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Quality Assurance of Diamond Radiation Detectors

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Tiivistelmä — Referat — Abstract

Halvledarstrålningsdetektorer är anordningar menade för detektering av elektromagnetisk strålning och partikelstrålning. Signalformationen i dem baserar sig på transport av laddningar mellan valens- och ledningsbanden. Växelverkan mellan detektormaterialet och strålningen producerar fria negativt laddade elektroner och positivt laddade hål som rör sig i motsatt riktning i elfältet mellan detektorns elektroder. Rörelsen inducerar en ström i den yttre elkretsen, som kan användas för identifiering av partikelstrålning, bestämning av deras energi eller rörelsemängd, samt deras bana.

Det finns många olika detektormaterial och -system, och nya planeras hela tiden. Ett material som har väckt intresse inom flera olika områden är diamant. Diamantdetektorer är ett lockande alternativ för flera olika applikationer tack vare sina unika egenskaper. Många av dessa egenskaper härstammar från diamantens kristallstruktur och styrkan hos bindningarna mellan kolatomerna. Den täta och rigida strukturen gör diamant till ett hårt och hållbart material, vilket möjliggör användningen av diamantdetektorer i krävande strålningsförhållanden. Detta kombinerat med snabba transporten av laddingar och den korta responstiden gör diamantdetektorer ett utmärkt val för tillämpningar inom högenergifysik. Diamantens kristallstruktur leder också till ett brett bandgap. Tack vare det breda bandgapet har diamantdetektorer liten läckström och de kan användas t.o.m. vid höga temperaturer utan skydd för omgivande ljus.

Speciellt de elektriska egenskaperna hos halvledare beror starkt på mängden orenheter och kristalldefekter. Därmed är bestämningen av de elektriska egenskaperna ett bra sätt att få en bild av kristallens kvalitet. Materialets elektriska egenskaper bestämmer spänningsområdet inom vilket anordningen kan användas på ett säkert sätt, och för optimerad användning av halvledardetektorer behövs kunskap om anordningens läckström och transportmekanismerna för elektroner och hål. Därför är karakterisering av materialets egenskaper en viktig del av framställningen av halvledaranordningar. Karakterisering bör göras i olika skeden av framställningen för att märka när eventuella problem uppstått och lättare förstå orsaken till dem. I det här arbetet beskrivs processen för kvalitetskontrollen av singlekristall CVD (kemisk förågningssdeposition, chemical vapour deposition) diamantdetektorer för CMS-experimentets PPS-detektor.

Processen inkluderar visuell inspektion av diamantens ytor och dimensioner m.h.a. optiskt och korspolariserat ljus mikroskop, samt elektrisk karakterisering genom mätning av läckström och laddningsinsamlingse□ektivitet (CCE, charge collection e□ciency). CCE mätapparaturen förbättrades med en styrbar plattform, som möjliggör automatisk mätning av diamanten i flera positioner. Den nya apparaturens funktion och resultatens upprepbarhet undersöktes via upprepade mätningar av en referensdiamant. Mätapparaturen kunde framgångsrikt användas för att mäta CCE över hela diamantens yta. Resultatens osäkerheter är dock stora. Resultaten var stabila och liknande för de olika mätpunkterna. Ytterligare arbete krävs för att minska mätningarnas osäkerhet och för att klargöra korrelationen mellan observerade defekter och mätta elektriska egenskaper.

Avainsanat — Nyckelord — Keywords
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1. Introduction

Radiation detectors are devices used to detect electromagnetic and particle radiation. Di erent detector systems can be built depending on the goal of the measurement. Detector systems can be used for particle identi cation, measurement of energy or momentum, timing, or tracking. Operation of radiation detectors is based on the interaction of the ionizing radiation with the detector medium, which can be liquid, gas or solid. This thesis studies solid semiconductor detectors. In semiconductor detectors information about the traversing radiation is deduced from the current generated by the movement of charge carriers produced by the radiation.

Semiconductor detectors are used in many elds in science and technology, for example medicine, particle and nuclear physics, energy production, material characterization and imaging in astronomy. Their wide use is due to some unique advantages over other detector types. These advantages include good energy resolution, precise position measurements, small size and relatively fast response. In addition, semiconductor detectors are mechanically rigid so they don't need support structures, and the detector thickness can be changed according to application requirements. However, semiconductor detectors are more expensive and their use is sometimes limited by the small size. Also, many semiconductor materials are relatively sensitive to radiation damage.

There are several options for detector designs and material, and new options are continuously developed and studied. One detector material that has obtained a large amount of interest in many elds is arti cial diamond grown by chemical vapor deposition (CVD). This is due to the many unique properties of diamond, such as low leakage current, fast response, the combination of low electrical conduction and high thermal conduction, and radiation tolerance. The radiation tolerance is a particularly intriguing property, since it means that the detector can be operated for a long time without signi cant changes in the response.

Key factors in semiconductor detector operation is a perfect crystal structure and the energy bands resulting from the formation of a crystal lattice. Small concentrations of impurities and irregularities in the crystal structure can have a signi cant e ect on semiconductor properties, such as charge carrier mobility,

conductivity and charge carrier lifetime. These properties de ne the safe operational region of the device, and a ect the detector operation and stability. Optimal operation of a detector requires knowledge of these properties, which is why characterization, especially determination of electrical properties, is an important part of detector fabrication and system design. This thesis describes characterization of CVD diamond detectors designed for the Precision Proton Spectrometer (PPS) detectors for the CMS-experiment at CERN.

1.1 Diamond detectors in TOTEM and CMS

Diamond detectors are used as time-of- ight detectors in the CMS-TOTEM Precision Proton Spectrometer (CT-PPS) timing layer and in TOTEM timing. The detectors measure the time-of- ight from the point of collision of proton beams colliding in the Large Hadron Collider (LHC) to the detector location inside the Roman Pots (RP) about 200m from the interaction point. RPs are movable devices consisting of vacuum vessels called pots, detectors for tracking and timing, and vacuum bellows for connecting the pot to the beam line vacuum.[1, 3] The detectors are designed to measure inelastic, elastic and total cross sections of proton-proton collisions. Together with the CMS detectors they are used to study di ractive dissociation and central exclusive processes at the LHC.[4] The time-of- ight measurements make it possible to determine the longitudinal position of the proton interaction point and to associate it with one of the vertices that the CMS detectors have reconstructed even when events are piled-up. In case of event pile-up, the timing detectors can be used to determine the di erence in arrival time, which is directly proportional to the longitudinal position of the collision point. The di erence in arrival time can be used to determine the position of the interaction vertex with an accuracy of a few cm even when several protons are detected at once.[3,4]

The timing detectors need to have timing precision less than 100 ps and excellent e ciency. Also, the detector system for the timing has to be small due to the limited space in the RP. These requirements can be met with single crystal CVD diamond.[4] Besides fast signal properties, diamond is more radiation tolerant than many other detector materials. Both detectors and electronics need to be radiation tolerant in order to provide precise information in the harsh radiation environments of high energy physics experiments.[1,2,5] Silicon, which is a widely used detector material, has very mature processing technology, but it does not have good enough radiation tolerance to withstand the harsh environments, even though its radiation hardness

Figure 1.1: Segmentation of the detector planes in the vertical Roman Pot (left) and the CT-PPS (right). Image source [4]

can be increased by di erent processing methods.[6] Irradiation studies have shown that diamond detectors can be operated for years with high e ciency and good spatial resolution close to the interaction region in the LHC, making it well suited for particle detection in high energy physics.[2,5] The radiation tolerance combined with the fact that CVD diamond can be produced in thicknesses of several hundred μm make it possible to produce self supporting detector systems that can be installed close to the interaction position in particle colliders. The low dielectric constant, small leakage current, the radiation hardness and fast response are the reasons why diamond detectors have found their way into experiments in the LHC.[2,7]

The TOTEM-experiment consists of two sets of detectors placed symmetrically around the interaction point. Each set originally consisted of a RP system, and T1 and T2 telescopes. The T1 telescope consisting of Cathode Strip Chambers was later removed and no upgrades have been planned. The T2 telescope was previously built of Gas Electron Multipliers, but these have now been replaced with segmented plastic scintillators. Both telescopes detect charged particles in the forward region. The RP system consists of two RP stations installed at 210m and 220m from the interaction point. The stations consists of 2 units consisting of 3 RPs, one horizontal and two vertical. One RP is used for timing and the other two, placed on opposite sides of the timing RP, are used for tracking of leading protons. The RPs housing the timing detectors for the CT-PPS are installed in the RP station at 220m between the two units described earlier. In the latest upgrade a second timing RP will be built in each RP unit.[3,4,8]

Detectors for tracking were previously edgeless silicon detectors, but these have been gradually replaced with 3D silicon pixel detectors. Timing measurements are

done with single crystal CVD diamond detectors. In year 2017 one diamond detector plane was temporarily replaced with a ultrafast silicon detector (UFSD). The timing detectors in TOTEM are installed in the vertical RPs, and the ones of CT-PPS in the horizontal RPs. Each Roman Pot unit has four segmented sensor planes for timing. Dividing the detector system into four planes improves the precision of the measurement, while segmenting improves the spatial resolution. Segmenting also reduces event pile-up. The detector geometry for TOTEM consists of twelve detector pads with di erent thickness, arranged so that the thinner pads are in the high activity area. Each detector plane is segmented as shown on the left in Figure 1.1 and consists of eight single crystal CVD diamond detectors. In the detector geometry for the CT-PPS each plane is divided into twelve segments as shown on the right in Figure 1.1.[3,4,8] In order to improve the time resolution, the diamonds of CT-PPS are gradually being changed to double-diamond structures. Half of the diamond planes had been changed to double-diamond in 2018.[3] The signals are read out using dedicated fast low noise electronics.[3]

1.2 Scope of this thesis

This thesis presents the quality assurance of CVD diamond detectors during their fabrication process. All measurements were done at the University of Helsinki. The electrical measurements were done with measurement setups in the Detector Laboratory. The setup for the charge collection e ciency (CCE) measurement was improved to allow automatic and repeatable measurements of several samples at the same time. The visual inspections were done with an optical microscope in the Detector Laboratory and with a cross polarized light microscope in the Geology Laboratory. This thesis describes the quality assurance process and measurements. The focus is on the CCE measurements and the improvements made to the setup.

The structure of this thesis is as follows. Chapter 2 explains important concepts of semiconductor physics and the operational principle of semiconductor radiation detectors. Diamond as detector material, as well as the production of CVD diamond and diamond detectors are presented in Chapter 3. Chapter 4 describes di erent types of defects present in crystalline materials and their e ect on semiconductor properties. The quality assurance process and the measurements are described in Chapter 5. Finally, Chapters 6 and 7 present and discuss the obtained results. Chapter 6 includes also the e orts to reduce the measurement uncertainty.

2. Semiconductor radiation detectors

This chapter presents the basic operational principles of semiconductor radiation detectors, explaining generation of charge carriers in the detector and the signal formation. Discussion about radiation damage and its e ects on detector operation is also included. The chapter is based on books by Lutz [10] and Knoll [11]. Additional sources are mentioned when they are used.

For understanding operation of semiconductor detectors, is it important to have some knowledge about semiconductor physics, especially the concept of energy bands. The energy bands are a result of the periodicity of the crystal lattice and they determine where the electrons can be found within the lattice. The formation of these bands can be explained by imagining that crystal lattices consist of atoms that were originally far apart. Atoms that are far apart have the same discrete energy levels and they will not in uence each other. But when N number of atoms are brought closer to form a lattice, their energy levels start to overlap. The Pauli exclusion principle states that two electrons can not be in the same quantum state. Therefore the atomic energy levels split into N closely packed molecular energy levels. When $N \to 1$ the space between each energy level becomes very small and the energy levels become energy bands. As the distance between atoms is reduced, the energy levels overlap more, which leads to broadening of the energy bands. If the distance is reduced further the bands merge before they split again to a lower and upper energy band. The separation between the bands in a material depends on the distance between the atoms.

The band with higher energy is called the conduction band and the band with lower energy the valence band. The valence band corresponds to the electrons that are bound to speci c sites in the crystal lattice, while the conduction band corresponds to the electrons that are free to migrate through the crystal and contribute to the electrical conductivity of the material. The conduction and valence band are separated by a band gap (E_g). Because the band gap is forbidden for electrons, those can only be found in the energy bands. The size of the band gap determines whether the material is an insulator, conductor or semiconductor. Insulators have a large band gap, typically 5 eV or more, and conductors have either a partially

lled conduction band or overlapping bands. Semiconductors are something between conductors and insulators. In semiconductors the energy bands are separated, but the band gap is smaller than in insulators. The band gap is typically less than 2 eV, which means that charge carriers can be thermally excited and cross the band gap from the valence band to the conduction band. Figure 2.1 shows the energy bands of insulators, conductors and semiconductors. The dotted area represents bands that are lled with electrons.

Figure 2.1: Energy bands of insulators, semiconductors and conductors.

2.1 Generation of charge carriers in semiconductor materials

At low temperatures electrons are bound to their lattice sites leading to a completely full valence band and an empty conduction band. At higher temperatures thermal vibrations can break covalent bonds and electrons can be excited to the conduction band. The probability of excitation is small in materials with large band gap and high in materials with small band gap. Each electron excited to the conduction band will leave one hole on the valence band. Both the electron and hole are available for conduction. The probability for thermal excitation depends on the temperature and the size of the band gap. The probability increases with decreasing band gap and increasing temperature. Materials with low probability of excitation will have few electrons on the conduction band and low conductivity, while materials with high excitation probability will have many electrons on the conduction band and high conductivity.

Thermal generation of charges means that semiconductor detectors show some conductivity and steady state leakage current even in absence of ionizing radiation when an electric eld is applied over the device. Leakage current and its uctuations

Figure 2.2: Excitation of charge carriers through intermediate energy levels within the band gap.

are a source of noise superimposed on the signal and lead to signal blurring, which have a detrimental e ect on semiconductor detector operation. In semiconductors with small band gap thermal generation of charges leads to such large leakage currents that they can not be properly operated in normal room temperature without cooling. The leakage current of a device can be reduced with structures like the reversed biased PN-junction.[12,13] Materials with large band gap can show leakage current even in lower temperatures than the band gap suggests in case there are intermediate energy levels inside the band gap, e.g. due to impurities. These energy levels allow excitation of charges to the conduction band with energy less than the band gap energy. The excitation of charge carriers through intermediate energy levels is illustrated in Figure 2.2.

In radiation detectors one is interested in the number of charge carriers produced by radiation hitting the detector.[14] The operation of any type of radiation detector is based on interactions between the detector material and the studied radiation. Therefore, knowledge of how radiation interacts with matter is a central part of understanding the operation of radiation detectors. Photons interact with matter mainly through photoelectric absorption, Compton scattering and pair production, see Figures 2.3a-2.3c.[15] Photons are absorbed in the detector and the energy they deposit is used to excite valence electrons to the conduction band. If the absorbed photon has energy higher than the band gap, the excess energy is emitted as lattice vibrations (phonons) or lower energy photons. Photons with energy smaller than the band gap can also be absorbed if there are suitable intermediate states within the band gap. Electrons interact with matter mainly through excitation, ionization, Coulombic interactions and radiative losses, called bremsstrahlung. Bremsstrahlung is the emission of photons during deceleration of electrons in their interactions with atomic nuclei, see Figure 2.3d.[15] The total energy deposition is the sum of all these processes. Because electrons have the same mass as orbital electrons, they will

(a) Photoelectric absorption (b) Compton scattering (c) Pair production

(d) Bremsstrahlung (e) Excitation (f) Ionization

Figure 2.3: Mechanisms by which radiation interacts with matter.

scatter in di erent angles in the interactions and their paths can be very non-linear.

Charged particles deposit their energy mainly through Coulombic interactions with orbital electrons. In each interaction the particle delivers part of its energy to the electrons and slows down. The energy deposition can either lead to excitation of electrons or ionization of atoms, see Figures 2.3e-2.3f. If the electrons obtain large enough energy they can cause further ionization. These electrons are called delta rays. Delta rays have short range and will not travel far from the primary particle track. The energy deposition of charged particles is described by the Bethe-Bloch formula. The formula gives the energy $d(E_p)$ deposited per path length dx, called speci c energy loss.

$$\frac{dE_p}{dx} = \frac{4\,e^4 z^2}{m_0 v} N Z \left[\ln \frac{2 m_0 v^2}{I_0} - \ln\left(1 - \frac{v^2}{c^2}\right) - \frac{v^2}{c^2} \right] \tag{2.1}$$

In the formula v is the primary particle velocity and ze is its charge, N is the number density of the absorbing material and Z is atomic number. The electron mass is denoted by m_0, speed of light by c, and the elementary charge by e. I_0 is the average

ionization and excitation potential which is experimentally determined for an element. At low particle energies the energy deposition is inversely proportional to the square of the velocity. The energy deposition decreases rapidly with increasing velocity. When the velocity approaches the speed of light (about 0.95c)[14] the energy deposition reaches a near constant minimum. Charged particles reach this minimum when their energy is several hundreds of MeV and electrons when their energy is around 1 MeV. At this point the particles are called minimum ionizing particles (MIP). Further increase of the particle velocity leads to a logarithmic increase in the energy deposition, until it saturates due to polarization of the absorbing material.[14] When the energy deposition of charged particles is large the energy loss is well described by the Bethe-Bloch formula in the form given above. However, if the energy deposition is low, e.g. in thin detectors in which particles deposit only part of their energy, additional terms need to be added to account for the high energy tail of the energy distribution. Additional terms are also needed if delta electrons are able to leave the detector without depositing all of their energy.[13,14] The Bethe-Bloch formula also fails to describe the energy deposition of very low energetic charged particles, for which charge exchange with the absorbing material becomes important.

2.2 Operational principle of semiconductor radiation detectors

Interactions between ionizing radiation and matter lead to formation of electron-hole pairs in the detector active volume. The operational principle of semiconductor detectors is based on collection and measurement of charge carriers along the particle track. The number of generated electron-hole pairs depends on the energy required to form one pair, which in turn depends on the size of the band gap. The number of produced electron-hole pairs depends on the amount of energy deposited by the traversing radiation.[14 18]

After their formation charge carriers undergo random thermal motion within the lattice. The motion is driven by di erences in charge concentrations between regions in the lattice.[15,16] The probability for a carrier to move is the same in all directions, so the mean distance carriers travel is zero and charges quickly disappear by recombination if no external electric eld is applied.[14,15] However, there is a probability for the carrier to move between regions with di erent charge concentration. The probability for charges to move from the high concentration region to the lower concentration region is higher so di usion leads to smoothing of charge carrier

di erences. The charge carrier ux (F) due to di usion is described by

$$F = \quad D r \quad q; \tag{2.2}$$

where $r \quad q$ is the concentration gradient and D the di usion coe cient. The di usion coe cient is related to charge carrier mobility .

$$D = \frac{kT}{e} \tag{2.3}$$

Here k is the Boltzmann's constant and T the absolute temperature. Mobility describes how fast carriers travel across the device. Materials with high mobility will hence have fast response. The mobility depends on both temperature and defect concentration. Defects introduce scattering sites that reduce the drift velocity.[19] Because of di usion charges do not move in a straight line to the electrodes from their point of origin. Charges arrive at the electrodes at slightly di erent positions, which limits position measurements and leads to broadening of the charge collection time. In many cases the e ects of di usion are so small that they can be neglected, but in detectors with large volume, and in timing or position measurements such e ects can be signi cant.

Voltage is applied to the detector to generate a drift eld and to remove free charge carriers. Even when an electric eld is applied across the detector some free carriers will be present in the detector volume due to thermal generation of charges, but these quickly drift to the electrodes.[13,17] Generated electrons and holes will drift in opposite directions in the eld with mean velocity v.[16] During their drift, carriers will collide with lattice atoms. Between every collision the charge carriers will accelerate due to the in uence of the electric eld. The mean drift velocity is determined by the electric eld strength and number of interactions between carriers and lattice atoms.[14] When the time between collisions is independent of the applied electric eld, and the energy carriers obtain in the acceleration is small compared to the thermal energy, the drift velocity will increase linearly with increasing electric eld strength. The drift velocity v is given by

$$v = \quad E; \tag{2.4}$$

where E the electric eld. [20]

However, at high eld strengths the linear relation doesn't apply anymore. Charge carriers undergo more collisions with lattice atoms, and the energy they

obtain in the acceleration becomes large compared to the thermal energy. The velocity increases more slowly with increasing eld strength, until it saturates and becomes independent of the applied electric eld. In the non-linear region the drift velocity follows the empirical formula

$$v = \frac{_0 E}{1 + \frac{E \; _0}{v_{sat}}}; \tag{2.5}$$

where $_0$ is the low eld mobility and v_{sat} the saturation drift velocity.[17,20]

Electrons and holes will migrate in opposite directions in the electric eld applied across the detector until they are collected at the electrodes. The time it takes to collect the charges depends on the distance carriers have to travel before reaching the electrodes, and on the carrier mobilities.[14,17,18] The movement of charges induces a current at the electrodes.[21,22] Both drift and di usion contribute to the current generation, and the current lasts until all charge carriers are collected. Electrons and holes have di erent mobility, so the carrier types will have slightly di erent collection times.[14] An expression for the generated current can be derived by imagining two charges Q and $+Q$ that move apart a distance x in an electric eld E applied between two parallel plates. The potential between the plates separated by distance l is

$$V = El: \tag{2.6}$$

The work required to move the charges a distance x in the electric eld is

$$W = QxE = Qx\frac{V}{l}: \tag{2.7}$$

Work is also related to the current I running in the external circuit by

$$W = VIt; \tag{2.8}$$

where t is the time during which charges are collected. Solving I and inserting Equation 2.7 gives an expression for the current generated by the traversing radiation.[14]

$$I = \frac{W}{Vt} = \frac{Qx\frac{V}{l}}{Vt} = Q\frac{x}{lt} \tag{2.9}$$

Expressing this with the drift velocity v gives

$$I = Q\frac{v}{l} = q_{gen} l \frac{v}{l}: \tag{2.10}$$

In the final step the generated charge Q has been expressed with the number of electron-hole pairs created per unit length q_{gen} ($Q = q_{gen} l$).[15,17] Alternatively, the equation can be derived using Green's theorem and Gauss' law, as has been done in reference [21]. The number of generated charges is proportional to the deposited energy, hence measurement of the generated current can be used to determine the particle energy when it stops within the detector. Accurate and reliable determination of the deposited energy requires full collection of both electrons and holes.[14 16]

But not all charges reach the electrodes. Some carriers might be trapped for a certain time period within the crystal, or recombine with charges of opposite sign. Recombination removes charges from the signal lowering the measured energy deposition of each event. The time it takes on average until charge carriers recombine and disappear is called charge carrier lifetime. If trapped charges are accumulated in the detector bulk the device can suffer from polarization. Accumulation of charges in the interface between the detector bulk and metal contacts can also lead to polarization.[2,13,16,19,23] Polarization leads to reduced resistance and finally detector breakdown. Also, the electric field is no longer homogeneous because the accumulated charges create their own electric field in a direction opposite to the applied electric field. Accumulation of charges causes first a gradual decrease and then an abrupt drop in signal amplitude, charge collection efficiency, count rate and charge carrier velocity during detector operation. Polarization can be removed or reduced by switching the polarity of the bias voltage, switching the bias off and on again, by warming the crystal, or by irradiation with light of suitable wavelength. However, studies on irradiated samples have shown that these methods are not enough in samples irradiated with high fluxes. These samples require other methods, such as filling of traps (priming) and reprocessing, to fully counteract effects of polarization.[2,15,20,23] Traps can be filled by low flux irradiation. Traps are filled with electrons produced by the radiation and passivated. The device can remain passivated for months if kept in dark and the traps are deep within the band gap. Exposure to light will release the trapped charges and depassivate the detector.[5]

2.3 Radiation damage

Semiconductor crystals always contain defects and impurities originating from the detector manufacturing and crystal growth. These defects are discussed in Chapter 4. In addition, there might be defects caused by radiation damage. Radiation detectors will suffer from radiation damage after some time, especially in high

radiation environments. Proper operation of semiconductor detectors is based on nearly perfect crystal structures with no defects. Radiation damage changes the crystal structure of semiconductors by formation of defects, which can lead to changes in the electrical properties of the material.[13] The e ects of impurities and defects in the crystal structure are discussed in more detail in Section 4.1. Generally, radiation damage has a negative e ect on semiconductor properties and leads to degraded detector performance and shortened lifetime.[16] In low radiation environments these e ects are usually small, but in high radiation conditions the changes can be signi cant. One way to increase radiation tolerance is to reduce the detector thickness. This shortens the charge collection distance and the distance the radiation interacts with the material. However, since the amount of charge generated by radiation is proportional to the detector thickness, reducing the device thickness will also a ect its sensitivity.[1]

Interactions of ionizing radiation with the detector material can lead to both reversible and irreversible changes in the crystal structure. Energy transfer through ionization and formation of electron-hole pairs used in the detection is a reversible change, while non-ionizing energy transfer leads to irreversible changes.[15] These irreversible changes are commonly displacements of atoms from their lattice sites, which are called a Frenkel defects and lead to interstitial lattice atoms and neutral vacancies. Lattice atoms are displaced when the radiation scatters from the atom and gives it enough energy to break free from its bond. The defects produces additional energy levels that are generally deep within the band gap. These defects act as trapping and generation-recombination centers and a ect charge carrier lifetimes and collection of both charge carrier types. The charge collection e ciency can be reduced even further by radiation damage in the interface between the detector bulk and the metal contacts.[1,2,12,15,24]

In semiconductor detectors radiation damage leads to increased leakage current.[24,25] The additional energy levels in the band gap reduce the energy charge carriers need to move between the valence and conduction band. This shortens the charge carrier generation lifetime and increases the charge ow between the bands. Defects that act as traps capture charges and reduce the charge collection e ciency.[12,25] This leads to shortening of carrier recombination lifetime and signal reduction.[25] Because of the increased leakage current and reduced charge collection e ciency, detectors su ering from radiation damage will have worse energy resolution than non-damaged radiation detectors.

Radiation damage can also be observed as a change in e ective doping density.

Point defects produced by the radiation can form defect complexes with either positive or negative charge. These complexes are called e ective donors and acceptors. Point defects can also remove original donors by binding them in defect complexes. Examples of this type of complexes are vacancy-boron and vacancy-phosphorous complexes in silicon. In worst cases, after long term radiation exposure, the change in e ective doping density can in N-type semiconductor detectors leads to type inversion, which means that the N-type semiconductor becomes P-type. P-type detectors don't undergo type inversion and instead become increasingly P-type after long term radiation exposure[26].

3. Diamond radiation detectors

Diamond has unique properties, e.g. breakdown voltage, wide band gap, high charge carrier mobility and radiation hardness, that make diamond attractive for many applications in both science and technology. The high quality of single crystal diamond produced with chemical vapour deposition techniques leads to additional advantages for radiation detection applications, e.g. reduced polarization e ects and smaller need for detector priming (i.e. lling of traps by e.g. irradiation, see Sections 2.2 and 4.1). The many unique properties of diamond make it seem like an ideal material. However, the use of diamond in some applications is limited by the wide band gap, and the small signal resulting from the larger energy required to form one electron hole pair.[5,15,17,27] But the main disadvantage of especially single crystal diamond is its high price.[4] Table 3.1 lists some properties of diamond and silicon that are important for detector applications.

Many of the unique properties of diamond are a result of the crystal structure and the way atoms are bound to each other. Diamond consists of sp^3-hybridized carbon atoms and each carbon atom is covalently bound to four other carbon atoms in a tetrahedral geometry.[13,14,28] Because carbon atoms are small they can come close to each other before experiencing repulsive forces from each other. This results in relatively short atomic bonds and tight packing of atoms, giving diamond its high density and low compressibility.[13 15,29] The strength of the bond between the atoms makes the lattice rigid and strong.[14,28] Combined with the high density, the rigidity and strength of the crystal make diamond stable, hard and wear resistant.[11,14,30] The stability allows operation of diamond detectors even in high temperatures under high magnetic elds and voltages.[27] The strength of the atomic bonds makes dislocation of the carbon atoms hard, which is why diamond is hard to scratch, and it usually won't break due to dislocation creep or crack propagation.[14,30] In dislocation creep a part of the crystal moves relative to the rest of the crystal. The movement occurs point by point along a plane.[31,32] Crack propagation is the growth of cracks due to external loading. There are three growth modes; opening, sliding and tearing. In opening mode the crack surfaces are moved apart from each other. In sliding the crack surfaces move parallel to the

Property	Diamond	Silicon
Atomic number	6	14
Density [g=cm^3]	3.5	2.33
Band gap [eV]	5.47	1.12
Resistivity [cm]	10^{13} 10^{16}	$2.3\ 10^3$
Intrinsic carrier density [cm ^{3}]	< 10^3	$1.5\ 10^{10}$
Breakdown eld [V=cm]	10^7	$3\ 10^5$
Electron mobility [cm^2=(Vs)]	1800 2200	1500
Hole mobility [cm^2=(Vs)]	1200 1600	500
Saturation velocity [cm=s]	$2.20\ 10^7$	$1.00\ 10^7$
Dielectric constant	5.7	11.9
Electron-hole pair creation energy [eV]	13	3.6
Displacement energy [eV=atom]	43	13 20
Thermal conductivity [W=(cmK)]	20 24	1.5

Table 3.1: Properties of diamond and silicon.[12,14,16 18,25,27,30]

crack direction, while in tear mode the surfaces move perpendicular to the crack direction.[32]

The structure of the crystal gives diamond a large band gap of 5.47 eV. The size of the band gap makes diamond an insulator, but because diamond has many similarities with conventional semiconductor materials it is often categorized as a semiconductor.[12,14,15,17,23] Electrical properties of semiconductors are mainly determined by the band gap.[14] Important properties resulting from the large band gap are the low intrinsic carrier density and the low leakage current. The large band gap combined with the bond strength makes thermal excitation of charge carriers to the conduction band unlikely. Because leakage current is proportional to the intrinsic carrier density, diamond detectors have smaller leakage current than corresponding detectors made of other semiconductor materials. At room temperature leakage current of natural diamond is usually less than 10^{12} A for voltages up to several hundred volts.[11,12,15,17,23] This leads to low power consumption and hence low energy dissipation[4,17], and low noise even at room temperature.[1,18,23] Diamond is suited for detector applications at high temperatures and its use at temperatures of 400 600°C has been reported.[33] The band gap energy corresponds to a wavelength of 225nm, which is within the deep ultraviolet region. This makes diamond optically transparent for radiation ranging from the deeper half of deep ultraviolet region to far infrared and even radio frequencies. Because diamond is transparent to a wide range of wavelengths detectors often don't need windows to select a speci c radiation type, or screening or packing to stop surrounding light. Solar-blind detectors for measurement of ultraviolet light take advantage of the improved discrimination between ultraviolet

light above the band gap energy and visible light.[4,15,16,18,28,29] A disadvantage followed by the large band gap is that the energy required to produce one electron-hole pair is quite large compared to other semiconductor materials. Because the energy required to form one electron-hole pair is larger, the number of charge carriers, and hence also the signal, is smaller in diamond than in many other semiconductor materials. The signal is further reduced by charge trapping.[5,17,18,34]

Diamond has high charge carrier mobilities and saturation drift velocities.[17,23] The saturation drift velocity is about $2:2 \quad 10^7$ cm=s, which is a factor of 2 higher than in silicon.[12,15,23,28] The mobilities can be very di erent depending on the crystal quality and diamond type, but typical values are $1800 \quad 2200$ cm^2=(Vs) for electrons and $1200 \quad 1600$ cm^2=(Vs) for holes.[14,18] High mobilities and drift velocities lead to fast charge collection and short response times. Also, because electrons and holes have similar mobility they are collected at almost the same time.[11,14,15,23,34] These lead to less signal pileup and summation of events.[18] In many semiconductor materials, e.g. silicon, breakdown happens before the saturation drift velocity is reached. But with diamond the saturation drift velocity can be reached. This is due to the high breakdown electric eld, which can be up to 10^7 V/cm , more than one order of magnitude higher than in silicon. The high breakdown eld also allows operation of diamond detectors over a fairly wide voltage range.[12,25,28] The fast signals and high breakdown electric eld make it possible to design systems for high speed and count rate measurements.[17,18] Diamond also has a smaller dielectric constant compared to many other semiconductor materials. The detector capacitance is determined by the dielectric constant and the device geometry. The capacitance in turn a ects the noise level of the readout. Thanks to the smaller dielectric constant and lower capacitance, diamond detectors have less noise than silicon detectors of corresponding geometry.[5,15,23,25,34] The product of the input resistance of the circuit and the combined capacitance of the detector and the measurement circuit determines the time constant of the output signal. A small time constant produces fast signals, which is important in high event rates and when timing information is important. Low capacitance is therefore an important factor in timing applications.[4,11]

Diamond detectors can be used to detect any radiation with energy higher than the band gap energy, but the sensitivity of the detector strongly depends on the measured radiation type and energy.[1,18] The small atomic number of carbon reduces multiple scattering, which is preferred in tracking where particles should travel in near straight line for accurate position determination, but it also

makes measurement of highly penetrating radiation, such as high energy gamma radiation, difficult. The small atomic size makes the interaction cross section for highly penetrating radiation small, which reduces the detection efficiency. The sensitivity is reduced further by the high energy required to form one electron-hole pair. Thanks to the tight diamond lattice there are many atoms to interact with, but the higher density is not able to fully compensate for the smaller cross section and large energy required to form one electron-hole pair. Therefore diamond detectors are not that well suited for measurements of very penetrating radiation.[13,18,34]

Diamond has high thermal conductivity.[5,14,17,28,30] This property allows operation of diamond detectors in environments where the active cooling of the detector is not practically achievable or impossible.[5,15,17] Diamond has an unique combination of high thermal conductivity and low electrical conductivity, which is a rare combination in nature. This combination is explained by the heat transport mechanism.[13,14] In many semiconductor materials heat is mainly transported by electrons, hence high thermal conductivity comes with high electrical conductivity. However, in diamond the heat is mainly transported by lattice vibrations because there are very few free charge carriers that can transport heat due to the large band gap.[14,15,28,30] But because heat is mainly transported by phonons, thermal conductivity of diamond is more sensitive to crystal defects and crystal quality. Defects lead to increased phonon scattering and reduced thermal conductivity.[30] High thermal conduction is important in cooling applications. Electronics often require transportation of heat away from a small region it is produced at. The fast heat transportation makes diamond well suited for electronics cooling, especially in particle colliders due to its radiation hardness. In addition, diamond itself will not produce much heat due to the its high resistivity.[14]

Thanks to the strength of the atomic bonds and rigidity of the lattice, diamond is more resistant to radiation damage than many other semiconductor materials.[11,12,14,23,35] Radiation damage leads to atom dislocations and other crystal defects, which requires relatively high energy in diamond.[23] The energy required to permanently displace an atom from the lattice is around 43 eV in diamond and 13 – 20 eV in silicon.[17,28] Thanks to the relatively high binding energy of carbon atoms in the diamond lattice, the number of atom dislocations in diamond is smaller than in other detector materials exposed to the same amount of irradiation.[12,15] Radiation damage won't affect the leakage current of diamond as much as in e.g. silicon, due to the large band gap and naturally low leakage current of diamond, but formed traps affect carrier drift and signal size.[24] The radiation hardness makes it possible

to operate diamond detectors in high radiation environments[13,25], which is why they are well suited for tracking in high energy physics.[11]

Another field for which diamond is an attractive detector material is medicine. The atomic number of diamond ($Z = 6$) is similar to the effective atomic number of human soft tissue ($Z \approx 7.5$).[11,14,18] This makes diamond tissue equivalent, which simplifies dose calculations since the dose to tissue can be obtained directly.[18,36] Diamond and human tissue also have similar response to photon radiation.[29] Because diamond is chemically inert and non-toxic, devices made of diamond won't react with the body or have harmful effects in the patient.[14,36] The better resistance to radiation damage means that the detectors can be used for a longer period of time before they need to be replaced.[11] Other appreciated properties are the small size, good energy resolution and efficiency.[36]

3.1 Classification of diamond

There are different types and quality of natural diamond, which is why a classification system has been developed. The classification system is shown in Figure 3.1. It is good to know about this classification system since many earlier applications used natural diamond and older literature often refer to natural diamond.[14] Even though the classification system was developed for natural diamond, the system can also be applied to synthetic diamond. However, this simple classification system can not distinguish between different synthetic diamond types with tailored properties manufactured today.[28,37] The classification is based on the impurities present in diamond. Due to variations in both impurity types and and concentrations, different diamond types have different properties. For example electrical conductivity of type IIb diamond is 13 times larger than type I diamond.[14] Impurities and their effects on properties of diamond and other semiconductor materials are discussed in more detail in Chapter 4.

Nitrogen is the most common impurity in natural diamond and the concentration of nitrogen is the base of the classification system. Depending on the presence of nitrogen, diamond can be divided into type I and type II diamond. These two main types are further divided into subtypes according to the arrangement of the nitrogen impurities and the presence of boron, which is another common impurity in diamond. Natural diamond can also contain other impurity atoms, such as iron or nickel, but these are not included in the classification system.[37]

Diamond that contains nitrogen impurities is categorized as type I. The nitrogen

Figure 3.1: The classi cation system of natural diamond.

concentration is larger than 5 ppm, typically 100 3000 ppm. If the nitrogen is present as aggregates the diamond is type Ia, and if the nitrogen occurs as isolated atoms the diamond is type Ib. Type Ia is the most common diamond type in nature. Over 98% of natural diamond is type Ia. Type Ia can be further divided into type IaA and type IaB.[28,37] In type A the aggregates are pairs of nitrogen atoms, while in type B the aggregates consist of four nitrogen atoms symmetrically organized around a vacancy. There are also other nitrogen aggregates, such as nitrogen-vacancy pairs, nitrogen-vacancy-nitrogen aggregates, and charged aggregates, but these are not included in the classi cation system. Figure 3.2 shows some examples of nitrogen aggregates present in diamond. Type I diamond is transparent to UV-light below about 300 nm, but due to the nitrogen impurities it strongly absorbs IR-light in some regions.[37]

Type II diamond does not contain nitrogen. In practice the diamond may not be completely free of nitrogen, the concentration is just so low that it can't be observed in IR absorption spectroscopy, typically less than 5 ppm. Type II diamond is rare in nature. Type II is subdivided into type IIa and type IIb based on the presence of boron. Type IIa is free of nitrogen and boron impurities. Synthetic diamonds produced by chemical vapour deposition are usually type IIa diamonds. In type IIb there are boron impurities but no nitrogen impurities. The increased electrical conductivity of type IIb diamond is due to the boron impurities. P-type diamond doped with boron falls within this category.[28,37]

Figure 3.2: Examples of nitrogen aggregates present in diamond.

3.2 CVD diamond

The use of diamond in radiation detection applications was previously small due to the limitations of natural diamond. Natural diamond is expensive and and single crystal diamond is rarely found as large crystals. It often contains high concentrations of impurities and crystal defects that limit carrier lifetimes and charge collection. One disadvantage with natural diamond is the lack of control of material properties.[12,16,18,28,29] The wider use of diamond was made possible by development of production methods of arti cial diamond. Synthesis of diamond has reduced the price of diamond and it allows better control of material properties. Arti cial diamond can be produced in larger sizes with reproducible properties and lower concentration of impurities and crystal defects.[1,12,14,15,30,38]

Today arti cial diamond is mainly produced by chemical vapour deposition (CVD) techniques. [28 30] CVD is a technique in which the crystal is slowly grown layer by layer as a result of chemical reactions happening in the gas phase above a solid surface under controlled conditions.[14 16,39] The method requires activation of the gas phase with combustion ame (e.g. oxygen acetylene torch), thermal methods (e.g. hot lament) or electric discharge (e.g. microwaves).[15,17] There are di erent CVD techniques with di erent parameter values and details, but they all have some similarities e.g. the substrate is heated to temperatures above 700°C to guarantee formation of diamond instead of amorphous carbon, and most use a methane-hydrogen gas mixture.[15,29,39] The used gas mixture, temperature and pressure determine the number of defects, and therefore the properties of the CVD diamond.[13] Special care must be taken during the growth to not include nitrogen impurities, since they have been proven to have a negative e ect on detector properties.[35]

In the synthesis process the substrate and the gases are placed inside a chamber,

Figure 3.3: The chemical and physical processes in production of CVD diamond.

where the gas is mixed, see Figure 3.3. The gas di uses towards the substrate surface. As the gas di uses downwards, it passes the activation region where the gas is heated up to a few thousand kelvin, and the molecules are provided with additional energy by e.g. a hot lament, laser, direct current or microwaves.[14 16,29] The additional energy excites the molecules and breaks them into ions and electrons, leading to formation of reactive radicals and atoms that continue to di use towards the substrate. The species mix and undergo chemical reactions until they reach the substrate surface, where several processes can happen. The species can be absorbed and react with the surface, they can be desorbed back to the gas phase, or they can di use on the surface until they hit a suitable reaction site.[29] If the processing conditions are right, the reactions lead to formation of diamond.[14,15,29]

The gas is a mixture of carbon compounds hydrogen and oxygen. Commonly the gas mixture consists of methane and hydrogen, in which the methane fraction is typically 1 15%. The carbon compounds supply the process with carbon atoms in form of radicals that nucleate when they come in contact with the substrate.[15,16,29] Hydrogen has several important roles in the gas phase. Hydrogen undergoes thermal dissociation and forms reactive radicals when it reacts with neutral species in the gas mixture. It terminates dangling bonds of carbon atoms close to the surface, and it breaks long hydrocarbon chains preventing formation of large rings and polymers in the gas phase. Hydrogen also reduces the formation of graphite, since it is more e ective at etching graphite than diamond.[15,16,29,39] Dopants are usually added

in the gas phase if they are needed.[16]

Diamond can be grown on di erent substrate materials, e.g. silicon, molybdenum or diamond, but the material has be able to withstand the processing conditions. The melting point at the processing pressure should be higher than the temperature the diamond is grown at. The substrate temperature depends on the technique, but it is between 770K and 1470K.[29,39] The substrate material and diamond should have similar thermal expansion coe cients. The substrate expands with rising temperature onto which the diamond is then grown. When the temperature is decreased both the substrate and diamond contract. If the expansion coe cients are di erent and the substrate contracts more, the diamond will experience signi cant compressive stress. This causes bowing and can result in cracking, aking and in worst cases delamination of the lm from the surface. If the goal is to produce an adherent lm, i.e. a lm that is attached to the surface, the substrate should be a material that can form a carbide layer. The interstitial carbide layer works like glue and binds the diamond to the substrate. In case one wants to form a free-standing diamond lm one should chose a substrate material that does not form a carbide layer.[29]

3.3 Polycrystalline and single crystal diamond

CVD techniques can be used to grow both polycrystalline and single crystal diamond. Single crystal diamond consists of only one crystal. It is formed when the diamond is grown on a single crystal diamond substrate. Polycrystalline diamond on the other hand consists of many single crystals bound together by a disoriented interface and it is typically formed when the substrate is non-diamond.[24,28,30] Because of the grain boundaries polycrystalline diamond has some disadvantages compared to single crystal diamond. The boundaries are also the reason why the use of polycrystalline diamond is limited in some applications.[20] Because of its better crystal quality, detector applications usually use single crystal diamond.[27]

The growth of polycrystalline diamond starts from many randomly positioned and oriented crystal seeds. The crystal grains grow in all directions until they meet another crystal. When the grains don't have room to grow to the sides they only grow upward from the surface. Larger crystal grains grow faster and tend to outgrow small crystals.[24,28,29] This leads to a columnar structure with grain sizes that increase with distance from the substrate. The larger grain size comes with reduced number of defects and grain boundaries, which results in improved crystal quality.[28,29,38]

Because of the change in crystal quality, charge collection distance and electrical properties of polycrystalline diamond vary with the distance from the substrate. The crystal quality is improved by growing thicker polycrystalline diamond that is thinned from the bottom by lapping to remove layers with poor crystal quality.[13,34]

Grain boundaries are the main source of leakage current in polycrystalline diamond. In single crystal diamond the leakage current is mainly due to point and line defects. For single crystal diamond the leakage current increases linearly with applied voltage, but for polycrystalline diamond the change is non-linear due to additional energy levels produced by grain boundaries.[27] Grain boundaries challenge uniform and smooth charge collection by acting as trapping and recombination centers.[13,25] Because of trapping and recombination charge collection e ciency of polycrystalline diamond is only around 50%. Single crystal diamond that has less defects and trapping centers typically has charge collection e ciency over 95% and charge collection distance close to the detector thickness.[24,30] Boundaries can also accumulate charges, which leads to formation of polarization elds that are superimposed on the applied drift eld.[25,27] All these processes remove charges from the signals and change the energy deposition of each event, which leads to lower pulse heights, or even disappearance of some characteristic peaks from the spectra.[27]

3.4 Structure of diamond detectors

Thanks to its high resistivity diamond doesn't need doping or reversed biased pn-junctions to reduce leakage current.[13,15,16,18] This makes fabrication of diamond detectors easier than fabrication of silicon detectors.[15] But processing is not trivial due to the hardness of diamond.[28] The processing starts with lapping and cutting of the diamond to size and thickness suitable for the application.[38] Next the surface is polished in order to create a smooth surface for the metallization. The polishing technique should be selected correctly, since some techniques can lead to surface damage that a ect the detector operation down to depths of a few μm.[7,17,18] Processing after the growth produces surface contamination, such as graphite phases, and smoothing of the surface leads to hydrogen termination of the diamond surface. These both lead to increased surface leakage current. Radiation detectors need an insulating surface, which can be achieved by oxygen termination of the surface.[15] Therefore removal of the contaminants and oxidization of the surface are important parts of the processing. These are achieved by wet chemical cleaning protocol

that involves e.g. cleaning with di erent acids and organic solvents.[14,15] Diamond detectors typically have metal-semiconductor-metal structure, in which the diamond, usually intrinsic CVD diamond, is sandwiched between two metal electrodes, see Figure 3.4. The metallic contacts are added to allow collection of charges from the surface with the help of an electric eld, and to avoid accumulation of charges on the surface. Similar structures made of other semiconductor materials, such as silicon, require doping in order to reduce leakage current, which is not needed with diamond thanks to its high resistivity and naturally low leakage current.[11,14,18,34,35]

Figure 3.4: Structure of diamond radiation detectors (not to scale).

The metallic contacts can be either ohmic or Schottky (rectifying) contacts. In an ohmic contact, the contact resistance is small compared to the semiconductor bulk resistance. In a Schottky contact, the di erence in the Fermi levels of the metal and the semiconductor forms a potential barrier that restricts the ow of charges. Schottky contacts conduct well with one polarity and poorly with the other. Ohmic contacts on the other hand conduct the same with both voltage polarities. Due to the inertness and wide band gap, there are not many techniques and metals available that can form good ohmic contacts with diamond. The production of good ohmic contacts can be challenging. Bad contacts result often in Schottky barriers and increase polarization e ects.[14,15] Most materials form Schottky contacts on clean diamond surfaces.[40] The size of the Shottky barrier depends on the termination of the diamond surface. Studies have shown that the barrier is the smallest for clean diamond surfaces and the largest for oxygen terminated surfaces. Hydrogen termination of the surface will lead to a barrier between these two. From this one can conclude that cleaning and termination of the surface has a signi cant e ect on the Schottky barrier height.[41]

Ohmic contacts are usually obtained by modifying the diamond surface in some way. The surface can be modi ed by e.g. sputtering with argon, or formation of a carbide layer between the diamond and the metal. Argon sputtering damages the surface and leads to formation of amorphous carbon and graphite. Deposition of e.g. gold on the damaged surface will produce an ohmic contact. However, annealing

makes these contacts rectifying. Commonly ohmic contacts are obtained by forming a carbide layer between the metal and the diamond. As previously mentioned most materials form rectifying contacts with diamond. However, some materials, such as titanium, chromium, molybdenum and tantalium, form carbides upon annealing.[40] Carbide forming metals are the best way to produce ohmic contacts on diamond.[41] The carbide layer reduces the contact resistivity and allows the formation of an ohmic contact. To be noted is that the carbide layer is not necessarily complete, but instead in patches.[33,41] It is believed that the carbide layer prevents the contact from becoming rectifying again.[40]

Previously, when the techniques were less developed, metallization was challenged by the hardness and chemical inertness of diamond.[16] Today, metals are added by sputtering or evaporation.[14,15,17,38] Contacts need to be designed so that charges can easily flow out from the diamond bulk, but the flow from the metal to the diamond is stopped.[15] The exact requirements for the metallic contacts depends on the application, but most application require stability at elevated temperatures and good adhesion, i.e. the metal should be well attached to the surface. Good adhesion requires a reaction between the diamond and the metal, which explains why metallization of diamond can be challenging. Good attachment is usually achieved by depositing a thin adhesion layer beneath the thicker contact metal layer.[41] The material for the adhesion layer should be a carbide forming metal, common choices are chromium and titanium. A thicker interconnect metal layer is deposited on top of the adhesion layer. The interconnect layer is made of a stable and inert metal, e.g. gold, and allows good contact with the electrodes and protects the underlying layers from oxidation.[14,14,17,28,38,41] Studies on Ti/Au contacts have shown that titanium can diffuse into the gold layer, reducing the quality of the contact. Mixing of the two layers can be stopped by depositing a thin barrier layer between the gold and the titanium. The barrier material should have slow diffusion in gold or non-reactive to oxygen, or both. A common material choice for the barrier is platinum, because it diffuses slowly in gold and does not easily form oxides.[33]

The samples in this study have contacts made of 10w% titanium and 90w% tungsten alloy. The contact on the top consists of a pad that covers most of the diamond surface, and four strips. The bottom contacts consists only of the metal pad. The diamonds are etched and polished before deposition of the alloy by sputtering. 100nm thick layers are deposited on both sides. After deposition the samples are annealed at 700°C for 4 minutes to form an ohmic contact. There are two options for the deposition of the metal, shadow masking and lithography. With shadow masking

the edges of the metallized area are not as clear as with lithography and aligning the pads can be challenging. However, using a mask makes the processing faster since 20 samples, instead of only one, can be processed at once. For the studied samples the pad is done by shadow masking and the strips by lithography. Figure 3.5 shows the processed detectors glued and wirebonded to the readout board.

Figure 3.5: Diamond detectors glued and wirebonded to the readout board. Image source [8].

4. Defects

Ideal crystals have a continuous periodic structure and contain no foreign atoms or lattice irregularities. There are no perfect crystals in nature. Natural crystals always contain impurities or lattice defects. Because atoms are relatively immobile in solids, defects are hard to remove once they have been formed. Depending on their concentration defects can have a signi cant e ect on semiconductor properties. The impurity concentration tend to determine electrical properties of semiconductors. This is why characterization of defects and knowledge of their e ects is important.[11, 19,31,32,42]

Crystal defects are classi ed according to their dimensions. Zero dimensional defects are isolated errors in the crystal that are called point defects. One dimensional defects are lines that break the crystal periodicity and are called dislocations. Two dimensional defects are surfaces and are called interfacial defects. In three dimensional defects the crystal irregularity extends over some volume. These are called volume or bulk defects.[31,32]

Point defects can be vacancies, impurities or self-interstitials, see Figure 4.1. Vacancies are empty sites in the crystal lattice that should contain atoms. These are always present in crystals.[31,32] Vacancies govern di usion of atoms in solids, since easy migration of atoms requires that atoms move to positions that are free of other atoms.[31] When the defect is an atom placed in a position that normally is free the defect is called a self-interstitial. Atoms are larger than the free space between the atoms so self-interstitials cause large distortions in the crystal. This is also why self-interstitials are not as common as vacancies. Impurities are foreign atoms that are intentionally or unintentionally added into the crystal. Impurities can substitute lattice atoms or be placed in interstitial positions.[31,32] Substitution is more likely when the impurity atom and lattice atoms have similar size. Interstitial atoms on the other hand must be small due to the limited space between lattice atoms. In order not to alter the crystal too much interstitial atoms must be smaller than the host atoms.[31,32,43] Intentional addition of impurities is called doping and it is used to modify some material property, e.g. corrosion resistance, electrical conductivity, or mechanical property.[31,32]

Figure 4.1: Point defects

Linear defects, or dislocations, are misalignments that break the periodicity of the crystal. These can be screw dislocations, edge dislocations or mixed dislocations. Edge and screw dislocations are illustrated in Figure 4.2. If a part of the crystal is shifted relative to other parts of the crystal, the defect is called a screw dislocation. Edge dislocations are defects in which a plane of atoms ends within the crystal. Mixed dislocations are a combination of screw and edge dislocations. These are the most common linear defects.[31,32] Dislocations are always present in crystals and they can be formed e.g. during crystal growth, during deformation, or due to thermal stress.[32] Dislocations are generally unwanted in semiconductor applications since they have a negative e ect on electrical properties.[31]

(a) Edge dislocation (b) Screw dislocation

Figure 4.2: Examples of linear defects in crystals.

Interfacial defects are two dimensional boundaries.[31,32] There are three types of surface defects, free surfaces, intercrystalline boundaries and internal defects. Figure 4.3 shows a free surface, a boundary and two types of internal defects. Free surfaces are external surfaces that terminate the crystal and determine the shape of the crystal. Intercrystalline boundaries interrupt the periodicity of the crystal and separate crystal grains that can also have di erent composition or crystal structure. Free surfaces and intercrystalline boundaries both contain atoms that are not bounded to the maximum number of neighbours.[31,32] The atoms with dangling bonds want to get rid of the asymmetry and are favorable locations for adsorption of foreign atoms from the surrounding.[31] Atoms at the boundaries are

(a) Free surface (b) Boundary (c) Stacking fault (d) Antiphase boundary

Figure 4.3: Examples of interfacial defects in crystals.

irregularly bonded and both bond length and angle vary.[32] Two common types of internal defects are stacking faults and antiphase boundaries. Stacking faults are errors in the stacking of close-packed planes. Antiphase boundaries are only present in ordered compounds.[31]

Volume defects are larger than the defects described so far.[32] These are three dimensional aggregates of vacancies and atoms. There are four types of volume defects. Precipitates are very small volumes, with di erent crystal structure. These are typically a fraction of one µm in size. Dispersants are second-phase particles that can have very di erent sizes, from a fraction of 1 µm to up to 100 µm. Inclusions are dirt that have entered the crystal during its growth or precipitated atoms. These come in di erent sizes, from a few µm to macroscopic size, and are quite large. Inclusions are unwanted in most applications. Voids, or pores, are formed either when vacancies accumulated at one place or by trapped gasses. Voids are also generally unwanted defects e.g. because they decrease the mechanical strength of the material.[31] Volume defects can also be cracks, other phases or other larger crystal deformations.[32] Volume and lower dimension defects reduce the mechanical strength of the material and can make device manufacturing challenging. Defects can e.g. a ect the di usion of dopants, work as impurity sinks or generation sites for linear defects. Inclusions and precipitates can also alter the electrical properties of the material.[31]

4.1 E ect on semiconductor properties

Usually, defects don't signi cantly change essential properties of materials, such as melting point and the elastic modulus. But electrical properties, such as conductivity, charge carrier mobility and charge carrier lifetime, are signi cantly a ected by variations in the crystal structure.[10,42] Whether the change in the property is

wanted or not strongly depends on the application. For example short charge carrier lifetimes are wanted in switches but not in radiation detectors. Today structural defects and impurities are intentionally added to material in order to produce materials with desired properties. For example charge carrier lifetimes can be controlled by growing structurally perfect pure crystals and intentionally introducing lifetime shortening defects. It is important to study defects and their properties in order to be able to add defects with wanted properties and remove those with undesired properties.[42]

The change in electrical properties are due to defect energy levels. In perfect crystals there are no energy levels in the band gap and charge carriers need to move directly between the valence and conduction band. Defects alter the crystal structure and lead to formation of additional energy levels within the band gap. These energy levels allow charges to move between the valence and conduction band with energies less than the band gap energy, see Figure 2.12.[9,42] This impacts carrier densities and mobility, as well as carrier lifetimes and trapping probability.[10] How defects a ect the electrical properties depends on the location of the energy levels within the band gap.[42]

Defects are divided into shallow and deep defects. Shallow defects are divided into acceptors and donors. The simplest de nition is that shallow defects have energy levels close to the band gap edges, see Figure 4.4. The states are usually within a few tens of meV from the band edge. Deep defects mostly have energy levels deep inside the band gap, usually within the middle third.[11,42] But deep defects are also found that have energy levels close, or even inside, the conduction or valence band. A generally applicable de nition is that deep defects have highly localized wave functions, while shallow defects have extended wave functions.[42] Wave functions of highly localized states overlap very little with the wave functions of the neighbouring states. The wave functions of extended states on the other hand overlap signi cantly with the neighbouring wave functions. Impurity atoms that t well in the lattice have large overlapping of orbitals, and produce shallow energy levels. Badly tting impurity atoms form deep levels because they cause large distortions in the lattice and have orbitals that overlap much less with the neighbouring orbitals. Conductivity requires signi cant overlapping of neighbouring orbitals. Therefore the concept of localized states explains why highly disordered crystals don't show conductivity.[42,44]

Deep defects have some properties that make them generally unwanted.[23] However, in some applications they are intentionally added to improve some property,

Figure 4.4: Simple de nition of deep and shallow defects.

e.g. to shorten carrier lifetimes in switches.[19] Deep defects can act as traps or generation-recombination centers.[11,15,19] Whether a deep defect acts as a trap or generation-recombination center depends on many factors, e.g. temperature and capture cross sections, but a general rule is that defects in the middle of the band gap act as recombination-generation centers and those closer to the edges work as traps. Generation-recombination centers generate charges when the charge carrier density is less than the equilibrium value, and recombine charges when the carrier concentration exceeds the equilibrium density. [19]

Recombination centers rst capture a charge from either the conduction or valence band, e.g. an electron from the conduction band. Next the center captures a charge carrier with opposite sign from the other band, e.g. an hole from the valence band, which leads to annihilation of the two charge carriers. Generation centers rst emit an electron to the conduction band and then an hole to the valence band. The hole emission is followed by capture of an electron from the valence band. Traps capture charges from the energy bands and emit them after some time.[11,19] The longer distance the charges have to travel through the detector, the higher the probability that they are trapped before they are collected.[23] Both traps and recombination centers remove charges and contribute to signal reduction. Deep defects reduce the distance charge carriers travel before they are trapped and are the most e ective reducers of carrier lifetimes.[10,11,42] In detector applications deep defects are highly unwanted since they lower detector performance by shortening carrier lifetimes and drift distances, and by removing charges before they are collected.[11]

Shallow defects are often used to control the type and charge of charge carriers in semiconductors.[11] This changes the electrical properties of the material and is achieved by intentional addition of impurities into the crystal in a process called doping. Doping can change semiconductor properties by several orders of

magnitude.[10,31,42] Impurities can be added into the crystal during crystal growth or later during processing. Ideally dopants are substituted into the crystal without changing the chemical bonds nor distorting the lattice.[10] This is easier to achieve with impurities that have similar size as the host atoms.[43] Addition of atoms with fewer valence atoms than the host atom leads to incomplete bonding and holes. By exchanging with holes electrons can move from bond to bond across the lattice. This process is called conduction by holes. Dopants that accept electrons from the valence band and increase conduction by holes are called acceptors. Semiconductors with excess holes are P-type semiconductors. Addition of atoms with more valence electrons than the host atom leads to saturated bonding and forces electrons into excited states. The excited electrons are free to move in lattice. Dopants that donate electrons to the conduction band and increase conduction by electrons are called donors. Semiconductors with excess electrons are N-type semiconductors.[10,31,42]

Deep defects can to some degree compensate e ects of shallow defects if they act as trapping centers. Shallow defects increase movement of charges between the energy bands, while deep trapping centers reduce the charge ow. Therefore formation deep defects e.g. by radiation damage, can be observed as decreased leakage current. But if the deep defect act as a recombination-generation center, it will increase the charge ow between the bands and have the same e ect as the shallow defect.[15]

Impurities and irregularities in the crystal structure lead to reduced and unstable detector response. There are several reasons for this change. As mentioned in Section 2.2, charges can be trapped within the detector by defects. If charge carriers are captured by traps the detector response will slowly decrease during operation as the number of lled traps increases. In case the traps are deep inside the band gap, charges will accumulate within the detector and form an additional electric eld that a ects the charge carrier drift. In su ciently high temperatures, the thermal energy can excite the charge carriers to the conduction band and release them from the traps. This leads to an increase in the signal amplitudes.[35] The signal instability caused by charge trapping can be countered by lling traps before the measurement e.g. by irradiation. When the measurement is started the traps are already lled and will not capture charges forming the signal, which will lead to better charge collection e ciency, higher signals and increased detector stability.[13,15,35] Studies on CVD diamond have shown that lling of traps before the measurement can increase the signal by 30 100%.[34]

4.2 Defects in diamond

Even synthetic diamond grown in very restricted environments contains defects. Just like defects in other semiconductor materials, these defects can have a signi cant e ect on electrical properties of the diamond.[39] These can be e.g. crystal boundaries, vacancy clusters or dislocations, self-interstitials. Some polishing techniques can also lead to lifetime reducing surface defects. Due to the atomic density and rigidity of the lattice, there is very little room for foreign atoms in the diamond crystal. Still it is possible for impurities to substitute carbon atoms, or to take interstitial positions in the lattice.[15,30] Two common impurities are nitrogen and boron, but diamond can also contain e.g. silicon, phosphorus, nickel, iron or sulfur.[30,36,37] Boron and nitrogen both have size close to the size of carbon atoms, which is why they are easily incorporated into the diamond crystal. Nitrogen is a major impurity in diamond. Usually nitrogen substitutes carbon atoms and can be present either as individual atoms or as aggregates. Nitrogen acts as a trapping center, a ecting e.g. charge carrier lifetimes and detector sensitivity, which is why the concentration of nitrogen should be kept as low as possible. However nitrogen is very di cult to remove from crystal growth and processing.[15,18,30,36] Sometimes small amounts of boron are added into the crystal to compensate some of the negative e ects of nitrogen and to produce P-type diamond. Boron can also enter the crystal due to contamination during the processing. However, boron impurities are shallow defects and can have a negative e ect on detector performance.[15,36]

Modi cation of diamond properties by doping isn't as exible as for silicon. Doping of diamond is challenging mainly due to the low mobility of dopants. This hinders the use of di usion doping techniques commonly used with silicon.[14] P-type diamond has been successfully obtained with boron doping by incorporating boron compounds in the gas phase during crystal growth. Doping with boron produces energy levels 0.37 eV above the valence band. N-type diamond, however, is a challenge.[14,28,39,43] Nitrogen is a N-type dopant, but it forms quite deep energy levels when it bonds with four carbon atoms. An option is to use phosphorus which doesn't form as deep energy levels as nitrogen. The energy levels of phosphorus and nitrogen dopants are 0.6 eV and 1.7 eV below the conduction band.[28,39,43] But incorporation of phosphorus is more di cult because it has a larger covalent radius than carbon. Since N-type doping hasn't been successful, diamond can not be used to build bipolar structures such as PN-junctions.[43] However, due to its naturally high resistivity, diamond doesn't need doping or PN-junctions in radiation detector applications.[14]

5. Characterization

For optimal operation of a semiconductor detector one should have knowledge of the generation of leakage current and the charge carrier transport mechanism in the detector material. Properties such as charge carrier velocities and lifetimes, e ective space charge concentration (i.e. the concentration of excess charges accumulated in a speci c region, e.g. concentration of ionized dopants in a PN-junction) and dielectric strength determine the safe operational region of the device, and how much of the charges generated by the traversing radiation is collected. Many of the important electrical properties depend on the defect concentration, therefore the measurements give an idea of the crystal quality of the sample. Characterization of electrical properties allows selection of operational conditions and a device geometry such that the charge carrier drift time is shorter than their lifetime.[15,45]

The characterization should be done at di erent stages of the detector fabrication, in order to detect problems at an early stage and to get an idea of what could have caused it. This work describes the characterization and quality assurance process of CVD diamond detectors. The process starts with visual inspection of the samples by optical and cross-polarized light microscopy, after which the samples are sent for pre-metallization. The next step is to check the quality of the coating by optical microscopy and to perform a leakage current and charge collection e ciency measurement. The same measurements are repeated in the nal step, after the metallization of strips. The main focus of this thesis is on the charge collection distance measurement. The other measurements are described for completeness.

5.1 Visual inspection

The purpose of visual inspections is to check whether the crystal is good enough to proceed in the processing. In the rst step an optical microscope is used to make sure that there are no large deformations on the sample surface or pieces missing in the corners. The microscope was also used to check that the sample dimensions are correct. The samples have a truncated pyramid shape, i.e. a shape where one