described below in this appendix, semiconductors may be for example investigated in terms of purity and doping by characterizing the semiconductor/electrolyte interface. In this thesis such techniques have been used to study the properties of the grown NCD layers and of the devices in which they are integrated.

The experimental setup used for electrochemical characterization of diamond used here is the standard electrochemical cell, which includes 3 electrodes: the counter, the reference and the working electrode. The diamond layer is the working electrode to be characterized, while the counter electrode is a metal electrode used to apply potentials to the electrolyte and to measure currents through it. The reference electrode is an electrode which has a stable and well-known potential; such electrode is electrically de-coupled from the counter electrode and does not pass DC current by reactions with the electrolyte. The reference electrode is therefore used to determine the potential in the electrolyte. In this appendix an introduction to the diamond/electrolyte interface and to the used measurement techniques is therefore given. Moreover the advantages of diamond in respect of other electrode materials are highlighted.

### A.2 Diamond/Electrolyte interface

When a semiconductor is immersed in electrolyte, the solvated or the solvent charged ions are adsorbed at the electrode surface; this adsorption may be due to electrostatic attraction or to bond formation between the electrode surface and the charged molecule in the liquid. The adsorption of the charged molecules depends strongly on the electrode material and on its termination. The behaviour of the resulting semiconductor/electrolyte interface can be represented by an electrical equivalent circuit, the elements of which depend on the electrode properties as well; such equivalent circuit can be therefore used for the electrochemical characterization of the semiconductor.

When a semiconductor such as silicon, germanium or III-nitrides is immersed in electrolyte, the bulk and the surface can undergo oxidation in certain conditions because of reactions in the material. The formation of these oxide layers may complicate dramatically the electrochemical characterization since it may generate a very complicated equivalent circuit, where the oxide layer is also included.
In contrast to the above mentioned semiconductors, diamond is chemically inert and does not form an oxide in any circumstances in electrolyte; this means that the diamond/electrolyte interface can be generally represented by a simpler equivalent circuit and is therefore easier to study or characterize.

A further advantage of diamond among other semiconductors is that both carbon-hydrogen (C-H) and carbon-oxygen (C-O) surface groups are stable in aqueous solutions, and show a completely different behaviour in terms of wetting by water and of the resulting charge state. In this thesis only the oxygen terminated boron doped diamond surface is analyzed; hence the diamond/electrolyte interface is here described for such material.

When oxygen terminated boron doped diamond is immersed in electrolyte, the resulting interface consists of a depletion layer in the material and of the Helmholtz (or double layer) in the electrolyte, named after its first introduction by the German Scientist H. Helmholtz. The formation of these layers is related to the position of the charged ions of the electrolyte at the electrode surface, as shown in figure A.1 for boron doped diamond in water with $\text{H}_2\text{SO}_4$.

The depletion or space charge layer in diamond is caused by the surface state pinning due to the oxygen termination, which depletes holes as already mentioned in chapter 3.5 [100]; this layer is characterized by an RC circuit with space charge capacitance $C_{\text{SC}}$ and space charge resistance $R_{\text{SC}}$, as shown in figure A.1. The double layer is formed by the charged ions of the electrolyte which face the diamond surface; the double layer can as well be represented by an RC circuit with double layer capacitance $C_{\text{DL}}$ and double layer resistance $R_{\text{DL}}$, which is a representation of the activity occurring on the surface. The capacitance and resistance values of the interface can be extracted by impedance spectroscopy measurements combined with fitting by an equivalent circuit, as will be described in section A.4.

![Diamond/Electrolyte interface diagram.](image)
The electric potential at the diamond surface depends on the type and on the concentration of the charged ions in the electrolyte; such potential depends therefore on the pH of the electrolyte. The mechanism which correlates the pH and the electric potential is the surface state pinning and is expressed by the Nernst equation (A.1), which sets a theoretical maximum of 59.2 mV/pH at room temperature independently from the sensitive layer material [133] (A.2):

$$\Delta V = \frac{kT}{q} \ln(C_{H_3O^+})$$  \hspace{1cm} (A.1)$$

$$\Delta V = -2.303 \frac{kT}{q} \cdot \Delta pH = -59.2mV \cdot \Delta pH \text{ at R.T.}$$  \hspace{1cm} (A.2)$$

In equations A.1 and A.2 $k$ is the Boltzmann constant, $T$ temperature and $C_{H_3O^+}$ the concentration of $H_3O^+$ in the electrolyte.

The correlation between pH and potential is called pH sensitivity and is measured in mV/pH. The pH sensitivity has then a maximum of 59.2 mV/pH, but the effective value depends also on the electrochemical activity of the electrode material which constitutes the sensitive layer.

The effect of the electrolyte pH can be observed in figure A.2, which shows the correlation between electrochemical potentials (left) and energy levels (right) in electrolytes with different pH. The 0 V electrochemical potential is defined at the hydrogen evolution of water dissociation in respect of SHE (Standard Hydrogen Electrode); the corresponding energy to this point depends on the electrolyte’s pH, varying from 4.44 eV to 3.7 eV in respect of the vacuum level respectively for pH 0 and pH 14. The oxygen evolution lies at $-1.23$ V and defines, with the hydrogen evolution, the potential window of water dissociation in electrolyte. The “SCE” electrochemical potential level in figure A.2 corresponds to the Standard Calomel Electrode, which is further discussed in appendix B. A typical voltammogram of highly boron doped diamond electrode is placed between $-1$ V and $+2$ V in the electrochemical potentials scale (left).
A.3 Cyclic Voltammetry

In absence of redox reactions the current through the electrode/electrolyte interface presents a low current range in which the rate of water electrolysis is negligible; this range is called potential window and its width is defined by the hydrogen and the oxygen evolution of water dissociation. The evaluation of the potential window is performed by scanning the potential between the working and the counter electrode from the hydrogen to the oxygen evolution and vice versa; the resulting graph is therefore named cyclic voltammogram.

The potential window is very useful for studying electrochemical reactions; the low current in the window gives in fact the possibility to measure current peaks due to many other redox reactions with potentials within the window. As a consequence of this, the possibility to detect reactions is strongly affected by two parameters: the width of the potential window and the background current within it. These two features are strongly related to the material of the electrode as can be observed in figure A.3 [138]; here the hydrogen and oxygen evolutions are shown in the mA/cm$^2$ range for polycrystalline diamond, highly oriented pyrolytic graphite and for platinum, which is a standard metal electrode in electrochemistry.

The figure shows clearly that high quality diamond possesses a very wide potential window and shows very low background current. Therefore diamond is recognized as ideal material for electrochemistry since it allows the detection of redox reactions at high overpotentials. Oxidation energies of histamine [139] and phenol [140] are for example shown to be observable only with diamond electrodes. The difference between diamond and platinum can be easily seen in figure A.4, where the cyclic voltammograms of NCD and platinum are superimposed. It can be seen that even in the case of NCD, with grain
size below 200 nm, the cyclic voltammogram of diamond shows a larger potential window and a lower background current.

\[ I_{\text{background}} = C \frac{dV}{dt} + I_{\text{activity}} \]  \hspace{1cm} (A.3)

Without any redox reaction the background current within the potential window can be defined by the combination of two factors (A.3): a capacitive charging current, defined by the total interface capacitance and by the voltage scan rate, and an activity current related to chemical activity of defects or other states.

For a platinum electrode such as the one shown in figure A.4, the high background current is given by a large double layer capacitance \( C_{\text{DL}} \), in the range of 20 \( \mu \text{F/cm}^2 \), and by surface activities like adsorptions and desorptions.

For the diamond electrode in figure A.4 there are two capacitances in series: the double layer capacitance \( C_{\text{DL}} \), in the range between 5 and 20 \( \mu \text{F/cm}^2 \) \([102][129][141]\), and the space charge capacitance \( C_{\text{SC}} \) which is generally in the range of 1 – 3 \( \mu \text{F/cm}^2 \) for highly boron doped diamond \( (N_A > 10^{20} \text{ cm}^{-3}) \). The space charge capacitance is therefore dominating and the capacitive current in equation A.3 is then much lower for diamond than for platinum.

Referring again to figure A.3, one can observe that the cyclic voltammogram of the same electrode material can vary considerably according to its quality, as illustrated by the difference between high quality and low quality polycrystalline diamond in terms of background current and width of the potential window. In polycrystalline and nanocrystalline diamond the differences in the voltammograms stem from the different density in the material of surface defects and of carbon phases, like graphite or amorphous carbon. These foreign phases in diamond can narrow the potential window width and increase the background current by adding new surface states which result in new chemical activities within the window. The characterization of diamond can be thus carried out by investigating the cyclic voltammograms in terms of width of the potential window and background current within it.
If the voltammograms of different diamond electrodes with comparable doping are taken using the same voltage scan rate, the difference in the background current is mainly determined by the activity current and therefore such measurements can give important information on the diamond layer quality. For easier comparison of cyclic voltammetry graphs in this thesis, all the measurements are performed at the same scan rate of 20 mV/s and using the same doping level for the NCD layers; the current due to chemical activity could be therefore correlated with the quality of the NCD layers.

**A.4 Impedance spectroscopy**

The values of the resistances and of the capacitances of the double and space charge layers can be obtained by impedance spectroscopy in electrolyte. This measurement is achieved by applying a sinusoidal potential between the working and the counter electrode at different frequencies and by measuring the total complex impedance of the circuit and its phase shift. The impedance module and the phase shift are then plotted versus the frequency and the curves are fitted with simulated data from which the equivalent circuit of the system can be extracted.

The diamond/electrolyte interface can be however represented also by other elements related to surface defects, pin-holes, grain boundaries or impurities. These different phases on the diamond surface can induce new chemical surface activities which have to be represented by further electrical elements in addition to the two RC circuits of the equivalent circuits. Such electrical elements must be necessarily known in order to use the correct equivalent circuit for the characterization of the diamond surface. Impedance spectroscopy in electrolyte is also a powerful instrument to investigate these additional elements.

**A.5 Capacitance-Voltage measurement**

As for semiconductor characterization in air, capacitance-voltage measurement in electrolyte allows to extract the doping profile of the diamond electrode from the space charge capacitance. The measurement is performed by applying a voltage between the counter and the working electrode (diamond) and by extracting the space charge capacitance from the measured total capacitance, being the double layer capacitance known from impedance spectroscopy. Such voltage is composed by two components: a DC voltage which is scanned within the diamond potential window and an AC component at a certain frequency. Plotting the space charge capacitance versus the DC voltage for a certain frequency allows extracting the doping profile of the diamond layer by using the equations of metal-semiconductor junction theory [104].

The measurement of the space charge capacitance at each DC voltage point and at a certain frequency requires that the equivalent circuit of the system as well as the circuit elements values are known. The equivalent circuit can be determined by impedance
spectroscopy, as discussed in the previous section, and is generally composed by two RC circuits in series as described in section A.2. Figures 3.18 B and C in section 3.5.2 shows an example of equivalent circuit used for the characterization of a delta doped NCD layer.
Appendix B

Electrochemical cell setup

Electrochemical characterization of NCD electrodes and ISFETs is performed in a standard three electrode glass cell with a platinum wire as counter electrode and a saturated calomel reference electrode (SCE) in a grounded Faraday cage. The measurements are made using two water-based electrolytes: 0.1M H₂SO₄ and 0.1M KOH with respectively pH 1 and pH 13. Data are acquired with a PARSTAT® 2273 potentiostat (Princeton Applied Research) for electrode measurements and with three Keithley SourceMeter instruments (2420, 2400 and 238) for ISFET measurements. The platinum counter electrode is used for applying potentials to the electrolyte and for measuring currents through it. This electrode is pH sensitive and therefore cannot be used as reference for electrochemical characterization in electrolytes with different pH; for this purpose a second electrode is used, the Saturated Calomel Electrode (SCE). As it is also shown in figure A.2, the SCE electrode is pH insensitive and is therefore used as reference for defining the correct voltage applied to the sample (V vs. SCE).

Figure B.1 shows the setup for electrode characterization. In this case a voltage is applied between the sample and the platinum electrode and the current through the electrolyte/sample interface is measured; this current is then correlated to the sample surface potential Vₓ versus the reference electrode SCE. Such measurement is called Cyclic Voltammetry and gives information about surface activity on the NCD layer. The same setup is used for capacitance-voltage (C-V) measurements and for impedance spectroscopy, in order to calculate the equivalent circuit of the system and to evaluate doping concentrations in case of semiconductors.

For ISFET’s electrode characterization source and drain are short-circuited as shown in figure B.2; current and capacitance measurements are performed as in the case of electrode samples described above.

Output and transfer characteristics of ISFET devices are measured with the setup shown in figure B.3. Here two voltages are applied, VₓDS between source and drain of the ISFET and VₓG between platinum electrode and source. The gate source voltage is then defined as the potential of the reference electrode SCE (representing the gate) versus the surface potential at the source contact; this voltage correlates thus with −Vₓ in electrode configuration.
In ISFET configuration two current values are measured; the drain-source current of the ISFET $I_D$ and the gate leakage current $I_g$.

Fig. B.1: Electrochemical cell setup for electrode characterization

Fig. B.2: Electrochemical cell setup for ISFET’s electrode characterization

Fig. B.3: Electrochemical cell setup for ISFET characterization
Appendix C

Schematic growth method for boron $\delta$-doped NCD

The growth of boron $\delta$-doped NCD in HFCVD relies on the fact that the TMB and CH$_4$ concentrations in H$_2$ reach the required values for growing and doping NCD only after a certain time that the growth phase is started.
References


[7]  Takeshi Kondo, Hiroyuki Ito, Kazuhide Kusakabe, Kazuhiro Ohkawa, Kensuke  
    Honda, Yasuaki Einaga, Akira Fujishima, Takeshi Kawai, “Characterization and  
    electrochemical properties of CF₄ plasma-treated boron-doped diamond surfaces”,  
    Diamond and Related Materials, Volume 17, Issue 1, January 2008, Pages 48-54

[8]  Jian, Sheng-Rui, Fang, Te-Hua, Chuu, Der-San, “Analysis of physical properties of  

[9]  Physical Constants for Transport Studies of the Group III-Nitrides,  
    http://iiiv.tn.cornell.edu/www/foutz/nitride.html#mrs1

[10]  Physical properties of Silicon, Si – Silicon,  


    Whitehead, S.E. Coe and G.A. Scarsbrook “High carrier mobility in single–crystal  

    Nitride (GaN)” in M.E. Levinshtein, S.L. Rumyantsev and M.S. Shur (eds.),  
    “Properties of advanced semiconductor materials: GaN, AlN, InN, BN, SiC, SiGe”  
    (JohnWiley & Sons, 2001) 1.


[37] Williams, Oliver A.; Douhéret, Olivier; Daenen, Michael; Haenen, Ken; Ōsawa, Eiji; Takahashi, Makoto, “Enhanced diamond nucleation on monodispersed nanocrystalline diamond”, Chemical Physics, Volume 445, Issue 4-6, p. 255-258


comparison of Raman and electrical measurements”, Diamond and Related Materials, 1994, Pages 623-627


[79] F. Silva, J. Achard, X. Bonnin, A. Michau, A. Tallaire, O. Brinza, A. Gicquel, "3D crystal growth model for understanding the role of plasma pre-treatment on CVD diamond crystal shape", Volume 203 Issue 12, Pages 3049 - 3055


[84] Q. Yang, S. Yang, Y.S. Li, X. Lu, A. Hirose, “NEXAFS characterization of nanocrystalline diamond thin films synthesized with high methane concentrations”,
Diamond and Related Materials, Volume 16, Issues 4-7, April-July 2007, Pages 730-734


[123] W. Wroblewski, Warsaw University of Technology, csrg.ch.pw.edu.pl/tutorials/isfet/


[125] Infineon Technologies, Max Planck Institute


[130] Diplomarbeit Carsten Pietzka, 2006, University of Ulm


Tables

Chapter 3

<table>
<thead>
<tr>
<th>Sample</th>
<th>$\text{N}_2/\text{H}_2$ ratio</th>
<th>Filament temperature</th>
<th>Substrate temperature</th>
<th>Pressure</th>
<th>Growth time</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>-</td>
<td>2050</td>
<td>810</td>
<td>2</td>
<td>20</td>
</tr>
<tr>
<td>B</td>
<td>-</td>
<td>2030</td>
<td>810</td>
<td>2</td>
<td>20</td>
</tr>
<tr>
<td>C</td>
<td>-</td>
<td>2050</td>
<td>815</td>
<td>2</td>
<td>25</td>
</tr>
<tr>
<td>D</td>
<td>1.5</td>
<td>2050</td>
<td>810</td>
<td>2</td>
<td>30</td>
</tr>
</tbody>
</table>

Table 3.1: Growth parameters for the samples used for $\text{CH}_4$ concentration/quality investigation

<table>
<thead>
<tr>
<th>Sample</th>
<th>$\text{CH}_4/\text{H}_2$ ratio</th>
<th>TMB/$\text{H}_2$ ratio</th>
<th>Filament temperature</th>
<th>Substrate temperature</th>
<th>Pressure</th>
<th>Growth time</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>1.5</td>
<td>2</td>
<td>2050</td>
<td>750</td>
<td>2</td>
<td>20</td>
</tr>
<tr>
<td>B</td>
<td>1.2</td>
<td>2</td>
<td>2030</td>
<td>740</td>
<td>2</td>
<td>20</td>
</tr>
<tr>
<td>C</td>
<td>0.9</td>
<td>2</td>
<td>2050</td>
<td>740</td>
<td>2</td>
<td>18</td>
</tr>
<tr>
<td>D</td>
<td>0.6</td>
<td>2</td>
<td>2020</td>
<td>750</td>
<td>2</td>
<td>18</td>
</tr>
<tr>
<td>E</td>
<td>0.3</td>
<td>2</td>
<td>2020</td>
<td>740</td>
<td>2</td>
<td>15</td>
</tr>
</tbody>
</table>

Table 3.2: Growth parameters for boron doped NCD layers with different grain size

<table>
<thead>
<tr>
<th>$\text{CH}_4/\text{H}_2$ ratio</th>
<th>TMB/$\text{H}_2$ ratio</th>
<th>Filament temperature</th>
<th>Substrate temperature</th>
<th>Pressure</th>
<th>Growth time</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.3</td>
<td>1</td>
<td>2050$^\circ$ C</td>
<td>740$^\circ$ C</td>
<td>2</td>
<td>8</td>
</tr>
</tbody>
</table>

Table 3.4: Growth parameters of boron doped NCD for intrinsic cap layer growth
### Table 3.5: Growth parameters of intrinsic cap NCD layers (samples Cap1, Cap2, Cap3)

<table>
<thead>
<tr>
<th>CH&lt;sub&gt;4&lt;/sub&gt;/H&lt;sub&gt;2&lt;/sub&gt; ratio</th>
<th>Filament temperature</th>
<th>Substrate temperature</th>
<th>Pressure</th>
</tr>
</thead>
<tbody>
<tr>
<td>%</td>
<td>°C</td>
<td>°C</td>
<td>kPa</td>
</tr>
<tr>
<td>0.3</td>
<td>2050°C</td>
<td>810°C</td>
<td>2.5</td>
</tr>
</tbody>
</table>

### Table 3.7: RIE etching parameters of delta doped NCD

<table>
<thead>
<tr>
<th>Power</th>
<th>Ar flux</th>
<th>O&lt;sub&gt;2&lt;/sub&gt; flux</th>
<th>Pressure</th>
</tr>
</thead>
<tbody>
<tr>
<td>25 W</td>
<td>17 sccm</td>
<td>1.7 sccm</td>
<td>40 mTorr</td>
</tr>
</tbody>
</table>

### Table 3.8: Growth parameters for boron delta doped NCD layers

<table>
<thead>
<tr>
<th>Sample</th>
<th>Growth phase time</th>
<th>CH&lt;sub&gt;4&lt;/sub&gt; flux</th>
<th>TMB flux</th>
<th>TMB opening time</th>
</tr>
</thead>
<tbody>
<tr>
<td>60M</td>
<td>60 min.</td>
<td>1.2 sccm</td>
<td>3 sccm</td>
<td>After 30 min.</td>
</tr>
<tr>
<td>30M</td>
<td>30 min.</td>
<td>1.2 sccm</td>
<td>8 sccm</td>
<td>After 15 min.</td>
</tr>
</tbody>
</table>

### Table 3.9: BEN nucleation on InAlN/GaN with and without SiO<sub>2</sub> interlayer

<table>
<thead>
<tr>
<th>CH&lt;sub&gt;4&lt;/sub&gt;/H&lt;sub&gt;2&lt;/sub&gt; ratio</th>
<th>Filament temperature</th>
<th>Substrate temperature</th>
<th>Pressure</th>
<th>Maximum bias current</th>
<th>Time</th>
</tr>
</thead>
<tbody>
<tr>
<td>%</td>
<td>°C</td>
<td>°C</td>
<td>kPa</td>
<td>mA</td>
<td>h</td>
</tr>
<tr>
<td>1.5</td>
<td>2000°C</td>
<td>750°C</td>
<td>2.5</td>
<td>97</td>
<td>1.5</td>
</tr>
</tbody>
</table>

### Table 3.10: low temperature growth parameters of NCD on InAlN/GaN

<table>
<thead>
<tr>
<th>CH&lt;sub&gt;4&lt;/sub&gt;/H&lt;sub&gt;2&lt;/sub&gt; ratio</th>
<th>Plasma power</th>
<th>Pressure</th>
<th>Growth time</th>
</tr>
</thead>
<tbody>
<tr>
<td>%</td>
<td>W</td>
<td>mTorr</td>
<td>Min.</td>
</tr>
<tr>
<td>1</td>
<td>700</td>
<td>30</td>
<td>60</td>
</tr>
</tbody>
</table>
Chapter 4

<table>
<thead>
<tr>
<th>CH$_4$/H$_2$ ratio</th>
<th>Filament temperature $^\circ$C</th>
<th>Substrate temperature $^\circ$C</th>
<th>Pressure kPa</th>
<th>Growth time h</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.0</td>
<td>2100</td>
<td>820</td>
<td>2</td>
<td>40</td>
</tr>
</tbody>
</table>

Table 4.1: intrinsic NCD ISFET buffer growth parameters

Chapter 5

<table>
<thead>
<tr>
<th>CH$_4$/H$_2$ ratio</th>
<th>Filament temperature $^\circ$C</th>
<th>Substrate temperature $^\circ$C</th>
<th>Pressure kPa</th>
<th>Growth time h</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.3</td>
<td>2000</td>
<td>740</td>
<td>2</td>
<td>5</td>
</tr>
</tbody>
</table>

Table 5.1: Growth parameters of NCD on EPFL InAlN/GaN layer for HEMT

<table>
<thead>
<tr>
<th>CH$_4$/H$_2$ ratio</th>
<th>Filament temperature $^\circ$C</th>
<th>Substrate temperature $^\circ$C</th>
<th>Pressure kPa</th>
<th>Growth time h</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.3</td>
<td>2020</td>
<td>750</td>
<td>2</td>
<td>4</td>
</tr>
</tbody>
</table>

Table 5.2: Growth parameters of NCD on Thales InAlN/GaN layer for HEMT
List of publications

N-type doped nano-diamond in a first MEMS application,
M. Dipalo, J. Kusterer, K. Janischowsky, and E. Kohn,

Thermally Actuated Nanocrystalline Diamond Micro-Bridges for Microwave and High Power RF Applications,
S. Balachandran, J. Kusterer, R. Connick, T. M. Weller, D. Maier, M. Dipalo, E. Kohn,

O-terminated Nano-Diamond ISFET for applications in Harsh Environment,
M. Dipalo, C. Pietzka, A. Denisenko, H. El-Hajj, E. Kohn,

Characterization of UV irradiated nanocrystalline diamond,

Planar NCD microelectrodes for detecting quantal release of catecholamines from chromaffin cells
A. Pasquarelli, M. Dipalo, E. Kohn, A. Marcantoni, V. Carabelli and E. Carbone,
6th International Meeting on Substrate-Integrated Micro Electrode Arrays, 2007

Nanodiamond Microbridges for RF-Applications
J. Kusterer, S. Balachandran, D. Maier, M. Dipalo, R. Connick, T. M. Weller, E. Kohn,
2nd Int. Industrial Diamond Conf., Rome 19/20 April 2007

Grain size dependence of the optical properties of nanocrystalline diamond films

O-Terminated boron doped NCD electrode with low background current
C. Pietzka, M. Dipalo, A. Denisenko, Z. Gao, E. Kohn,
SBDDXIII 2008, Hasselt, Belgium

A Concept for Diamond Overlayers on Nitride Heterostructures
E. Kohn1, M. Dipalo1, M. Alomari1, F. Medjdoub1, J.-F. Carlin2, N. Grandjean2, S. Delage3, Device Research Conference 2008, Santa Barbara, California, 2008
Diamond-on-GaN Heterostructures, Toward a New Class of Extreme performance Hybrid Devices
E. Kohn, M. Dipalo, M. Alomari, F. Medjdoub, C. Pietzka, J-F. Carlin, N. Grandjean,
ICEM 2008, Sydney, Australia

Combining Diamond Electrodes with GaN Heterostructures for harsh Environment ISFETs
Denisenko, J.-F. Carlin, N. Grandjean and E. Kohn,
Diamond Conference 2008, Sitges, Spain

High Temperature Diamond Growth on GaN heterostructure
M. Dipalo¹, F. Medjdoub¹, M. Alomari¹, S. Rossi¹, H. El-Hajj¹, J.-F. Carlin², N.
Grandjean², E. Kohn¹,
NDNC 2008, Taipei, Taiwan

Mikromechanisches diamante-basierendes Stempelwerkzeug zum Einsatz in der Feinstbearbeitung im Mikro- bis Nanometerbereich
J. Kusterer, Schmid, M. Dipalo, S. Balachandran, D. Maier, W. Ebert, E. Kohn,
Industrie Diamanten Rundschau 11/08

High power nanocrystalline diamond RF MEMS- A combined look at mechanical and microwave properties
Balachandran, S.; Kusterer, J.; Maier, D.; Dipalo, M.; Weller, T.; Kohn, E.; Microwaves,

High Power Nanocrystalline Diamond RF-MEMS
S.Balachandran, J.Kusterer, D.Maier, M. Dipalo, A.Kumar, T.M.Weller, and E.Kohn,
Lester Eastman Conference 2008, University of Delaware

XPS and UPS investigation of the diamond surface oxidation by UV irradiation,
S. Torrengo¹, L. Minati¹, M. Filippi¹, A. Miotello², M. Ferrari³, A. Chiasera³, E. Vittone⁴,
A. Pasquarelli⁵, M. Dipalo⁵, E. Kohn⁵, G. Speranza¹, Diamond Conference 2008, Sitges,
Spain

Planar NCD microarray for the amperometric detection of catecholamines from single chromaffin Cells, A. Pasquarelli*, V. Carabelli, M. Dipalo, A. Marcantoni, E.
Kohn, E Carbone, Diamond Conference 2008, Sitges, Spain
Patents

**Chemical Sensor on Diamond Film**
E. Kohn, M. Dipalo, A. Denisenko, application number 10 2007 039 706.4, German Patent Office

**Semiconductor Device**
E. Kohn, M. Dipalo, F. Medjdoub, application number EP 08003665.0, European Patent Office