Electronic Characterization of CVD Diamond

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Abstract

Diamond is a promising material for high-power, high-frequency and high-temperature electronics applications, where its outstanding physical properties can be fully exploited. It exhibits an extremely high energy gap, very high carrier mobilities, high breakdown field strength, and the highest thermal conductivity of any wide bandgap material. It could therefore produce the fastest switching, the highest power density, and the most efficient electronic devices obtainable, with applications in the RF power, automotive and aerospace industries. Lightweight diamond devices, capable of high temperature operation in harsh environments, could also be used in radiation detectors and particle physics applications where no other semiconductor devices would survive.

The high defect and impurity concentration in natural diamond or polycrystalline high-pressure-high-temperature (HPHT) diamond substrates has made it difficult to establish reliable results when studying the electronic properties of diamond. However, recent progress in the growth of high purity Single-Crystal Chemical Vapor Deposited Diamond (SC-CVD) has opened the perspective of applications under such extreme conditions based on this type of artificial diamond.

Despite the improvements, there are still many questions which must be answered. This work will focus on electrical characterization of (SC-CVD) diamond by different measurements techniques such as internal photoemission, $I-V$, $C-V$, Hall and in particular, time-of-flight (TOF) carrier drift velocity measurements. With the mentioned techniques, some important properties of diamond such as drift mobilities, lateral carrier transit velocities, compensation ratio and Schottky barrier heights have been investigated. Low compensation ratios $(N_D/N_A) < 10^{-4}$ have been achieved in boron-doped diamond and a drift mobility of about 860 cm$^2$/V for the hole transit near the surface in a lateral TOF configuration could be measured.
To my wonderful son Elias
List of Papers

This thesis is based on the following papers, which are referred to in the text by their Roman numerals.


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### Abbreviations and Symbols

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
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<tbody>
<tr>
<td>$a_0$</td>
<td>Bohr radius</td>
</tr>
<tr>
<td>$A$</td>
<td>Contact area</td>
</tr>
<tr>
<td>$A^*$</td>
<td>Richardson’s constant</td>
</tr>
<tr>
<td>$A_{it}$</td>
<td>Gold</td>
</tr>
<tr>
<td>Al</td>
<td>Aluminum</td>
</tr>
<tr>
<td>AC</td>
<td>Alternating current</td>
</tr>
<tr>
<td>B</td>
<td>Boron</td>
</tr>
<tr>
<td>B$_2$H$_6$</td>
<td>Diborane</td>
</tr>
<tr>
<td>BJT</td>
<td>Bipolar Junction Transistor</td>
</tr>
<tr>
<td>C</td>
<td>Carbon/diamond</td>
</tr>
<tr>
<td>C</td>
<td>Capacitance</td>
</tr>
<tr>
<td>C$_j$</td>
<td>Depletion layer capacitance</td>
</tr>
<tr>
<td>CV</td>
<td>Capacitance voltage measurement</td>
</tr>
<tr>
<td>CVD</td>
<td>Chemical vapor deposition</td>
</tr>
<tr>
<td>d</td>
<td>Sample thickness</td>
</tr>
<tr>
<td>DC</td>
<td>Direct current</td>
</tr>
<tr>
<td>DOS</td>
<td>Density of states</td>
</tr>
<tr>
<td>DSO</td>
<td>Digital sampling oscilloscope</td>
</tr>
<tr>
<td>DLTS</td>
<td>Deep level transient spectroscopy</td>
</tr>
<tr>
<td>e</td>
<td>Electron (index)</td>
</tr>
<tr>
<td>E</td>
<td>Electric field</td>
</tr>
<tr>
<td>$\varepsilon_0$</td>
<td>Vacuum permittivity</td>
</tr>
<tr>
<td>$\varepsilon_s$</td>
<td>Relative dielectric constant</td>
</tr>
<tr>
<td>$E_F$</td>
<td>Fermi level</td>
</tr>
<tr>
<td>$E_g$</td>
<td>Indirect bandgap energy</td>
</tr>
<tr>
<td>$E_A$</td>
<td>Acceptor ionization energy</td>
</tr>
<tr>
<td>$E_D$</td>
<td>Donor ionization energy</td>
</tr>
<tr>
<td>FCC</td>
<td>Face centered cubic</td>
</tr>
<tr>
<td>FWHM</td>
<td>Full width half maximum</td>
</tr>
<tr>
<td>$g_a$</td>
<td>Spin degeneracy factor</td>
</tr>
<tr>
<td>GaN</td>
<td>Gallium nitride</td>
</tr>
<tr>
<td>h</td>
<td>Hole (index)</td>
</tr>
<tr>
<td>$\hbar$</td>
<td>Planck’s constant</td>
</tr>
<tr>
<td>HF</td>
<td>Hot-filament</td>
</tr>
<tr>
<td>H</td>
<td>Hydrogen</td>
</tr>
<tr>
<td>HPHT</td>
<td>High-pressure high-temperature</td>
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</table>
High voltage
Intrinsic layer
Intrinsic layer on p-doped layer
Noise current
Current signal
Saturation current
Photoemission current
Infrared
Current voltage measurement
Current temperature measurement
Internal photo-emission
Current density
Junction field effect transistor
Boltzmann’s constant
Wavelength
Light emitting diode
Effective mass
Microwave plasma
Microwave plasma enhanced reactor
Metal oxide semiconductor field effect transistor
Hole and electron mobility
Ideality factor
Free electron concentration
Intrinsic carrier concentration
Nitrogen
Acceptor doping concentration
Donor doping concentration
Effective density of defects
Nickel
Effective DOS in the valence band
Hole density
Phosphorous
Photocurrent
Photoemission
Elementary charge
Absolute temperature
Room temperature
Time-of-flight
Lateral time-of-flight
Thermally simulated current
Drift time
Hole drift time
Sulphur
<table>
<thead>
<tr>
<th>Notation</th>
<th>Description</th>
</tr>
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<tbody>
<tr>
<td>$Si$</td>
<td>Silicon</td>
</tr>
<tr>
<td>$SiC$</td>
<td>Silicon carbide</td>
</tr>
<tr>
<td>$SC$</td>
<td>Single crystal</td>
</tr>
<tr>
<td>$SBH$</td>
<td>Schottky barrier height</td>
</tr>
<tr>
<td>$SIMS$</td>
<td>Secondary ion mass spectrometry</td>
</tr>
<tr>
<td>$\Phi_B$</td>
<td>Schottky barrier height</td>
</tr>
<tr>
<td>$U$</td>
<td>Bias</td>
</tr>
<tr>
<td>$UV$</td>
<td>Ultraviolet</td>
</tr>
<tr>
<td>$v_{dr}$</td>
<td>Drift velocity</td>
</tr>
<tr>
<td>$v_{sat}$</td>
<td>Saturation velocity</td>
</tr>
<tr>
<td>$V_{bi}$</td>
<td>Built-in potential</td>
</tr>
</tbody>
</table>
1 Introduction

The exceptional properties of diamond make it suitable in a variety of applications [1]. Diamond is the hardest natural material. The Mohs hardness scale, on which diamond is a ‘10’ and corundum (sapphire) is a ‘9’, does not adequately attest to its incredible hardness, as diamond is very much harder than corundum. Diamond is also the least compressible and stiffest substance. It is an exceptional thermal conductor - 4 times better than copper.

Diamond has an extremely low thermal expansion, is chemically inert with respect to most acids and alkalis, is transparent from the far infrared through to the deep ultraviolet [2], except for an absorption band, around (\(\lambda = 3 \, \mu m\)) and is one of only a few materials with a negative electron affinity.

Natural diamonds do not conduct electricity well, although some are semiconductors. Diamond can burn if subjected to a high temperature in the presence of oxygen. Diamond has a high specific gravity; it is amazingly dense given the low atomic weight of carbon. The brilliance and fire of a diamond are due to its high dispersion and high refractive index. Diamond has the highest reflectance and highest index of refraction of any transparent substance.

1.1 Diamond lattice structure

There are two stable isotopes of carbon in natural diamond, 98.9% of the natural abundance is \(^{12}\)C and the rest is 1.1% \(^{13}\)C. The nuclear spins are respectively zero and one-half. The simple chemical nature of diamond allowed its chemistry to be determined very early on [3]. The crystal structure of a diamond is a face-centered cubic or FCC lattice with a cube edge length denoted by \(a_0\) (Bohr radius). The two populated atoms in the FCC lattice are separated by \(\sqrt{3/4a_0}\) [4].

Each carbon atom joins four other carbon atoms in regular tetrahedrons (triangular pyramids). Based on the cubic form and its highly symmetrical arrangement of atoms, diamond crystals can develop into several different shapes. The most common crystal form is the eight-sided octahedron or diamond shape. Diamond crystals can also form cubes, dodecahedra, and combinations of these shapes.
Figure 1.1 The diamond lattice (formed by the carbon atoms in a diamond crystal) consists of two interpenetrating face centered cubic Bravais lattices, displaced along the body diagonal of the cubic cell by one quarter the length of the diagonal.

1.2 Types of diamonds

From the beginning, electrical characterization of diamond was performed on natural diamond. There are four types of natural diamond (Ia, Ib, IIa, IIb), classified according to the presence of nitrogen in the crystal and certain other properties. Type-IIb diamonds contain so little nitrogen that the crystal is a $p$-type semiconductor due to trace amounts of boron. Unfortunately this type is very rare and expensive. To reduce the cost and increase the availability of diamond samples, synthetic methods were developed.

Graphite is said to be the most stable allotrope (different forms of the same element) of carbon. Diamond exists only due to the extremely large activation barrier for conversion between itself and graphite. This metastability causes complications when diamond synthesizes [5]. There are currently two main methods of synthesizing diamonds. One is the high pressure - high temperature (HPHT) method where graphite is subjected to conditions similar to those under which natural diamonds are formed in the Earth’s mantle. In HPHT synthesis, graphite and a metallic catalyst are placed in a hydraulic press under high temperatures and pressures. The resulting diamonds are usually a few millimeters in size and too flawed for use as gemstones, but they are extremely useful as edges on cutting tools and drill-bits and for generating very high pressures in diamond anvils. The first synthetic
diamond made using this process in 1953 [6] and since then, HPHT diamonds have been available for electrical characterization.

In order to achieve diamond crystals with higher purity and less defects, another method evolved, called chemical vapor deposition (CVD). This method of growth was first performed in the 1950s by Eversole [7]. Since the 1980s it is possible to synthesize diamond films with good control on the surface morphologies by chemical vapor deposition. Initially, this method resulted in polycrystalline material but nowadays one can buy freestanding single-crystal CVD (SC-CVD) diamond of a high quality. These diamond films are expected to be the most promising semiconducting material and the electronic characteristics of diamond films have greatly improved.

![Figure 1.2 Samples of single-crystal diamond grown by the CVD process.](image)

### 1.3 Applications

Due to the extraordinary properties of diamond such as extreme hardness, chemical inertness, optical transparency, high thermal conductivity in combination with electrical insulation or semiconducting properties more and more fields of application recognize the benefits provided by this material. Particularly in applications involving extremely high power densities, high mechanical loads or severe abrasive conditions, CVD diamond is often the only material that could meet the demanding requirements.
Some potential applications of CVD diamond films and related properties are listed in table 1.1.

Table 1.1 *List of some potential applications of CVD diamond.*

<table>
<thead>
<tr>
<th>Function</th>
<th>Field of application</th>
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<tbody>
<tr>
<td>High temperature semiconductor</td>
<td>Automobile and aircraft engines</td>
</tr>
<tr>
<td>High frequency/high power transistors</td>
<td>High speed transistors, High speed data process</td>
</tr>
<tr>
<td>High voltage transistors</td>
<td>Electric power control</td>
</tr>
<tr>
<td>Electron emission</td>
<td>Flat panel display</td>
</tr>
<tr>
<td>Light emission</td>
<td>LEDs and lasers in UV region, white luminescence and light source for printer</td>
</tr>
<tr>
<td>X-ray windows</td>
<td>X-ray lithography masks and IR windows</td>
</tr>
<tr>
<td>IR windows</td>
<td></td>
</tr>
<tr>
<td>Pressure sensing</td>
<td>Pressure sensor at high temperature</td>
</tr>
</tbody>
</table>
One of the most promising semiconducting materials, which can be used for many extreme performances in microelectronic applications, is diamond. The excellent chemical, thermal, electrical and mechanical properties are suitable for high-power, high-temperature and high-frequency devices. But before the realization of active devices in diamond, several problems must be overcome [8, 9].

Due to the negative effect of contamination and structural defect and grain size on the behavior of diamond [10], especially electrical performance, it is important to grow diamond into films or substrate of single-crystal quality. Until now most of the published results have been performed on polycrystalline diamond. However, free-standing CVD single-crystal diamonds are now commercially available through companies such as Element Six Ltd.

The fundamental problem of diamond synthesis is the allotropic nature of carbon. Under ordinary conditions diamond is not the thermodynamically stable crystalline phase of carbon. Hence, the main requirement of diamond CVD is to deposit carbon and simultaneously suppress the formation of graphitic sp²-bonds. This can be realized by establishing high concentrations of non-diamond carbon etchants such as atomic hydrogen. Usually, those conditions are achieved by admixing large amounts of hydrogen to the process gas and by activating the gas either thermally or by plasma [11].

2.1 Growth process

CVD processes for diamond synthesis can be used for the growth of both single crystal and polycrystalline forms of the material. The actual conditions required for making either type of diamond are very similar; it is the choice of substrate that determines which type will grow. For single crystal CVD diamond, a single crystal diamond substrate is required and the new diamond film grows epitaxially, with the deposited film taking on the same lattice structure and orientation as those of the substrate. For polycrystalline diamond, a non-diamond substrate is normally used.

In diamond CVD synthesis, the process generally takes place below atmospheric pressure. The CVD growth is based on the activation of a H₂/CH₄ gas mixture with a high hydrogen concentration [12]. Only a tiny amount of
hydrocarbon (methane), often between about 1 and 5%, is normally present in the gas mixture and provides the source of carbon from which the diamond is formed. The various diamond CVD techniques differ mainly in the way of gas phase activation and dissociation.

Table 2.1 *Example of required condition of growth CVD diamond films [44]*.

<table>
<thead>
<tr>
<th>Source gases</th>
<th>CH&lt;sub&gt;4&lt;/sub&gt;, H&lt;sub&gt;2&lt;/sub&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH&lt;sub&gt;4&lt;/sub&gt;/H&lt;sub&gt;2&lt;/sub&gt; (%)</td>
<td>0.05-0.075</td>
</tr>
<tr>
<td>Total gas pressure (kPa)</td>
<td>~10</td>
</tr>
<tr>
<td>Total gas flow rate (sccm)</td>
<td>400-1000</td>
</tr>
<tr>
<td>Substrate temperature (°C)</td>
<td>800-900</td>
</tr>
</tbody>
</table>

The first critical step of CVD diamond growth is nucleation and the control of it will decide the diamond film properties, such as transparency, grain size and roughness [13]. The most common nucleation techniques are microwave plasma (MP) assisted CVD and thermally assisted CVD, usually realized by gas activation with a hot filament (HF) (~ 2200°C). Plasma systems offer uniform films over larger substrate areas than hot filament CVD growth, with the possibility of industrial scale-up by using more powerful reactors.

*Figure 2.1* Examples of two of the most common types of low pressure CVD reactor. (a) Hot filament reactor, (b) Microwave Plasma Enhanced Reactor (MPER).
2.2 Impurities and doping

Diamond with its wide band-gap normally behaves as an insulator at room-temperature. Although the superior properties of diamond make it desirable to be used as a semiconductor, it is necessary to introduce shallow donors or acceptors. To achieve high activation in a doped semiconductor it is necessary to have a low degree of compensation. This puts a high demand on the achievement of a controlled doping process.

There are several existing substances which can be use as impurities in diamond. Hydrogen (H) related defects are very complex and exist due to the hydrogen-rich growth atmosphere. The passivation effect of hydrogen on diamond dopants has been investigated repeatedly [14, 15]. Silicon (Si) and sulfur (S) are two other elements which are common impurities in diamond. These are often unintentionally introduced into diamond during the growth process. Silicon is centered deep in the bandgap, having the ionization energy of 2 eV [16]. Unfortunately, in the case of sulfur this value is uncertain and varies significantly (0.77 eV [17] – 1.4 eV [18]).

These impurities are located deep in the bandgap and they do not act as dopants in diamond at room temperature. Other impurities which can be used as dopants, the \( p \)-type boron (B) and \( n \)-type phosphorous (P) and nitrogen (N), are described in following sections.

2.2.1 \( p \)-type doping

\( p \)-type diamonds containing boron, exist naturally in type IIb natural diamonds. Boron can easily be incorporated substitutionally into the diamond lattice during the CVD process [19]. This can e.g. be done by adding diborane \( \text{B}_2\text{H}_6 \) into the gas mixture.

A low boron concentration creates an acceptor level with an activation energy of 0.37 eV [20] and transforms insulating diamond to a \( p \)-type semiconductor. At higher boron concentration, diamond shows metallic properties due to the broadening of the acceptor level into a band [21]. Recent reports have shown a superconducting behavior in heavily boron doped diamond below 11 K [22]. This observation seems to be related to the strong electron-phonon coupling in diamond [23].

2.2.2 \( n \)-type doping

The majority of diamond samples used for optical and electrical studies around the world are \( p \)-type diamonds, despite the fact that the most common impurities in diamond are of an \( n \)-type nature (type Ib diamonds).

Nitrogen and phosphorous are candidates to act as a donor. They can easily replace carbon and fit substitutionally into the diamond crystal. However, nitrogen induces a deep energy level 1.7 eV below the conduction band min-
imum. Unfortunately this deep level does not donate significant numbers of electrons to the conduction band at room temperature [24].

Phosphorous, an element in group V, was proved to be an interesting donor in diamond, despite the rather deep level, 0.52 eV [25]. An early attempt to dope diamond with P by the CVD technique, turned out to be difficult with rather low electrical performance. Today it is possible to grow both polycrystalline heteroepitaxy and homoepitaxial high quality P-doped diamonds with electron mobilities up to 660 cm$^2$ V$^{-1}$ s$^{-1}$ [26].

![Figure 2.2 Bomor, n-doping and phosphorus ionization energies in CVD diamond.](image-url)
3 Characterization techniques

In this work several characterization techniques have been utilized to analyze single-crystal CVD diamond’s electrical properties. The main techniques used are: Time-of-flight (TOF), internal photo-emission (IPE), current-voltage measurements (IV), capacitance-voltage measurements (CV) and Hall measurements. In addition, we briefly describe secondary ion mass spectrometry (SIMS) which was used to determine doping levels.

3.1 Sample preparation

The samples described in Paper I-III were synthesized by Element Six Ltd. by CVD, first described in [27]. Initially, homoepitaxial boron-doped CVD diamond layers were deposited onto specially prepared high-pressure, high-temperature (HPHT) grown synthetic diamond substrates using a diborane ($\text{B}_2\text{H}_6$) addition to the $\text{H}_2/\text{CH}_4/\text{Ar}$ source gas mixture. A further CVD layer grown under conditions of high purity was deposited on this doped CVD material. The HPHT substrates were subsequently removed by laser cutting.

Before metallization, the samples were treated in a graphite etch ($\text{HNO}_3:\text{HClO}_4:\text{H}_2\text{SO}_4 = 1:1:1$, $180^\circ\text{C}$, 40min) and the surfaces were oxygen terminated in a mild oxygen plasma for 60 s. To form an Ohmic back contact for $I-V$, $C-V$ and $I-T$ measurements, Ti/Al contacts were deposited on the boron doped material under high vacuum ($10^{-7}$ Torr) in a Von Ardenne CS 730 Magnetron sputter. Circular Schottky contacts with a diameter between 0.25 mm to 2 mm were formed on the other side of the samples (see Fig. 3.1). The contacts were deposited by sputtering gold (Au) using a K675XD Turbo Sputter Coater. Nickel (Ni) and Aluminum (Al) contacts were deposited using a Von Ardenne CS 730 Magnetron sputter in high vacuum ($10^{-7}$ Torr). To pattern the samples, standard optical lithography and wet chemical etching were used. In the following characterization techniques, the same sequences of processing steps (except for the choice of metal) were used to prepare the samples.

To measure internal photoemission, semitransparent Schottky contacts (10-15 nm of Au, Al and Ni) were patterned on the top surface of the samples, while Ohmic back contacts were deposited in the manner previously described.
3.2 Current-Voltage measurements (IV)

Current-voltage measurements allow an estimation of the leakage current characteristics and the critical breakdown field of a dielectric. Study of $I$-$V$ measurements at different temperatures allows better understanding of the mechanism of the leakage current. The characterizations were performed on Schottky metal contacts without an edge-termination on both $p$-type material ($p$) and $p$-type material with a thin intrinsic overlayer ($i$-$p$).

Forward $I$–$V$ measurements were performed on several diodes on each sample at room temperature to investigate the homogeneity of the doping. A Keithley 6485 picoamperemeter in combination with a Keithley 2400 sourcemeter was used to measure $I$-$V$ characteristics of these diodes which were placed on a hotplate that can achieve temperatures in the interval 300-500 K.

3.3 Capacitance-Voltage measurements (CV)

Capacitance-voltage measurements are widely used to determine semiconductor parameters, particularly in MOSFET structures. However, other types of semiconductor devices and technologies can also be characterized with $C$-$V$ measurements, including bipolar junction transistors (BJTs), JFETs, III-V compound devices, photovoltaic cells, and many others.

A $C$-$V$ measurement of semiconductors and interfaces is a very sensitive and powerful technique for electrical characterization. This is based on monitoring capacitance for a varying DC voltage. In addition to the Hall-effect measurements, capacitance-voltage measurements were performed to get a different measurement of the donor concentration. The measurements were
made using an EG&G 7265 lock-in amplifier. The bias was applied using a Keithley 2400 sourcemeter.

3.4 Time-of-Flight (TOF)

Hall-effect measurements are generally used to measure the mobilities of the charge carriers in semiconductors. However, there are some difficulties to perform this technique on intrinsic wide bandgap semiconductors, such as intrinsic diamond. To overcome this, time-of-flight (ToF) measurements, also called the transient current technique (TCT) have been used by several groups. With this technique it is possible to investigate many important electrical properties of semiconductors, such as drift mobility, charge collection and trapping lifetimes. In order to create electron-hole pairs in intrinsic diamond, several methods such as pulsed electron beam [28], pulsed X-ray [29], α-particles [30] and UV-pulsed laser [27, 31-32] have been used. The time-of-flight technique allows to investigate the carrier transport through the diamond crystal (vertically) by preparing the sample in the following configuration:

- Deposition of a transparent net-contact (Au, Al or Ni) on one side of the sample followed by backside (Ti/Al) contact.

![Figure 3.2 Deposited semitransparent contact on CVD Diamond.](image)

This is shown in Fig. 3.2 and it is suitable for bulk studies. The carrier transport measurements can also be performed along the surface (laterally) with the sample in following configuration:

- Deposition of two parallel electrodes (metal contact made by Au, Al or Ni) on the same side of the sample
The unique advantage of this configuration allowed us to analyze transport characteristics of thin layer diamond films and delta-doped structures. The lateral time-of-flight system in **Paper II** uses a short (3 ns FWHM) UV pulsed laser (Nd-YAG laser) with a pulse of 213 nm produced at a 10 Hz repetition rate. A maximal intensity of 18 mJ can be achieved. The intensity can be controlled by several interference and attenuation filters. To focus the beam and achieve a line focus on the sample, a cylindrical square lens is used in conjunction with reflective optics, see Fig. 3.4.

**Figure 3.3** Deposited lateral contacts on CVD Diamond.

**Figure 3.4** Schematic of the ToF setup. The sample is illuminated with 3 ns (FWHM) 213 nm UV light from a quintupled Nd-YAG laser. The focusing optics are described in the text.
3.5 Internal Photo-emission (IPE)

Internal photo-emission (IPE) spectroscopy is a contactless, nondestructive method of probing the electronic structure of materials. IPE is defined as a process of optically induced transition of a mobile charge carrier across the interface between two solid phases, one is the emitter and the other is the collector. Light is directed onto a sample, where it is absorbed and imparts excess energy into the material in a process called photo-excitation.

For the IPE measurements, a halogen filament lamp attached to an Acton Research SP150 blazed grating monochromator was used to illuminate diodes through an optical fibre. A sharp cut-off coloured glass filter mounted between the lamp and the monochromator was used to eliminate higher orders from the grating. A Newport 818-BB-22 photodetector with well known photoresponsivity was used to measure the intensity vs. wavelength variation of the entire optical setup (lamp + filter + monochromator + fibre). The diamond diode IPE was measured with a Keithley 6485 picoamperemeter.

![Schematic of the photocurrent setup used to collect SBH data.](image)

Figure 3.5 Schematic of the photocurrent setup used to collect SBH data.
3.6 Complementary techniques

3.6.1 Hall-measurements

The key feature of Hall-measurements is the ability to determine the carrier density, the carrier type and the mobility with a relatively simple measurement. To determine the doping/drift parameters and degree of dopant compensation, Hall-measurements were applied using the van der Pauw configuration. The electrodes were formed at the four corners of each sample by ion implantation of boron. Ion implantation of the sample was performed by Anders Hallén at KTH (2.5×10^{16} cm^{-2} at 37keV), followed by annealing (15min at 1100°C), deposition of Ti/Al contacts (100/200 nm) and a final contact annealing (15min at 500°C) to obtain good Ohmic contacts. Hall-effect measurements were made in the temperature range of 80-450K in a magnetic field of 0.5 T.

![Figure 3.6](image)

(A) Schematic diagram of the Hall-effect. Current and a perpendicular magnetic field create a potential difference perpendicular to both the current and the magnetic field. this is known as the Hall-effect. (B) Schematic of a van der Pauw configuration used in the determination of the two characteristic resistances $R_A$ and $R_B$.

3.6.2 Secondary Ion Mass Spectrometry (SIMS)

Secondary ion mass spectrometry is used to provide accurate measurements to be able to distinguish differences in doping levels and presence of impurities or unintentional dopants. Due to its unique capabilities of high detection sensitivity for a variety of elements, SIMS is an essential tool for characterization of impurities in semiconductor materials.
SIMS measurements were performed by Margareta Linnarsson at KTH on homoepitaxial highly boron-doped CVD diamond samples, using a Cameca ims 4f micro-analyzer. A sputtering beam of 8.2 keV \((\text{O}_2)^+\) ions was rastered over an area of \(200 \times 200 \ \mu\text{m}^2\) and secondary ions of \(\text{B}^+\) were collected from the central region (~60 \(\mu\text{m}\)). In order to minimize the effect of sample charging, electron flooding was employed. The erosion rate was typically 10-20 Ås\(^{-1}\) as determined by crater depth measurements using a KLA-Tencor P15 profilometer.

*Figure 3.7* The principle of secondary ion mass spectrometry.
Diamond has long been considered to be an exceptional material for the fabrication of active electronic devices for the most demanding high-power and high-frequency applications. However, until recently it has not been available in sufficient quality or purity. Theoretical comparisons indicate that CVD diamond could offer a substantially higher level of performance than other established electronic materials, such as silicon or gallium arsenide. Due to the large bandgap and material purity, diamond is an excellent electrical insulator. By doping, however, CVD diamond can be made conducting.

Diamond is a wide bandgap semiconductor with a 5.47 eV indirect bandgap at 300 K. The highest drift mobility measured has been reported by Isberg et al. [27] and is 4500 cm²/Vs for electrons and 3800 cm²/Vs for holes. These are much higher than those of widely used conventional semiconductor material mobilities, such as Silicon (1450 cm²/Vs for electron mobility and 480 cm²/Vs for hole mobility) and other wide bandgap materials, such as Silicon carbide (SiC) (900 cm²/Vs for electrons and 120 cm²/Vs for holes) and Gallium nitride (GaN) (2000 cm²/Vs for electrons and 200 cm²/Vs for holes). Diamond has a very high electric breakdown field (20 MV/cm) [33] and high carrier saturation drift velocity (2.7x10⁷ cm/s for electrons and 1.4x10⁷ cm/s for holes) [34, 45]. Room-temperature values for the thermal conductivity of up to 24 W/cm K have been reported [35]. The latest results show that resistivity can exceed 10¹⁶ Ω cm [36] in pure diamond.

This chapter focuses on some of the basic theory behind electrical transport, carrier concentration dependence on the doping density and determination of Schottky barrier height by different methods in single-crystal CVD diamond.
4.1 Compensation in p-type diamond

Many of the extreme properties of diamond can be explained by looking at the crystal structure of diamond. Other parameters such as mobility depend on factors like concentration of extrinsic contaminations and dopants or intrinsic defects \textbf{Paper I}.

These defects and impurities exist in all semiconductors and even in very pure diamond crystals. Of course, in order to have any kind of conductivity a reasonable amount of dopants is needed and those can be introduced during growth or ion-implanted into the sample. During these processes it is inevitable to introduce undesirable levels into the bandgap which will affect the performance of the device either by compensation or passivation.

The relatively deep energy level of boron in the bandgap (0.37 eV) leads to a low activation at RT. The high activation energy is the reason for a strong temperature dependence of the carrier concentration. Because of the low activation it is highly important to keep the ratio between the dopants and the compensating defects concentration at a low level.

The carrier density in an uncompensated diamond at room-temperature is normally less than $10^{15}$ cm$^3$. Volume fractions lower than $10^{-3}$ between compensating donor ($N_D$) and the majority carrier concentration, in this case acceptor concentration ($N_A$) must be obtained to achieve diamond devices with high performances.

Here we will deal with a $p$-doped semiconductor where the acceptor doping $p >> n$, the influence of free electrons is negligible and holes are the "majority carriers" for current flow in a $p$-type semiconductor.

Several mechanisms affect the carrier transport in a semiconductor, due to the temperature dependence of the Fermi level $E_F$. At low temperature the main carrier transport in a $p$-type CVD diamond is dominated by a tunneling process called hopping conduction [36]. This is due to the existence of few holes at low temperatures. The process is quite slow and so the mobility is low. This phenomenon was observed in \textbf{Paper I} the low temperature range (80-150 K) Hall-measurements. Capacitance-voltage $C$-$V$ and secondary ion mass spectrometry SIMS were performed as complementary measurements.

In a compensated semiconductor, the difference in the concentration of donor and acceptor gives the effective density, $N_{eff}$.

$$ N_{eff} = N_A - N_D \quad (4.1) $$

If we consider a $p$-doped, wide bandgap semiconductor, such as diamond where $N_A > N_D$ the hole concentration $p$ can be calculated from:
\[
\frac{p(p + N_D) - n_i^2}{N_A - N_D - p - n_i^2 / p} = \frac{N_v}{g_a} \exp\left(-\frac{E_A}{k_B T}\right) \tag{4.2}
\]

where \(n_i, N_v, E_A, k_B, T\) and \(g_a\) are the intrinsic carrier concentration, the valence band effective density of states, the acceptor ionization energy, the Boltzmann constant, the absolute temperature and the spin degeneracy factor for the valence band, respectively. The latter is expected [37] to follow the expression below:

\[
g_a = 4 + 2 \exp\left(-\Delta / k_B T\right) \tag{4.3}
\]

Eq. 4.3 is valid in case of a non-degenerate semiconductor. For temperatures below 1000 K, due to the wide bandgap of diamond the intrinsic concentration, \(n_i\), can be neglected. \(N_v\), which represents the weighted sum of all states in the valence band, has the following temperature dependence:

\[
N_v = 2 \left(\frac{2 \pi m^*_h k_B T}{h^2}\right)^{3/2} \tag{4.4}
\]

where \(m^*_h\) is the density of states effective hole mass. The value of \(m^*_h\) is not well known and the assumption that \(m^*_h = m_0\) will be made. The carrier concentrations \(N_A\) and \(N_D\) and acceptor ionisation energy \(E_A\) were obtained by using Eq. (4.5) and performing a least-squares fit in the upper temperature range of the measured hole concentration data, by making the assumption that \(n_i\) is negligible in Eq. (4.2).

\[
p = \sqrt{\left(\frac{N_v' + N_D}{2}\right)^2 + N_v' \left(N_A - N_D\right)^2 \frac{N_v' + N_D}{2}} \tag{4.5}
\]

Where \(N_v'\) is the right side of the Eq. (4.2) and shows explicit temperature dependence.

\[
N_v' = \frac{2}{g_a} \left(\frac{2 \pi m^*_h k_B T}{h^2}\right)^{3/2} \exp\left(-\frac{E_A}{k_B T}\right). \tag{4.6}
\]

The behavior of the carrier concentration exhibits different behaviors for a compensated \(p\)-type diamond for different temperatures, Fig. 4.1.
i) Low temperatures, when $p << N_D$, $p << N_A - N_D$ and $p >> n_i$, we obtain:

$$p = \frac{N_A - N_D}{N_D} \cdot \frac{N_f}{g_a} \exp\left(-\frac{E_A}{k_B T}\right)$$  \hspace{1cm} (4.7)

Here the donor is partially compensated and the acceptor is incompletely ionized.

ii) Intermediate temperatures, when $p >> n_i$ and $N_A >> p >> N_D$

$$p = \sqrt{(N_A - N_D) \cdot \frac{N_f}{g_a}} \cdot \exp\left(-\frac{E_A}{2k_B T}\right)$$ \hspace{1cm} (4.8)

iii) High temperatures, when $E_A > k_B T$ and $p >> n_i$

$$p \equiv N_{\text{eff}} = N_A - N_D$$ \hspace{1cm} (4.9)

At this point the temperature dependence of the carrier concentration is negligible. For even higher temperature intervals (iv), the intrinsic region where $p \approx n_i$ is reached.

Figure 4.1 Sketch of the typical behaviour of the hole concentration vs. inverse temperature for CVD diamond.
The effective density of the defects can be obtained from \( C-V \) measurements on Schottky diodes. By fitting experimental data to Eq. (4.10) it is possible to determine the effective density \((N_A - N_D)\).

\[
\frac{1}{C_j^2} = \frac{2(V_{bi} - V)}{q\varepsilon_s(N_A - N_D)}
\]  \hspace{1cm} (4.10)

where \( C_j \) is the junction depletion layer capacitance per unit area, \( V_{bi} \) the built-in potential and \( \varepsilon_s = 5.7\varepsilon_0 \) the permittivity of diamond.

4.2 Schottky barrier height

One of the most important properties of a metal-semiconductor (MS) interface is its Schottky barrier height (SBH). The SBH is the rectifying barrier for electrical conduction across the MS junction and, therefore, it is of great importance to the successful operation of any MS device. The magnitude of the SBH reflects the mismatch in the energy position of the majority carrier band edge of the semiconductor and the metal Fermi level across the MS interface. The requirements for achieving high-voltage high-power switching devices are low forward losses, i.e. small threshold voltages, but also high reverse blocking voltages [38]. Ideally, for a \( p \)-type interface, the SBH is the difference between the valence band maximum of the semiconductor and the metal Fermi level. The Schottky barrier height has an influence on the leakage current and the breakdown voltage. This makes it an important parameter for adjusting the trade-off between low forward losses and high breakdown voltage in Schottky diodes.

Several methods can be use to determine the SBH. In Paper III photoemission, \( I-V \) and \( I-T \) measurements have been performed to obtain information on the SBH.

Internal photo-emission

Internal photo-emission (IPE) measurements were performed to determine the SBH. In this method the energy band offset at the interface is associated with the threshold \( \Phi \) determined as the minimal photon energy necessary for injection of a charge carrier. Unlike the \( C-V \) and \( I-V \) techniques that are often used to measure the barrier heights, the internal photoemission technique is not as sensitive to problems related to leakage currents, series resistance, thin interfacial layers, deep traps, and ideality factors and so it should in principle provide a more accurate measurement of the barrier height.

For photon energies slightly exceeding the barrier height, \( h\nu > \Phi_B \), the yield \( Y \) defined as the ratio of the photocurrent \( I_{ph} \) to the photon flux is expected to follow the Fowler law and it is given by Eq. (4.11) [39].
Extrapolation of the linear region to zero $Y^{1/2}$ in a Fowler plot ($Y^{1/2}$ vs. photon energy $h\nu$) extracts the SBH and this is visualized in Fig. 4.2.

\[ Y \propto (h\nu - q\Phi_B)^2 \quad (4.11) \]

**Current-voltage**

To calculate the barrier height, the reverse saturation current density $J_S = I_s/A$ was obtained by extrapolation of the forward characteristic at zero bias voltage. To investigate the homogeneity of the doping $I-V$ measurements were performed at room temperature. The thermionic current-voltage relationship of a Schottky barrier diode, neglecting series and shunt resistance [40], is given by:

\[
I = I_S \left( \exp \left( \frac{qV}{nkT} \right) - 1 \right) \quad (4.12)
\]

where

\[
I_S = AA^*T^2 \exp \left( -\frac{q\phi_B}{kT} \right) \quad (4.13)
\]

and
\[ A^* = \frac{4\pi qk^2 m^*}{h^3} = 120 \left( \frac{m^*}{m_0} \right) \text{A cm}^{-2} \text{K}^{-2} \] (4.14)

Where \( A \) is the diode area, \( T \) the absolute temperature, \( n \) the ideality factor, \( I_S \) being the saturation current, \( m^* \) is the effective mass and \( A^* \) the Richardson’s constant. The Schottky barrier height is denoted by \( \Phi_B \).

\[ \ln \left( \frac{I}{T^2} \right) = \ln(AA^*) - \frac{q(\Phi_B - V/n)}{kT} \] (4.15)

The barrier height is then given by:

**Figure 4.3** Theoretical I-V relationships for a p-type semiconductor at five different temperatures.

**Current-temperature**

In general defects might cause thermal activation of the reverse leakage. Due to this phenomenon it is important to study the current at different temperatures to achieve a better evaluation of the SBH.

By assuming that the ideality factor \( n \) is known (the result from the I-V fit can be used) one can determine SBH from the slope of a (Richardson) plot where \( \ln(I/T^2) \) is plotted versus \( I/T \) at a constant forward bias.

For \( V >> kT/q \), Eq. (4.12) & (4.13) can be written as:
\[ \phi_B = \frac{V}{n} - \frac{k}{q} \frac{\partial}{\partial (1/T^2)} \ln \left( \frac{I}{T^2} \right) \] (4.16)

In current-temperature relationship, the voltage is fixed and the temperature varies. Extraction of the SBH from the temperature dependence of the forward current density of a diode is determined by a linear fit to the data.

![Figure 4.4 Theoretical I-T relationships for a p-type semiconductor at three different voltages.](image)

4.3 Lateral time-of-flight

In comparison to polycrystalline diamond, single crystal diamond (SC-CVD) offers important advantages for applications in electronics and radiation detection. This is because SC-CVD diamond exhibits superior charge transport characteristics, specifically high drift mobility and an increased charge carrier lifetime. So far, only limited studies have dealt with the measurements of electrical transport parameters in SC-CVD diamond.

In Paper II a system is described that has been built to measure the carrier transport between two metal electrodes with certain distance on one side of a sample (Lateral alignment). The main purpose is to analyze electrical transport properties of thin intrinsic diamond films.

The main principle is to inject a short laser pulse into the sample, and to analyze the resulting current pulse at a contact at the distance \( d \) from the
injection point. Due to the wide bandgap of diamond (5.47 eV) the sample is illuminated by a 213 nm UV-pulsed laser. This provides the photon energy necessary to create electron-hole pairs.

**Figure 4.5** Device simulation of a carrier transit, showing the hole concentration at three different times. Electron-hole pairs are created near the right electrode and drift in an applied field towards the opposite electrode. Thermal diffusion broadens the carrier distribution during the transit.

### 4.3.1 Signal interpretation

By applying an electric field the electrons and holes begin to drift towards the anode and the cathode respectively. As soon as the charge carriers begin their motion, they induce a current. The TOF technique measures the duration of the current pulse induced by the drift of charge carriers, under the influence of the field.

The current pulse width equals the time the charge carriers need to traverse the detector \((t_{dr})\) under the assumption that the effective charge carrier lifetime \((\tau)\) is longer than the drift time. Depending on the direction of the electric field, one polarity of charge carrier drifts across the whole detector thickness while the other polarity carrier only drifts a short distance.

Simulation of the output signal was carried out to obtain an analysis method. The expression below is an approximation of the induced current by the laser, where \(\alpha\) and \(\beta\) are constants.

\[
I(t) = \alpha \cdot \left(1 + \text{erf}\left(\frac{t-t_0}{\sigma_0}\right)\right) \left(1 + \text{erf}\left(\frac{t_0-t}{\sigma_1}\right)\right) \exp(\mu t) + \\
+ \beta \cdot \exp\left(-\left(\frac{t-t_0}{\sigma_0}\right)^2\right) 
\]

(4.17)

Processes such as photoelectric effect, and plasma relaxation, which are shorter than the laser pulse duration, are taken into account by the last term in Eq. (4.17). The generation and extraction of charge is described by the two \(1 + \text{erf} (*)\) factors in the equation.
The effect of a homogeneous distributed space charge on the applied field and the extracted charge by the trapping or recombination are described by the \( \exp(\gamma t) \) factor. Fig. 4.6 shows example of fits, derived from Eq. (4.17) and current data obtained from experimental measurements.

![Figure 4.6 Example of fit of expression (4.17) to current calculated in a device simulation.](image)

### 4.3.2 Charge injection and mobility measurements

Before the measurement starts, some consideration should be made due to the use of the lateral TOF configuration. The charge created by illumination must be large enough so that the measured current can be distinguished from the thermal noise caused by the sample and external sources. To achieve a homogenous electric field across the sample:

\[
E = \frac{U}{d} \tag{4.18}
\]

the charge \( Q \) injected should satisfy \( Q \ll CU \), where \( U \) is the bias applied across the contacts and \( C \) is the capacitance (very small, typically \(< 1 \) pF). If \( Q \gg CU \) charge will appreciably effect the E-field and result in a time-varying E-field.

In the case of low-field injection, the current signal \( I_{\text{signal}} \) and sample’s noise current \( I_{\text{noise}} \) (from the preamplifier and input resistor R) can be calculated respectively using Eq. (4.19) and Eq. (4.20) where full charge collection and constant current have been presumed.
\[ I_{\text{signal}} = \frac{Q \mu U}{d^2} \]  
(4.19)

\[ I_{\text{noise}} = 4 \Delta f \sqrt{k_b T C} \]  
(4.20)

Here \( \mu \) is the carrier mobility and \( \Delta f \) is bandwidth of the RC circuit (\( \Delta f = 1/(4RC) \)). Having this information, the signal-to-noise-ratio can be used to estimate the exact charge \( Q \) needed in certain experimental situations.

To calculate the carrier mobility \( (\mu_h) \), in this case the low field hole mobility, the drift velocity must first be determined as a function of bias voltage. Assuming that the charge cloud is moving at constant speed, the average drift velocity can be calculated by extracting the transient time \( (\tau_h) \), from the pulse width (FWHM) of the signal in Fig. 4.6 as shown in Eq. (4.21).

\[ v_d = \frac{d}{\tau_h} \]  
(4.21)

There \( \tau_h \) is the transient time \( (t_1-t_0) \) from Eq. (4.17). An expression of the mobility can be utilized by analyzing the relation between the drift velocity and applied electric field when the velocity approaches the saturated regime:

\[ v_d = \frac{\mu_h E}{1 + \frac{\mu_h E}{v_{\text{sat}}}} \]  
(4.22)

and simplified by combing Eq. (4.18) and Eq. (4.21):

\[ \tau_h = \frac{d}{v_{\text{sat}}} + \frac{1}{U} \cdot \frac{d^2}{\mu_h} \]  
(4.23)

The slope and intercept of a linear fit of \( \tau_h \) to \( 1/U \), e.g. as exemplified in Fig. 4.7 can provide information needed to acquire mobility and saturation velocity.
Figure 4.7 Lateral hole TOF curve vs. inverse bias for a CVD diamond sample is shown in the plot. The hole mobility is $\mu_h = 860 \text{ cm}^2/\text{Vs}$. 
5 Summary of the results

Different electrical properties of single crystal CVD diamond have been studied by different measurement techniques. The results have been described in Papers I-III. A brief summary of these results will follow in this chapter.

5.1 Compensation in boron-doped diamond

From Hall-measurements in Paper I in the temperature range of 80-450K and best fit on Eq. 4.5, we managed to observe a volume fraction lower than $10^{-4}$ between compensating donor ($N_D$) and the dopant concentration, ($N_A$). The acceptor concentration obtained from fits to Hall data matched the result from capacitance-voltage measurements performed on Schottky contacts.

The secondary ion mass spectrometry was used as a complementary method to measure the total boron concentration in the samples. The results were in agreement with Hall-effect measurements and are summarized in Table 5.1.

Table 5.1 Summary of the results with 95% confidence interval. The Hall mobility at room temperature $\mu_H$ is also included.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$E_A$ (eV)</th>
<th>$N_A$ (cm$^{-3}$)</th>
<th>$N_D$ (cm$^{-3}$)</th>
<th>Comp. ratio</th>
<th>$\mu_H$ (cm$^2$/Vs)</th>
<th>$N_A$–$N_D$ (cm$^{-3}$)</th>
<th>[B] (cm$^{-3}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1$^*$</td>
<td>0.37±0.02</td>
<td>4.8±3.7×10$^{18}$</td>
<td>7.2±3.8×10$^{13}$</td>
<td>$&lt;10^{-4}$</td>
<td>435</td>
<td>7±1×10$^{17}$</td>
<td>1.5±0.3×10$^{18}$</td>
</tr>
<tr>
<td>2</td>
<td>0.34±0.01</td>
<td>1.5±0.5×10$^{18}$</td>
<td>6.0±2.7×10$^{16}$</td>
<td>$&lt;0.09$</td>
<td>365</td>
<td>2.4±0.3×10$^{18}$</td>
<td>-</td>
</tr>
<tr>
<td>3</td>
<td>0.32±0.01</td>
<td>9.6±3.3×10$^{17}$</td>
<td>4.6±3.7×10$^{12}$</td>
<td>$&lt;10^{-5}$</td>
<td>285</td>
<td>1.8±0.2×10$^{18}$</td>
<td>3.9±0.8×10$^{18}$</td>
</tr>
<tr>
<td>3$^{**}$</td>
<td>0.36±0.01</td>
<td>2.9±0.9×10$^{18}$</td>
<td>$&lt;2.7×10^{14}$</td>
<td>$&lt;10^{-4}$</td>
<td>285</td>
<td>1.8±0.2×10$^{18}$</td>
<td>3.9±0.8×10$^{18}$</td>
</tr>
</tbody>
</table>

$^*$ sample with $\approx 40\mu m$ boron layer on intrinsic diamond

$^{**}$ fitted only to values with $T > 250$ K

Table 5.1 shows that the activation energy values for all samples lie below 0.37 eV and exhibit a dependency on the boron concentration. From SIMS measurements the total boron concentration [B] could be obtained. These values were higher than the corresponding value obtained from $C$-$V$ measurements, indicating that boron has been partially passivated.
The hole concentration dependence on the temperature in Fig. 5.1 follows the semiconductor theory in wide bandgap materials described in chapter 4 (Fig. 4.1).

![Graph showing hole concentration versus reciprocal temperature including best fits to Eq. (4.5). Filled symbols denote data where valence band conduction is believed to be dominant.]

Figure 5.1 Hole concentration versus reciprocal temperature including best fits to Eq. (4.5). Filled symbols denote data where valence band conduction is believed to be dominant.

The concentration behavior at low temperature is most likely caused by hopping conduction. Samples 1 and 3 show extremely low compensation ratios but in sample 2 the high concentration of donors shifts the transition process from partially to completely ionized compensation to higher temperature.
5.2 Lateral time-of-flight measurements on thin SC-CVD layers

Charge carrier dynamics in intrinsic homoepitaxial diamond film were investigated using the lateral time-of-flight measurement system described in Paper II. Both bulk CVD diamond samples and samples consisting of a thin layer of CVD diamond on top of a $Ib$-substrate were used. Electron-hole pairs were created in between two parallel metal contacts on the surface with contact spacing of 0.3 mm, using a 213 nm UV pulsed laser. The line focus was parallel to the contacts and at a distance of 15 µm from one contact edge. Voltages in the range of 10-300 V were used. A hole transit could be observed in the current traces, this is shown in Fig. 5.2.

![Figure 5.2](image)

*Figure 5.2* Fits of Eq. (4.17) together with experimentally measured currents (hole transport, average over 100 shots) for two different bias voltages.

In the thin layer samples a linear relation between the drift velocity and bias voltage was revealed, by observing hole transit signals near the surface. A hole mobility of $\mu_h = 860 \, \text{cm}^2/\text{Vs}$ from the slope of the fit in Fig. 5.3 could be obtained in the best sample.
Figure 5.3 The transit time $\tau_{tof}$ from the fits in thin layer sample has been plotted vs. reciprocal bias voltage ($1/V$).

Figure 5.4 The transit time $\tau_{tof}$ from the fits in the bulk sample has been plotted vs. reciprocal bias voltage ($1/V$).

From the experimental data measured on the bulk sample a hole mobility of $\mu_h = 1200 \text{ cm}^2/\text{Vs}$ could be calculated from the slope of the fit in Fig. 5.4. The $\tau_{tof}$ in both cases is defined as $\tau_{tof} \equiv t_f - t_0$ from Eq. (4.17). In contrast to the vertical TOF, the obtained mobility values are much lower. Anisotropy in the observed carrier mobility could possibly be explained by the surface scattering effects and scattering caused by dislocations aligned in the growth direction.
5.3 Characterization of single crystal CVD diamond Schottky barrier diodes

In this work (Paper III), freestanding single crystal CVD diamond was used to make Schottky diodes both on $p$-type material ($p$) and $p$-type material with thin intrinsic ($p$-$i$) overlayer. Internal photo-emission (IPE) measurements in combination with other characterization techniques such as current-voltage ($I$-$V$) and current-temperature ($I$-$T$) were used to investigate the barrier height of the samples with different metallization (Au, Ni and Al).

The diodes showed a barrier height, attributed to the interface Schottky metal and boron doped diamond, ranging from $\Phi_B=1.78$-$2.10$ eV, using the internal photo-emission technique.

![Figure 5.2 A Fowler plot for sample A with three different metallizations. The inset is a detail of the linear regression region.](image)

Table 5.2 Schottky barrier heights as obtained from internal photo-emission spectroscopy measurements on two samples A & B for three different Schottky metals.

<table>
<thead>
<tr>
<th>$\Phi_B$(eV)</th>
<th>Au</th>
<th>Ni</th>
<th>Al</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>1.91</td>
<td>1.82</td>
<td>1.78</td>
</tr>
<tr>
<td>B</td>
<td>2.10</td>
<td>2.0</td>
<td>1.91</td>
</tr>
</tbody>
</table>
Lower Schottky barrier height values were obtained using \textit{I-V} or \textit{I-T} methods, i.e. $\Phi_B=1.00$-1.71 and also relatively high ideality factors, above 1.4 were observed. The presence of interfacial defect states might cause this behavior. A comparison between these methods showed that, $\Phi_B(I-T) \leq \Phi_B(I-V) < \Phi_B(\text{IPE})$. The lower sensitivity of IPE to interface damages which introduce interface states or recombination centers causing trap-assisted tunnel currents (larger $n \leftrightarrow$ lower $\Phi_B$) might be a reason for this difference.
6 Conclusion

The aim of this work has been to study some of the electrical properties of single-crystal CVD diamond. Although the quality of diamond thin films has been improved during the last decade, the way to achieving successful diamond based devices is still surrounded by many uncertainties.

The concentration of impurities and dopants and thereby the compensation ratio in the diamond thin films has been studied, using different characterization techniques.

From Hall-effect measurements, a very low compensation volume fraction in \textit{p-type} CVD diamond could be reported. The achievement was in agreement with data obtained from SIMS and \textit{C-V} measurements. An important consequence of the study is the realization of devices with reasonable carrier density and increased hole mobility.

To study the effect of surface properties on carrier transport close to the surface, a time-of-flight system with lateral configuration has been described and hole transport measurements on homoepitaxial diamond thin film have been performed.

It is obvious that the result is highly affected by surface scattering effects and scatter from dislocations, aligned in the growth direction. A better surface treatment method must be introduced. Furthermore the improvement of the growth control is essential to reduce as-growth dislocation and defects.

A Schottky barrier height study of different contact metals was performed on CVD diamond films because of the importance of understanding the current loss and voltage blocking.

The behavior of the Schottky contacts exhibits strong Fermi level pinning related to a high concentration of interface states.
7 Future work

This work included a study of some electrical properties of SC-CVD diamond. We have applied a variety of experimental techniques such as TOF, CV and PC to analyze diamond samples. There are many groups, in Uppsala specialized in different techniques, working with diamond; collaboration between these groups would benefit the development of diamond based devices and could address some unsolved problems. In this case there are some projects which have already been started, on which I will focus more.

7.1 Defect investigation of SC-CVD diamond

To understand the electrical behavior of CVD diamond it is very important to investigate the defects inside the crystal lattice. In most cases, defects have a stable configuration in semiconductors. Generally, only defects which introduce levels in the band gap affect the electrical and optical properties of a material and are unstable (charge state of the defect changes) are of great importance to investigate. Single-crystal CVD diamonds are fairly pure and almost free from crystal defects such as dislocations and boundary irregularities. However, there are several defects present in the non-equilibrium charge states with long lifetime, acting as deep traps for carriers [41, 42].

The conventional experimental techniques which have been used to analyze defect levels, such as Thermally Simulated Current (TSC) and especially Deep Level Transient Spectroscopy (DLTS) are rather difficult to perform on diamond. The requirement of having low defect concentration, as discussed in Paper I, might be one of the aspects. Another reason is the wide bandgap of diamond (5.47 eV), which requires extremely high temperature (~1000°C) to excite all trap centers.

To overcome the problem regarding the achievement of higher temperature, our group is trying to develop a high temperature DLTS-setup where the measurements will take place in a vacuum chamber at the temperature range of 700-1000°C. Fig 7.1 in the next page describes the schematics of the DLTS setup which is in progress.
7.2 High voltage (HV) breakdown diodes

There is great interest in the Division for Electricity in developing diamond-based diodes with low on-state resistance of the drift layer and high breakdown voltage to be used as rectifiers. The Division is working with renewable energies such as wave and wind power where a test farm of wave power generators has already been planned and prototypes are currently tested in Lysekil. One of the main electrical challenges is to be able to feed the current directly into electrical grid (50 Hz) due to the variation in both frequency and amplitude of the generators [43]. That is why it is desirable to design Schottky diodes which could perform e.g., at 1.7kV-50A. The diode should provide a path for the reverse current flow whenever inductive loads are switched off and must have good reverse recovery characteristics. Intrinsici single crystalline CVD diamond diodes could satisfy these demands.

To achieve such diode a termination technique must be developed to prevent premature breakdown at the surface of the device. The proper termination design distributes the electric field evenly by enlarging the space charge region at the edge of the junction. Having overcome these problems one can produce electrically and economically efficient converters.
First of all I would like to express my sincere gratitude to my supervisor, Assoc. Professor Jan Isberg for his guidance and encouragement and for involving me in this interesting field. Secondly, I would like to thank my assistant supervisor, Professor Mats Leijon, head of the Electricity Division for injecting positive energy into the Division and making me feel welcome.

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Finally I would like to express my gratitude to you Erika, my son Elias and my family for all their understanding and love. I would not be here without your support.
9 References


[13] C. E. Nebel, J. Ristein ”Thin-Film Diamonds I” Semiconductors and Semimetals, Volume 76


