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NEW GENERATION OF GRAPHENE BOLOMETERS

NOVÁ GENERACE GRAFENOVÝCH BOLOMETRŮ

DIZERTAČNÍ PRÁCE

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Abstract

Bolometer detectors are essential for sensing minute energy changes in radiation and are widely used in fields such as astronomy, materials science, and environmental monitoring. Their exceptional sensitivity at cryogenic temperatures enables the detection of extremely small thermal signals, advancing both scientific research and technology. This thesis presents the fabrication and characterization of advanced bolometer architectures based on chemical vapor deposition (CVD) graphene, exploiting its outstanding electrical conductivity, thermal properties, and mechanical strength.

Three major results are demonstrated. First, we report the successful fabrication of quantum dot bolometers using CVD-grown graphene, where the quantum confinement enhances temperature-dependent electrical resistance—an essential parameter for sensitive bolometric detection. Second, a novel design of multi-parallel quantum dot devices based on CVD graphene is fabricated, showing improved scalability and robustness. Third, we reveal that the back-gate voltage plays a critical role in tuning the temperature dependence of the graphene quantum dot resistance, thereby offering a tunable mechanism to optimize bolometer performance.

Importantly, the multi-parallel architecture enables optimization of the total impedance of the bolometer, facilitating its future integration with antennas for high-frequency applications. This design also allows for a significant increase in the total active graphene area while preserving the same level of responsivity, overcoming a common trade-off in miniaturized detectors.

Despite fabrication challenges such as maintaining uniform material properties and achieving high-resolution lithography at the nanoscale, the demonstrated devices pave the way for high-performance, scalable graphene-based bolometers. These advances show promising potential for applications ranging from sensitive detection of molecular magnets to high-resolution DNA sequencing and beyond.

Keywords

Graphene bolometer, quantum dot, CVD graphene, back-gate tuning, multi-parallel architecture, impedance matching, cryogenic sensors, nanofabrication, thermal sensitivity, high-responsivity detectors.

Abstrakt

Bolometrické detektory jsou klíčové pro detekci nepatrných změn energie záření a nacházejí široké uplatnění v astronomii, materiálových vědách a environmentálním monitoringu. Jejich výjimečná citlivost při kryogenních teplotách umožňuje detekci extrémně slabých tepelných signálů, což posouvá vpřed vědecký výzkum a technologii. Tato práce se zabývá výrobou a charakterizací pokročilých architektur bolometrů založených na grafenu připraveném metodou chemické depozice z plynné fáze (CVD), využívajících jeho vynikající elektrické vodivosti, tepelných vlastností a mechanické pevnosti.

Jsou demonstrovány tři hlavní výsledky. Za prvé, hlásíme úspěšnou výrobu bolometrů s kvantovými tečkami využívajících CVD grafen, kde kvantové uzamčení zesiluje teplotní závislost elektrického odporu – klíčový parametr pro citlivou bolometrickou detekci. Za druhé byl vyroben nový design zařízení s multi-paralelními kvantovými tečkami na bázi CVD grafenu, ukazující zlepšenou škálovatelnost a odolnost. Za třetí ukazujeme, že napětí na zadním hradle sehrává klíčovou roli při ladění teplotní závislosti odporu grafenové kvantové tečky, a tím poskytuje laditelný mechanismus pro optimalizaci výkonu bolometru.

Důležité je, že multi-paralelní architektura umožňuje optimalizaci celkové impedance bolometru, což usnadňuje jeho budoucí integraci s anténami pro vysokofrekvenční aplikace. Tento design zároveň umožňuje výrazné zvětšení celkové aktivní plochy grafenu při zachování stejné úrovně odezvy, čímž překonává běžný kompromis u miniaturizovaných detektorů.

Navzdory výzvam při fabrikaci, jako je zachování homogenních materiálových vlastností a dosažení vysokého rozlišení litografie na nanoměřítku, demonstrovaná zařízení představují důležitý krok směrem k výkonným a škálovatelným bolometrům na bázi grafenu. Tyto pokroky ukazují slibný potenciál pro aplikace sahající od citlivé detekce molekulárních magnetů až po sekvencování DNA s vysokým rozlišením a dále.

Klíčová slova

Grafenový bolometr, kvantová tečka, CVD grafen, ladění zadního hradla, multi-paralelní architektura, impedanční přizpůsobení, kryogenní senzory, nanofabrikace, teplotní citlivost, detektory s vysokou odezvou

I hereby declare that I have written my doctoral thesis topic on the theme of *nová generace grafenových bolometrů* independently, under the guidance of the thesis supervisor, doc. Dr. Ing. Petr Neugebauer, Ph.D., and using literature and other sources of information which are all properly quoted in the thesis and detailed in the list of literature at the end of the thesis.

Mgr. Oleh Martyniuk

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1. Introduction

The detection and analysis of electromagnetic radiation represent fundamental components underpinning modern technological advancements in sensing, imaging, and spectroscopic applications. Photodetectors, devices that transform incident radiation into measurable electrical signals, constitute the backbone of these technologies¹. Broadly, photodetection technologies can be classified into two principal categories: photonic and electronic detectors. Photonic detectors exploit the photoelectric effect to directly convert incident photons into electrical currents or voltages. These detectors are especially valuable in scenarios demanding rapid response times and high sensitivity, such as telecommunications and precision spectroscopy². Conversely, electronic detectors, commonly based on semiconductor materials, rely on the modulation of electronic properties, including conductivity and carrier mobility, in response to electromagnetic radiation. Together, these detector classes play pivotal roles in diverse technological domains, ranging from consumer imaging systems to advanced scientific instrumentation and security applications.

Let us recall that the electromagnetic spectrum spans a vast continuum of wavelengths, extending from long-wavelength radio waves to high-energy gamma rays. Within this extensive range, the terahertz (THz) spectral region — positioned between the microwave and infrared bands — presents unique and significant challenges for photodetection³. Often referred to as the "THz gap," this spectral region has traditionally been underexplored due to limitations in available sources and detection technologies. However, recent advancements have highlighted the considerable potential of THz radiation, particularly due to its non-ionizing characteristics. Unlike higher-energy radiation such as X-rays, THz waves pose minimal health risks, thus offering substantial advantages for applications involving human exposure, including medical imaging and security screening. For example, conventional imaging methods utilizing ionizing radiation carry inherent risks⁴, notably for vulnerable groups such as pregnant women. In contrast, THz-based detection methods promise safer, non-invasive alternatives,

providing high-resolution imaging capabilities without associated health hazards. Within the context of THz detection, bolometers have emerged as particularly effective sensing devices. Operating on the principle of thermal detection, bolometers measure minuscule temperature variations resulting from the absorption of electromagnetic radiation. These temperature changes are subsequently converted into electrical signals, enabling precise measurement of incident radiation energy. The inherent advantage of bolometer detectors lies in their exceptional sensitivity, a critical feature for detecting low-energy THz radiation. Such sensitivity is indispensable across a variety of applications, including scientific research, security surveillance, and non-destructive testing, where subtle thermal signatures may convey critical diagnostic information⁵.

Despite their significant promise, the fabrication and practical implementation of bolometer detectors present substantial technical challenges, primarily related to material engineering and device miniaturization. Achieving the necessary sensitivity for THz detection necessitates the precise control and uniformity of advanced materials — such as superconducting thin films and specialized semiconductor compounds — at nanoscale dimensions⁶. This precision requires advanced fabrication techniques, particularly high-resolution lithography⁷, to accurately define the intricate nanoscale structures essential for bolometer performance⁸. However, lithographic processes are highly sensitive to imperfections, which can introduce variability in the thermal and electrical characteristics of the detectors, thereby impairing their overall reliability and sensitivity. Moreover, integrating these nanoscale detectors with supportive electronic circuitry introduces additional complexities. Effective thermal isolation and minimal interference at the detector-circuit interface are crucial for maintaining accurate temperature measurements. Consequently, the fabrication processes must meticulously manage thermal losses and cross-talk among adjacent components. This requirement demands sophisticated cleanroom environments, stringent process control, and rigorous quality assurance protocols to consistently meet the high performance standards essential for both research-grade and commercial bolometer applications⁹.

The ongoing refinement and miniaturization of bolometer technologies, although challenging, hold substantial potential across multiple technological and scientific fields. In security and surveillance, bolometers offer safer, non-invasive detection alternatives

to conventional X-ray systems. Biomedical imaging stands to benefit significantly, providing diagnostic capabilities free from the risks associated with ionizing radiation exposure, thus enhancing patient safety. Furthermore, their extraordinary sensitivity positions bolometers as valuable instruments in environmental monitoring and fundamental scientific research, including the exploration of novel quantum phenomena¹⁰.

In summary, photodetectors — including both photonic and electronic types — constitute a crucial element in diverse modern technological applications. Addressing the persistent challenges associated with the THz gap highlights the unique advantages and complexities inherent to this spectral region. In addition, their exceptional thermal sensitivity, emerge as a promising solution for advancing THz photodetection technologies. Through continued advancements in materials science, nanofabrication, and integrated device engineering¹¹, bolometer-based detection systems are poised to significantly impact security, healthcare, and fundamental research, fostering substantial technological progress in the coming decades¹².

2. Aims of thesis

The goal of this doctoral thesis was to adapt the method of fabricating graphene quantum dot (GQD) bolometers on chemical vapour deposited (CVD) graphene. As impedance in graphene, especially when used in bolometers, plays a crucial role in performance, one of the aims was to decrease impedance and increase responsivity. This was achieved via optimization of the device architecture. Parallel dot arrays reduce net impedance with the combination of back gates for tuning the Fermi level to charge occupation and barrier heights to dynamically reduce resistance and improve matching, which are supposed to give us desired enhanced performance. Fabrication of such devices was carried out by applying a chain of techniques to achieve the required samples.

1. The first deliverable required research towards the instrumentation and techniques for nano-fabrication processes. Initially, the lithography technique using both positive and negative photoresists has been optimized to get the clean desired features on the substrate. To remove the excess materials both dry and wet etching techniques have been used and optimized for the best results. Finally, the electrode patterning was achieved by Ultra High Vacuum (UHV) physical vapor deposition system and the standard lift off procedure was used. Further, the samples were repeatedly characterized using optical microscopy, atomic force microscopy, and Raman spectroscopy after every step of fabrication process. The details of instrumentation and applied methods is precisely described below.
2. For fabrication and characterization of the samples, we used available in-house instruments located at the CEITEC Nano Core facility of the Brno University of Technology - Brno, Czech Republic. The fabrication process of the samples is complex and require several methods and equipment for fabrication. The preparation of the samples starts from dicing Si/SiO₂ wafer into smaller samples. For that purpose, I was trained to operate laser

dicer (LASERDICER). The whole fabrication process consists of several methods which are repeating and used in different stages of fabrication: resist spin-coating, baking, electron beam (e-beam) lithography and photolithography writing, resist development, metal deposition, lift-off process as well as wet and dry etching. For spin coating samples with resist and baking them on hot-plates was used lithographic wet bench for coating (SUSS-WETBENCH). For precise shaping of CVD graphene quantum dots bolometers was used e-beam lithography writing done one E-beam writer RAITH150 Two (RAITH) to create protective mask from negative resist. The metal contacts on the sample which did not require such precision was done during second step of photolithography writing by using ML3 Baby MicroWriter (ML3 BABY). Shaping of CVD graphene covered and protected by negative resist was done by dry etching, using reactive-ion etching (RIE) by Fluorine Chemistry (RIE-FLUORINE). While all the metal depositions were performed by using Electron beam evaporator BESTEC (EVAPORATOR).

3. Once a suitable sample was prepared the measurements and characterization of the properties of fabricated devices were performed. The characterization process, which took place between fabrication steps and in the final samples, used different equipment, such as atomic force microscopy (AFM) - Bruker Dimension Icon, Raman spectroscopy (RS) - WITec Alpha 300 R, scanning electron microscope (SEM) and MOTES research group laboratory: a home-built HF-ESR spectrometer featuring a Virginia diode (VDI) signal generator, amplifier-multiplier chain, a quasi-optical bridge (Thomas Keating), Cryogenics 16T solenoid cryomagnet and a VDI heterodyne detector.

3. Theoretical background

3.1. Bolometer principles

This subchapter provides an overview of bolometric detection principles, their historical development, and their relevance in various scientific and industrial applications. It discusses types of bolometers, key performance metrics (such as responsivity and noise-equivalent power), and the importance of thermal isolation and impedance matching.

A bolometer is a thermal detector that measures incident electromagnetic radiation by using an absorptive element whose electrical resistance changes with temperature. The first such device was developed by Samuel Pierpont Langley in 1880¹³. In his original implementation, Langley used two lampblack-coated platinum strips as adjacent arms of a Wheatstone bridge, forming the core of a highly sensitive detection circuit. These strips were connected to a galvanometer and a battery to register resistance changes. One strip was exposed to radiation, while the other was shielded, creating a differential response: the exposed strip experienced a rise in temperature and thus a change in resistance. This imbalance in the circuit allowed detection of extremely small variations in incident radiation. Later that year, a revised version of Langley's ¹³ bolometer was empirically shown to detect thermal radiation with remarkable sensitivity, laying the groundwork for modern thermal detection technologies.

Figure [3.1](#) illustrates a elementary bolometer device. A bolometer functions by absorbing radiation, where an energy from incoming photons stimulates the electrons inside the material, forcing them to move to higher energy levels. The energy is then transferred to the lattice as phonons, resulting in increased lattice vibrations and an increase in the material's temperature. The efficacy of this process is dependent on the

electron-phonon coupling, which determines the effectiveness of energy transfer from the electrons to the lattice. Materials showing strong electron-phonon coupling, such as semiconductors and graphene, are very proficient at converting radiation into thermal energy. The speed of heat loss via thermal conduction to a heat sink influences the bolometer's sensitivity. However, materials exhibiting low thermal conductivity allow prolonged heat retention, leading to a greater temperature increase for a given amount of absorbed radiation and therefore increasing sensitivity. The bolometer's output, generally a variation in resistance or capacitance, measures the absorbed radiation. The way the bolometer is built, including how the material reacts to heat and how well it stays connected to the heat sink, affects how quickly it responds and how sensitive it is, which are important for detecting small amounts of radiation. In the realm of photon detection, the absorption of a photon pulse with energy E results in a temperature rise in the absorber, which is determined by the following equation:

$$\Delta T = \frac{E}{C} \quad (3.1)$$

where C is the heat capacity of the absorber-thermometer assembly.

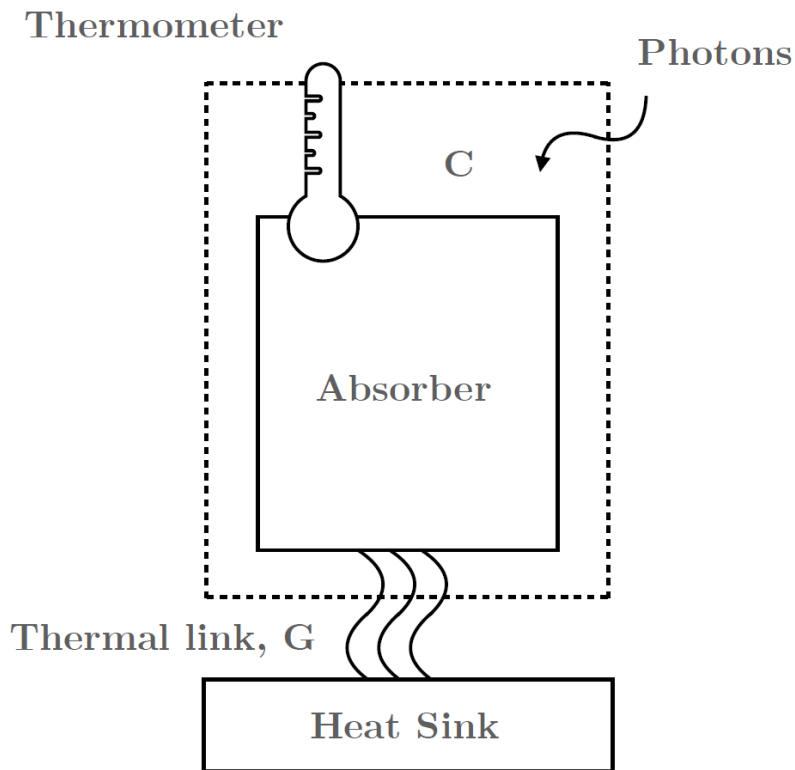


Figure 3.1: Schematic diagram of a bolometer device operations, outlining basic elements. Where C is capacity and G is thermal conductance.

The performance of an efficient detector is primarily characterized by its ability to respond effectively to incoming radiation, typically quantified through parameters such as responsivity, signal-to-noise ratio, and noise equivalent power (NEP). In the following subsections, we discuss these metrics, along with a comparison of different types of bolometers

3.1.1. Responsivity

The main function of a detector is to transform radiant input into an output signal of a convenient nature. In the context of our objectives, the resulting output consistently takes the form of electricity, either as an electric current or as an electric voltage. The responsivity r is defined as the quotient of the output signal and the radiant input. The irradiance E_e , which refers to the flux density at our detector, is commonly quantified in terms of either watts per square centimeter of detector area (W/cm^2) or photons per second per square centimeter [$\text{photons}/(\text{cm}^2 \text{ s})$]. The radiant input is calculated by multiplying the irradiance by the area of the detector (A_d).

$$r = \frac{\text{signal output}}{\text{IR input}} = \frac{S}{E_e A_d} \quad (3.2)$$

Responsivity is a crucial parameter that must be considered while evaluating a detector. Users can use it to pre-estimate the required sensitivity of a measurement circuit to detect the expected output or to predict the amplifier gain needed to enhance the signal to a desirable level. Alternatively, it provides instructions on how to estimate the observed irradiance level from the output signal¹⁴.

The output signal is typically expressed in volts, while the input signal is usually measured in watts. As a result, the standard unit of responsivity is volts per watt (V/W). However, the output can vary depending on the application requirements. It can be either current or voltage. The radiant input can be described in terms of total power, power density, photon arrival rate, or photon flux density. The fundamental principle remains unchanged: responsivity is equal to the ratio of output to input.

In these conditions, the responsivity r can be expressed as the ratio of the change in voltage across the device to the absorbed power at a constant bias current. The

relationship is based on the temperature dependency of resistance and thermal conductance G_{th} , as described by¹⁵:

$$r = \frac{\Delta V_{dc}}{\Delta P_{in}} = I_{dc} \frac{\Delta R}{\Delta P_{in}} = I_{dc} \frac{\Delta R}{\Delta T} \frac{1}{G_{th}} \quad (3.3)$$

3.1.2 Noise-Equivalent Power

Noise-Equivalent Power (NEP) is a metric that quantifies the maximum sensitivity of a specific detector. It provides a useful approximation of the signal-to-noise (S/N) ratio based on the available power. The NEP represents the minimum power required to provide a signal-to-noise ratio of 1 at the detector. If the power available is ten times the NEP, then the S/N will be 10.

It can be determined by dividing the system noise by the responsivity, which is defined as the output per power input:

$$NEP = \frac{noise}{responsivity} \quad (3.4)$$

The units of NEP are watts, but if the noise spectral density is used instead of the noise in the numerator of 3.4, the resulting units are watts per square root hertz ($W/Hz^{\frac{1}{2}}$).

The NEP formula is useful for estimating the minimal detectable power of a given system, but it has certain drawbacks. A high-quality detector would typically have a low NEP. It is important to note that the NEP of a detector might vary depending on its size and noise bandwidth. Therefore, it is not possible to determine the ideal NEP for a decent detector without specifying the area and noise bandwidth¹⁴.

The concept of specific detectivity $(D^*)^2$ was created to address two issues inherent in using NEP as a sole performance metric for photodetectors: first is that NEP is not normalized to detector size, so we can't compare the intrinsic sensitivity of detectors of different sizes using NEP alone. Second is that NEP depends on measurement bandwidth, so NEP doesn't give a fair comparison of detectors measured under different bandwidth conditions. That is why a high D^* is desirable, and all effective thermal detectors should

ideally have a similar D^* for a given field of view and effective temperature of the object or environment being observed by a thermal detector.

The value of D^* ^{16,17} can be calculated by multiplying the responsivity by the square root of the area, then dividing it by the noise spectral density (3.5a). Alternatively, D^* can be seen as a normalized signal-to-noise ratio (3.5b).

$$D^* = \frac{\text{responsivity} \times \sqrt{\text{area}}}{\text{noise} / \sqrt{\Delta f}} = \frac{R \sqrt{A_d}}{N / \sqrt{\Delta f}} \quad (3.5a)$$

$$= \frac{\text{signal} / \text{power}}{\text{noise} / \sqrt{A_s \nabla f}} \quad (3.5b)$$

3.1.3. Bolometer Applications

A bolometer is an exceptionally sensitive instrument used to measure the power of incoming electromagnetic radiation. It operates by detecting temperature changes in a material whose electrical resistance varies with temperature. Owing to its high sensitivity, the bolometer can detect even the slightest variations in temperature, making it useful in a wide range of applications.

In astronomy, bolometers are indispensable for detecting faint sources such as the cosmic microwave background radiation and other faint astronomical sources^{18,19}. They are employed in both satellite-based and ground-based telescopes²⁰ to measure the intensity of infrared and submillimeter radiation^{21,22} emitted by celestial objects. This enables scientists to explore the early universe, study star formation, and understand the properties of interstellar dust.

In environmental monitoring, bolometers are used to detect greenhouse gases and pollutants^{23–25}. Through remote sensing, they help assess Earth's radiation balance and monitor climate change by identifying changes in atmospheric temperature and composition. In the field of medical imaging, bolometers are applied in infrared thermography²⁶, to detect subtle temperature changes in human tissues²⁷. This non-invasive technique is valuable for diagnosing inflammation, tumors, and other abnormalities, providing thermal images that support early diagnosis and treatment

planning. Bolometers also have several industrial applications, particularly in materials science and quality control. They help assess thermal properties to detect defects and ensure consistency in manufacturing processes²⁸. Additionally, bolometers are used in gas detection systems to monitor hazardous gases²⁹, contributing to workplace safety.

To summarize, the versatility and remarkable sensitivity of bolometers make them indispensable tools in a wide range of scientific and practical applications. Depending on operational conditions, there are several types of bolometer detectors, each optimized for specific temperature ranges, radiation wavelengths, and readout techniques. These include thermal bolometers, which rely on resistive changes due to temperature rise; superconducting bolometers, which exploit the sharp transition between superconducting and normal states; and quantum dot or graphene-based bolometers, which offer enhanced sensitivity and faster response times due to their unique electronic properties.

3.1.4. Room temperature bolometers

Room temperature devices have mostly been designed for thermal imaging in industrial and security contexts, such as military operations, night vision, airport security, and equipment fault tolerance. Microbolometers, also known as thermal detectors, have become widely available in the commercial market, with leading manufacturers such as Lynred and Teledyne Flir Systems offering a range of products for various applications. These detectors utilize an oxide material, such as vanadium oxide, which has a high temperature coefficient of resistance, as the sensing element³⁰. These microbolometers designed for commercial use function at room temperature and experience limitations in terms of their sensitivities. Their spectral response is restricted to the wavelength range of 8 - 14 μm . In addition to this, numerous more designs have been developed that employ various principles to measure the temperature of an object. These devices encompass Golay cells, pyroelectric devices, and cantilever-based devices³¹. Golay cells employ the Golay principle³², which involves the expansion of a gas due to heating. They demonstrate greater sensitivity compared to the microbolometers available in the market.

3.1.5. Cryogenic bolometers

In order to achieve the required sensitivities, a cryogenic operation for a bolometer device is required for astronomical applications. Approximately 50% of the total brightness of the cosmic microwave background and 98% of the emitted photons lie in the sub-millimeter range of the electromagnetic spectrum.³³ The sub-mm wavelength spectral information can provide insights into the molecular composition of a celestial object.

Cooled bolometer devices are used in ground-based or space-based telescopes, depending on the extent to which the atmosphere absorbs far infrared radiation in the desired frequency range. For such research, developing cryogenic bolometers with background-constrained sensitivity poses a significant problem. This implies that the observations are solely constrained by the statistical noise associated with the arrival of photons. At frequencies above 1 THz, the NEP for cosmic microwave background radiation can be as low as $\sim 10^{-20} \text{ W/Hz}^{1/2}$ ³⁴. This is calculated using the formula $NEP_{ph} = h\nu\sqrt{2N_{ph}}$.

Fast bolometers are used in physical chemistry to investigate time-domain spectroscopy of molecular dynamics on the nanosecond scale. THz imaging has applications in both biological systems and the study of electrical properties in solid-state systems. In addition to THz detectors, there are kinetic inductance detectors (KIDs)³⁵, superconducting nano-wire single photon detectors (SNSPDs)³⁶, and superconductor-insulator-superconductor (SIS) mixers³⁷ etc.

3.2. Graphene-based Bolometers

This subchapter introduces graphene's unique properties—such as high carrier mobility, low heat capacity, and tunable resistance—and explains why it is a promising material for bolometric applications. It also reviews previous work in graphene bolometry, with a focus on both exfoliated and CVD-grown graphene devices, and sets the stage for the novel contributions of this thesis.

3.2.1 Basic electronic properties of graphene

Graphene is a monolayer of graphite composed of carbon atoms arranged in a hexagonal crystal lattice. Its distinctive electrical properties arise from the symmetry of the lattice and the atomic configuration of carbon³⁸. Carbon, a group IV element in the periodic table, has four valence electrons. In graphene, one electron from the s-orbital combines with two electrons from the p_x and p_y orbitals to form hybridized sp^2 orbitals. The strong in-plane carbon-carbon σ -bonds contribute to graphene's exceptional mechanical strength. The fourth valence electron occupies the p_z orbital, which extends perpendicular to the graphene plane. The lateral overlap of these orbitals creates weak π -bonds that govern the electrical conductivity of graphene.

To calculate the band structure of graphene using the tight-binding model, a unit cell consisting of two carbon atoms in a single layer is analyzed. These two atoms, located at positions labeled **A** and **B** (as shown in Figure 3.2), form the fundamental structure of a triangular lattice. Although chemically identical, these carbon atoms are physically inequivalent due to their different local environments. The two lattice vectors, denoted as **a**, and their corresponding reciprocal lattice vectors, denoted as **b**, are given by:

$$a_1 = \frac{a}{2}(\sqrt{3}, 1), a_2 = \frac{a}{2}(\sqrt{3}, -1) \quad (3.6)$$

$$b_1 = \frac{2\pi}{a}\left(\frac{1}{\sqrt{3}}, 1\right), b_2 = \frac{2\pi}{a}\left(\frac{1}{\sqrt{3}}, -1\right) \quad (3.7)$$

where $a = \sqrt{3}d_{c-c} = 2.46\text{\AA}$. d_{c-c} is the distance between two carbon atoms. Consider the carbon atom shown in green in Figure 3.2. Its three nearest neighbors are at coordinates given by,

$$\delta_1 = \left(\frac{a}{\sqrt{3}}, 0\right), \delta_2 = \left(-\frac{a}{2}, \frac{a}{2\sqrt{3}}\right), \delta_3 = \left(-\frac{a}{2}, -\frac{a}{2\sqrt{3}}\right) \quad (3.8)$$

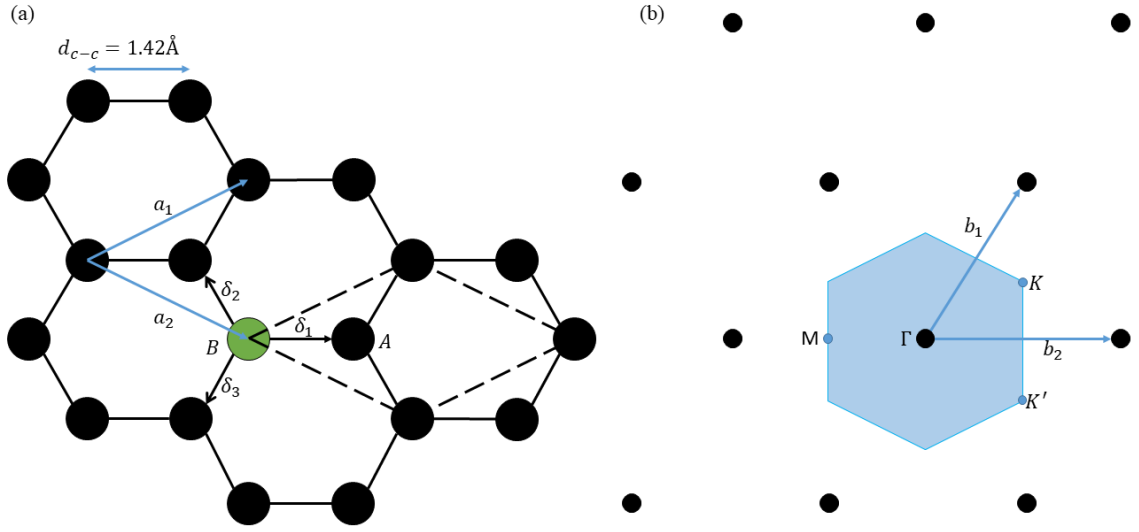


Figure 3.2: (a) Atomic structure of graphene. Each unit cell of the honeycomb lattice has two atomic sites (A and B). (b) First Brillouin zone of graphene with high symmetry points labeled Γ , M, K and K' .

The first Brillouin zone of graphene, as presented in Figure 3.2 (b), exhibits prominent symmetry points indicated as Γ , M, K, and K' . Among the six corners of the hexagonal Brillouin zone, only two are distinct, while the remaining four are connected by a reciprocal lattice vector.

In the tight-binding approximation, and considering that nearest-neighbor hopping is the main contribution to electron's energy, the energy bands of graphene are as follows³⁹

$$E_{\pm}(k) = \pm t \sqrt{1 + 4 \cos \frac{\sqrt{3}a}{2} k_x \cos \frac{a}{2} k_y + 4 \cos^2 \frac{a}{2} k_y}, \quad (3.9)$$

with the positive and negative signs representing the conduction and valence bands, respectively, and t the nearest-neighbor hopping energy, having a value of 3 eV³⁸. The valence and conduction bands intersect at the K and K' positions with zero energy. In undoped intrinsic graphene, the Fermi level coincides with the K and K' points, where the conduction and valence bands intersect. These locations are commonly known as the charge neutrality points (CNP). To obtain a low energy band structure, which is

significant in experimental scenarios, we can expand equation 3.10 at $k = K+q$, with $|q| \ll |K|$.

$$E_{\pm}(q) = \pm \hbar v_F |q| \quad (3.10)$$

Therefore, the energy dispersion shown in Figure 3.3 is a result of the honeycomb lattice's symmetry. We refer to the K and K' points as Dirac points, where an approximate linear and conical energy dispersion corresponds to a Hamiltonian.

$$\hat{H} = \pm v_F \vec{\sigma} \cdot \vec{P} \quad (3.11)$$

where $v_F = \frac{3ta}{2\hbar} \approx 10^6 \text{ m/s}$ is the Fermi velocity, $\vec{\sigma}$ are the Pauli matrices, and $\vec{P}$ is the momentum relative to the Dirac point. The wave functions can be shown as a spinor $\begin{pmatrix} \psi_A \\ \psi_B \end{pmatrix}$, where A and B are the two atomic sites. This is because each unit cell has two separate carbon atoms. This results in an extra level of independence, known as pseudospin, which characterizes the spread of the wavefunction between the two atomic locations. The pseudospin vector $\vec{\sigma}$ is either parallel or anti-parallel to the momentum vector, and $\vec{\sigma} \cdot \hat{P} = \pm 1$ ($\hat{P}$ being the unit vector of momentum) gives the chirality of the electronic excitations, the quasiparticles.

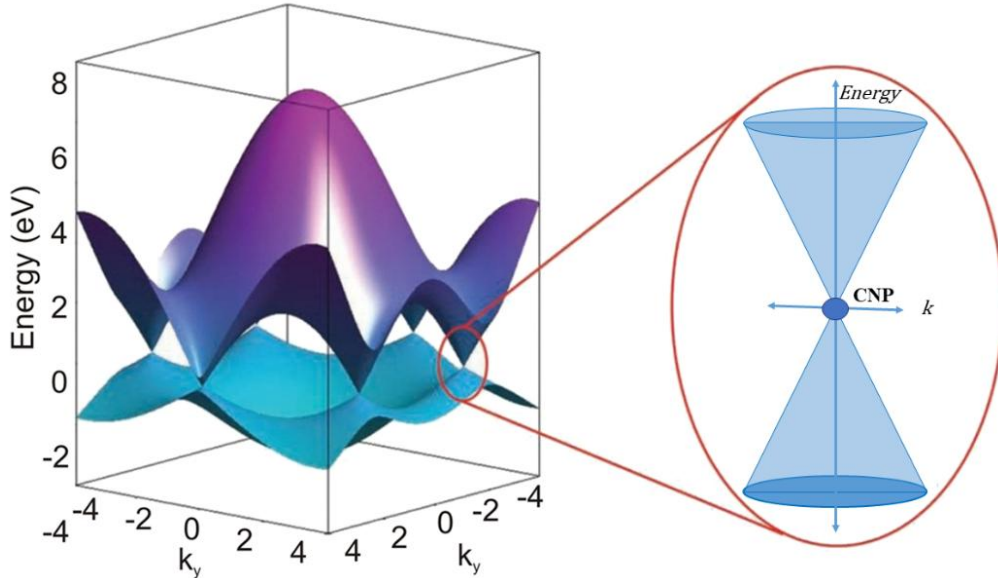


Figure 3.3: (left) Tight binding band structure of graphene, adapted from⁴⁰. Valence band and conduction band meet at the corners of Brillouin zone. (right) Low energy linear dispersion relation of graphene showing the Dirac energy spectrum with charge neutrality point (CNP) as the point where valence band and conduction band meet.

The impressive carrier mobility and saturation velocity in graphene attract electrical engineers, as these properties hold the potential for developing high-speed photonic devices based on graphene⁴¹. The utilization of graphene layer architectures with extended momentum relaxation time for both electrons and holes holds the potential to greatly improve the efficiency of the future optoelectronic devices. Graphene theoretically has an electron mobility of 250,000 cm²/Vs at ambient temperature. However, the local environment and processing methods greatly influence the material's transport behavior. Vacuum-suspended graphene, obtained through exfoliation, exhibits remarkably high carrier mobilities exceeding 200,000 cm²/Vs at room temperature. Regrettably, the films in question possess a minuscule surface area measuring 100 μm², rendering them costly for use in industrial settings. Charged impurity scattering and remote interfacial phonon scattering reduce the mobility when deposited onto a substrate Figure 3.4. Due to interfacial phonon scattering⁴², graphene's mobility on SiO₂ is limited to 40,000 cm²/Vs. Exposure to the atmosphere and the presence of pollutants, including resist residue, water, and metallic impurities, can also cause dispersion and reduce mobility.

Graphene is particularly noteworthy due to its exceptional thermal conductivity, which is around 10 times that of copper and 2 times that of diamond. Additionally, it exhibits outstanding electrical conductivity, which is roughly 100 times that of copper.

Unlike ordinary metals, which naturally have a high number of free charge carriers, graphene is a semimetal with fewer carriers. However, because of its two-dimensional structure, graphene allows easy tuning of its carrier concentration through chemical doping or electrical gating. This enables control over carrier densities in the range of 10¹² to 10¹³ cm⁻² - much lower than in typical metals like gold or silver. As a result, graphene offers electrical tunability that traditional metals cannot provide.

Graphene exhibits remarkable optical characteristics⁴³. The material's optical conductivity is characterized by its universal conductance, which is equal to $\pi\beta$. Here, β is defined as $(1/4\pi\epsilon_0)(e^2/\hbar c)$, where e represents the charge of an electron, $\hbar$ is Planck's constant, and c is the speed of light. Graphene exhibits a broadband linear absorption rate of 2.3% per monolayer, encompassing both visible and infrared wavelengths. With a

continuous monolayer thickness of 0.33 nm, it can absorb approximately 2.3% of the incoming light⁴⁴. This makes it significantly more absorbent, ranging from 10 to 1000 times, compared to semiconductors like Si and GaAs.

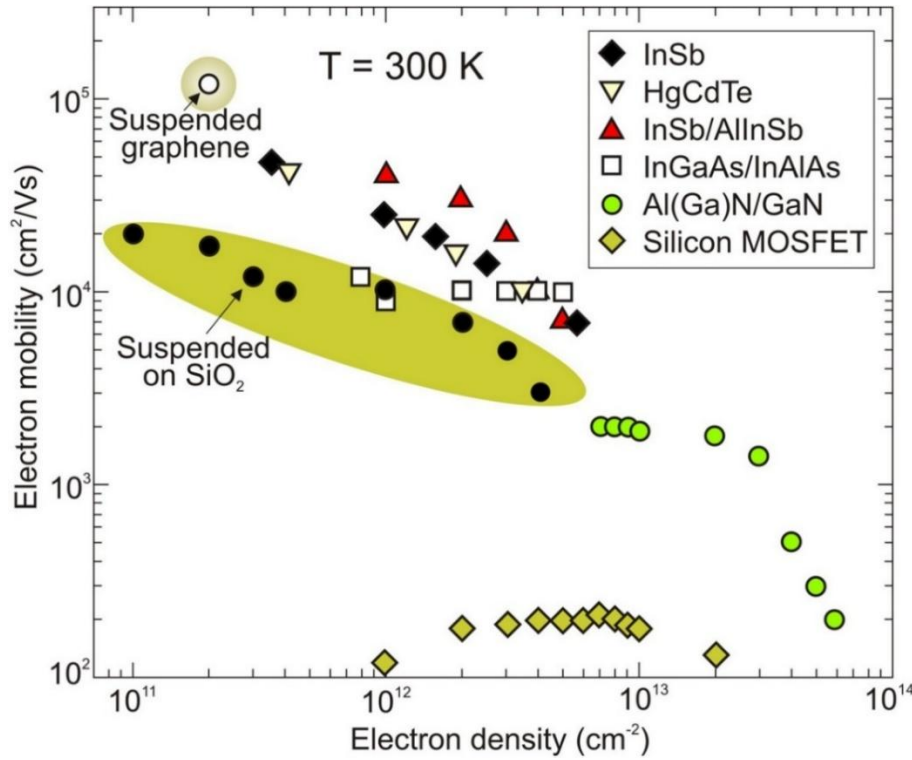


Figure 3.4: Electron mobility in graphene at room temperature in comparison with other material systems⁴⁵

Various methods can modify the bandgap structure of graphene, including the introduction of multiple layers Figure 3.5: Dirac Fermi cone Figure 3.5(a), substitutional doping Figure 3.5(b), the addition of two layers Figure 3.5(c), and the incorporation of a doped bilayer Figure 3.5(d). Doping the graphene layer can shift the Fermi level either upward or downward, reducing the mobility of both electrons and holes. The thickness limitation of graphene leads to a significant increase in resistance and chemical stability, which diminishes its suitability for applications requiring high conductivity.

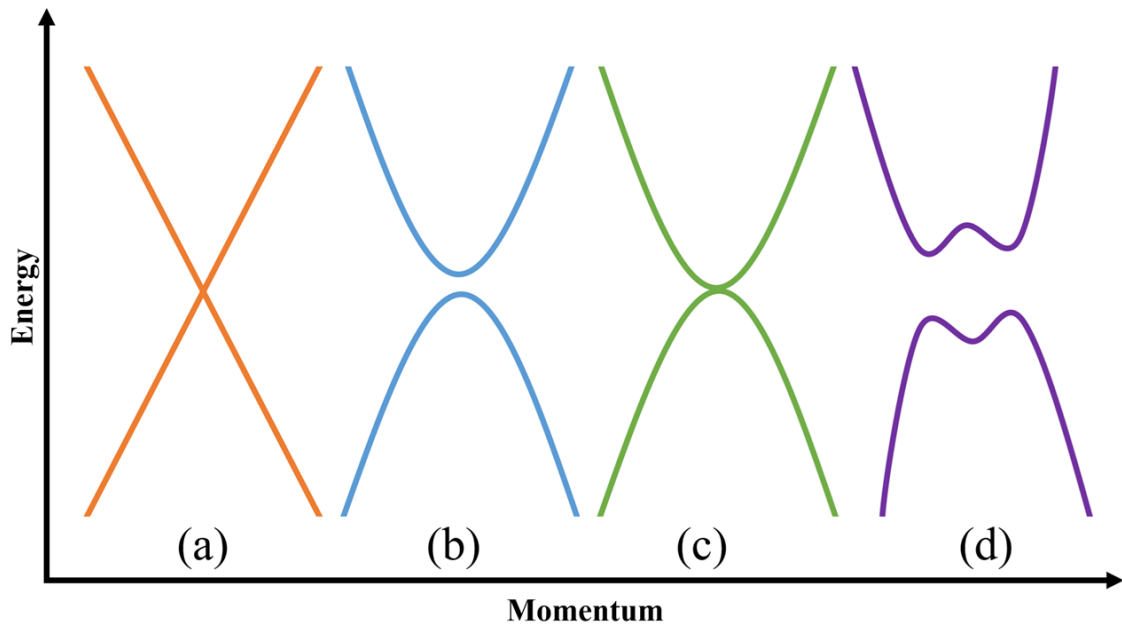


Figure 3.5: Modification of graphene's bandgap structure: (a) Dirac Fermi cone, (b) substitutional doping, (c) bilayer graphene, and (d) doped bilayers.

Out of all known substances, graphene has the highest specific interaction strength, which refers to the absorption per atom of material. Silicon has a typical absorption depth of 10 μm , resulting in 2.3% of the light being absorbed at a 200 nm thickness. In contrast, graphene, with its much smaller interplane spacing of 0.3 nm, exhibits the same optical absorption.

3.2.2. Advantages of a graphene absorber

In the conventional bolometer configuration described above, graphene acts as an active material. Using graphene absorbers for bolometer applications offers numerous benefits. The following characteristics are described below.

Graphene, consisting of a single layer of carbon atoms, has an exceptionally small physical volume. The electrons in graphene behave according to the Dirac-Weyl Hamiltonian, resulting in a linear energy dispersion. Additionally, graphene has a low electron density of states that increases linearly with energy. These characteristics — its

minimal volume and reduced density of states — lead to a significantly lower electronic heat capacity⁴⁶. This enables a high intrinsic energy resolution (R),

$$R = \frac{E}{\delta E} \quad (3.12)$$

where δE is the full-width-half-max (FWHM) energy width which is limited by the intrinsic energy resolution and the resolution of the readout mechanism, for single photon detection and a fast device response (small τ).

One additional benefit of graphene at low temperatures is its weak electron-phonon interaction, which is due to the narrow Fermi surface. This phenomenon is observed in transport measurements, where the resistance of graphene shows minimal dependence on temperature and a high level of mobility can be attained at low temperatures^{47,48}. At low temperatures, even a small amount of radiation can raise the temperature of the electrons in graphene above the temperature of the lattice. The electron and phonon subsystems coexist at distinct effective temperatures. The phenomenon known as the "hot-electron" refers to a state in which electrons in a material gain energy from an external source (such as light or electric field) and reach a higher effective temperature than the surrounding lattice. Such effect is utilized in devices called hot-electron bolometers to detect electromagnetic radiation. The weak interaction between electrons and phonons in graphene results in very low thermal conductance. This becomes the main obstacle to cooling heated electrons when all other thermal pathways have been limited. Graphene-based bolometers can reach high intrinsic sensitivity.

Graphene, as a two-dimensional (2D) material, has a larger contact surface, resulting in lower device resistance compared to one-dimensional nanomaterials like carbon nanotubes⁴⁹. Due to the small dimensions of the graphene bolometer device structure, an antenna is required to couple electromagnetic radiation to the graphene absorber. To achieve high coupling efficiency, a tight impedance match between the device and the antenna network is essential. The impedance of an amplifier is typically 50 Ω , whereas a planar antenna has an impedance of 100 Ω . The low and gate-tunable resistance of graphene allows for seamless integration with a planar antenna, enhancing coupling efficiency.

3.2.3. Challenges of employing a graphene absorber

Graphene is extremely attractive for detector applications due to the factors mentioned above. Nevertheless, there are fundamental technical obstacles to developing a bolometer that can fully use these features.

At low temperatures, the electron-phonon interaction in graphene is expected to be exceptionally weak. As previously stated, this decreases the thermal conductivity of the device and aids in achieving greater sensitivity. However, the resistance of a graphene flake doesn't show a substantial temperature dependency because of the weak-electron phonon scattering^{47,48}. Measuring the change in electron temperature caused by incoming radiation power becomes difficult as a result of this. A different electrical variable must be discovered that exhibits significant responses to variations in temperature.

In order to make a very sensitive bolometer, the next task is to stop the charged electrons from moving around inside the graphene channel and stop the heat from moving through the electron-phonon interaction. It would enable the investigation of electron-phonon interactions in graphene, a task that is otherwise challenging due to the weak correlation between temperature and resistance. A high contact resistance restricts the diffusion of hot electrons out of the electrical connections. In order to achieve high efficiencies, it is necessary to design the devices with low microwave impedance so that they can be properly matched with the antenna and external microwave readout circuit. Impedance matching with the antenna would not be possible if there is a high contact resistance, as this would hinder the reduction of thermal conductance. In the design of a graphene bolometer, it is important to consider the tradeoff between getting a high sensitivity and a high efficiency device.

3.2.4. State of the Art of graphene bolometer

Modern photon detectors are widely utilized in sensitive applications starting from astrophysical observations to quantum communications. The configurations thought-about so far for ultrasensitive Terahertz graphene detectors are thermal detectors at low temperatures, generally $T \leq 1K$.

As was mentioned previously about technical challenges that with weak electron-phonon scattering, the resistance is only weakly temperature dependent for pristine graphene. It is thus challenging to measure the electron temperature change due to incoming radiation power. Also, it is challenging to thermally isolate graphene to achieve the small electron-phonon thermal conductance^{50,51}, but there are ways to overcome this problem.

A stronger temperature dependence has been obtained either by using dual-gated bilayer graphene to create a tunable bandgap⁵² or by introducing defects to induce strong localization⁵³. Both schemes have successfully produced bolometric detection, with responsivities up to $2 \times 10^5 \text{ V.W}^{-1}$ and a temperature coefficient for the resistance as high as $22 \text{ k}\Omega.\text{K}^{-1}$ at 1.5 K. The hot electron bolometer (HEB) presented by A. El Fatimy et al. addressed the issue from a different angle by using graphene quantum dots^{15,54}. A bandgap is induced via quantum confinement and the graphene quantum dots device exhibits an extraordinarily high variation of resistance with temperature (higher than $430 \text{ M}\Omega.\text{K}^{-1}$), leading to responsivities of $1 \times 10^{10} \text{ V.W}^{-1}$. These devices required the use of multilayer structures, adding complexity. In the case of bilayer graphene, top and bottom gates were needed to induce a bandgap electrically⁵². In the case of disordered graphene⁵³, a boron nitride layer was used as a tunneling barrier between the graphene and the electrodes to reduce the thermal conductance due to diffusion of the electrons to the wires. Recently, A. Blaikie et al. have shown that graphene can challenge the state-of-the-art graphene bolometer at room temperature⁵⁵. They used a graphene nanoelectromechanical system to detect light via resonant sensing. In their approach, absorbed light heats and thermally tensions a suspended graphene resonator, thereby shifting its resonant frequency. Using the resonant frequency as a readout for photodetection, they achieve a room-temperature noise-equivalent power ($2 \text{ pW.Hz}^{-1/2}$) and bandwidth (from 10 kHz up to 1.3 MHz), challenging the state-of-the-art. Also, nano-bolometers based on superconducting transition edge sensors^{56,57} were proposed and already meet the single photon requirement regarding NEP, but they only operate in a very-low-temperature range around the superconducting transition temperature - around 0.1 Kelvin (See Table [1](#) for details).

Table 1: State-of-the-Art: of the graphene hot-electron bolometer

Graphene bolometer	Responsivity V/W	NEP $W/\sqrt{Hz}$	T (K)	References
Commercial InSb bolometer	5×10^3	5.0×10^{-13}	4.2 K	QMC Instruments Ltd.
Dual gate on bilayer graphene	2×10^5	3.3×10^{-14}	5 K	52
Defects in graphene	6×10^6	1.2×10^{-15}	1.5 K	53
Graphene quantum dot	1×10^{10}	5.0×10^{-16}	2.5 K	15
Magnetic tunnel junction	4×10^6	2.4×10^{-12}	Uncooled	58
Graphene Josephson junction		7.0×10^{-19}	19 mK	59
Superconductor graphene junction		3.0×10^{-20}	50 mK	60

3.2.5. Graphene quantum dot bolometer

In this work we focus on fabricating and using graphene quantum dot bolometers. As previously indicated, graphene is a promising material for quantum dot applications due to its distinctive electrical features, including high carrier mobility and adjustable electronic structure. Graphene, when restricted to nanoscale dimensions and transformed into quantum dots, undergoes significant changes in its electrical properties as a result of the quantum confinement effect⁶¹. The observed phenomenon occurs because the electron's wavefunctions are trapped within the quantum dot, resulting in the discrete quantization of energy levels. The discrete energy levels in graphene are markedly different from the continuous bands observed in bulk graphene. These discrete energy levels are essential for improving the sensitivity and selectivity of bolometers based on graphene.

Quantum confinement greatly affects the optical and electrical behavior of GQDs⁶², resulting in a strong sensitivity to particular wavelengths of incoming radiation. As the quantum dot's size reduces, the energy separation between its quantized levels

grows, enabling adjustable absorption and emission features. The ability to adjust this property is especially beneficial for applications that involve measuring heat radiation, where the capability to identify and distinguish between closely positioned wavelengths of light is crucial. The quantum confinement effect alters both the inherent electrical structure of graphene and its interaction with electromagnetic radiation, thereby enhancing the bolometer's responsiveness and overall performance.

The structures we use contain constrictions that attach the dot to the remaining part of the construction. The constrictions act as tunneling barriers, and although electrons have the ability to tunnel through the barrier, the capacitance of the dot is so low that the tunneling electron can generate a significant accumulation of potential, thereby preventing other electrons from tunneling. The quantum dot has a small self-capacitance, which results in a significant charging energy required for adding an electron to the dot. This charging energy can be calculated using the formula $U = e^2/C$, where C represents the self-capacitance of the quantum dot⁶³. The Coulomb blockade effect is responsible for the significant temperature dependence required for achieving high responsivity. If the thermal energy is lower than the charging energy $k_B T < e^2/C$, the current flowing through the dot is restricted by thermal activation across this energy barrier. This limitation persists until a voltage of sufficient magnitude is applied to align the energy levels of the quantum dot with those of the source and drain electrodes, as shown in Figure [3.6](#).

At low bias voltages, the Coulomb blockade phenomenon causes a noticeable reduction in current. Only when the applied voltage aligns the energy levels of the quantum dot with the Fermi levels of the electrodes can we detect current peaks. In the context of GQD bolometers, we can utilize Coulomb blockade to enhance the device's sensitivity by precisely controlling the electron flow in response to incoming radiation. The discrete energy levels and the Coulomb charging energy work together to develop an exceptionally sensitive detection mechanism.

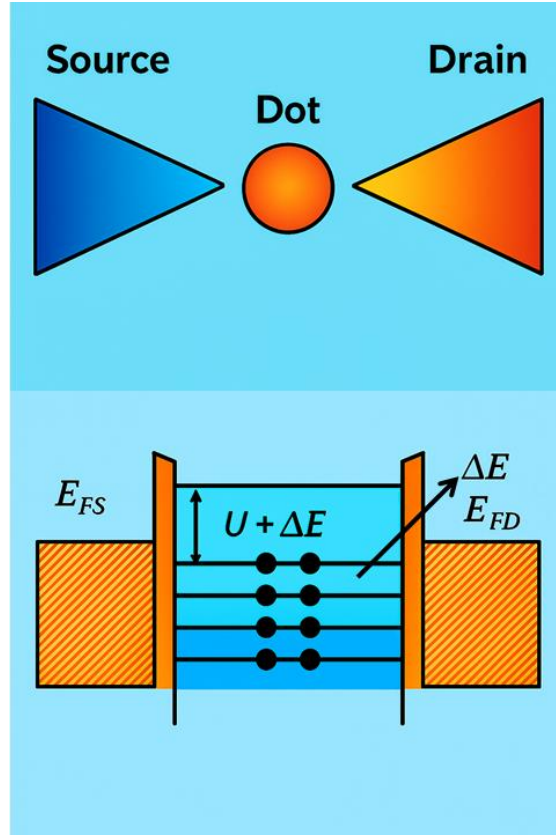


Figure 3.6 : Adapted from⁶⁴ (Top) Schematic of a quantum dot connected by source and drain electrodes. (Bottom) Schematic of electron transport across graphene quantum dot bolometer. The source and drain electrodes have Fermi energies of E_{FS} and E_{FD} , respectively. For an electron to be pushed from the source onto the Coulomb blockaded island formed by the dot, it must be thermally activated over a barrier determined by the charging energy $U = e^2/C$ where C is the capacitance of the dot.

Adding quantum confinement and Coulomb blockade effects to graphene quantum dots makes it possible to make a bolometric device that is more sensitive, selective, and tuneable. By precisely controlling the size, shape, and external gate voltage of quantum dots, we may regulate quantum mechanical events. This opens up new opportunities for the development of next-generation bolometers that can be used in infrared imaging, spectroscopy, and quantum sensing.

3.3 Conclusion

This section elaborates the theoretical underpinnings of bolometric detection with an emphasis on GQD bolometers. A bolometer functions as a thermal detector that transduces incident electromagnetic radiation into a measurable electrical signal via temperature-induced resistance changes in an absorber. The absorber's thermal linkage to a heat sink governs both the thermal time constant and device sensitivity. Key performance metrics include responsivity (V/W)—the ratio of output voltage to incident radiant power—and NEP, defining the minimal input power required for a signal-to-noise ratio of unity. Graphene's unique Dirac-Weyl electronic structure, with linear dispersion near the K-points, leads to exceptional carrier mobility, low density of states, and reduced electronic heat capacity, making it highly responsive to thermal excitation. Additionally, its weak electron-phonon coupling at cryogenic temperatures results in thermally isolated electron systems, enhancing sensitivity for hot-electron bolometry. The limitations of pristine graphene—specifically its weak temperature-dependent resistance due to low electron-phonon scattering—necessitate alternative mechanisms for temperature readout. Graphene quantum dots address this by introducing quantum confinement and Coulomb blockade effects, resulting in discrete energy levels and significant charging energies. These characteristics induce strong temperature-dependent transport behavior, critical for high responsivity and sharp current modulation in response to absorbed radiation. Device architectures leverage tunnel barriers formed by nanoconstrictions to confine electrons within the quantum dot. Radiation absorption perturbs electron temperature, modulating tunneling probability and hence the current, which is enhanced by the large resistance-temperature coefficient inherent to GQDs. Reported GQD-based devices demonstrate responsivity up to $10^{10} V/W$ and NEP values as low as $5 \times 10^{-16} W/Hz^{1/2}$. This integration of graphene's tunable band structure, nanoscale confinement, and hot-electron physics yields bolometric platforms with high sensitivity, scalability, and potential for quantum-limited infrared detection across diverse scientific and industrial applications.

4. Fabrication of Multi-Parallel Quantum Dot-Based Graphene Bolometers

This chapter presents the fabrication process of quantum dot bolometers using CVD graphene, including substrate preparation, lithographic patterning, and quantum dot formation. The design and fabrication of the multi-parallel quantum dot architecture are described in detail, highlighting the improvements in scalability, impedance tuning, and integration potential with RF antennas

The general fabrication process is shown on Figure 4.1. The process begins with substrate preparation, followed by the spin-coating of an e-beam resist layer, which is subsequently soft-baked on a hot plate to remove residual solvents and enhance adhesion. Upon resist application, e-beam lithography is employed to expose the desired pattern onto the resist. The sample is then subjected to a development process, wherein the exposed resist regions are selectively dissolved in the developer solution, leaving the unexposed regions intact to serve as an etch or deposition mask. Following development, metallic thin films are deposited onto the sample surface via electron-beam evaporation or sputtering, depending on the material and thickness requirements. Post-deposition, a lift-off process is conducted to remove the remaining resist along with the overlying metal, resulting in well-defined metallic structures on the substrate. This sequence can be iteratively repeated by reapplying the e-beam resist to enable the fabrication of multi-layered or complex device architectures.

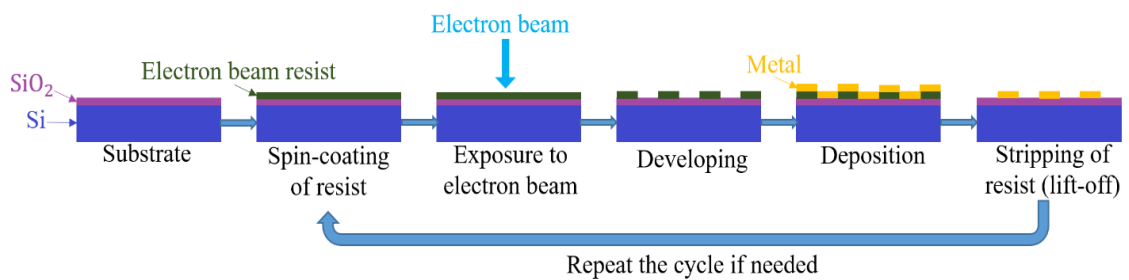


Figure 4.1 Schematic of the general fabrication process.

4.1. Fabrication techniques

4.1.1. Photolithography

In the 1820s, Nicéphore Niepce created a photographic technique that employed Bitumen of Judea, a naturally occurring asphalt, as the very first photoresist. When a sheet of metal, glass, or stone is coated with a thin layer of bitumen, the areas exposed to light become less soluble. The sections that were not exposed to light can subsequently be removed by rinsing with an appropriate solvent, revealing the material underneath. This exposed material is then chemically etched in an acid bath to create a printing plate. The light-sensitivity of bitumen was extremely limited, necessitating very long exposure times. However, despite the subsequent development of more sensitive alternatives, its affordability and exceptional resistance to powerful acids allowed it to remain commercially viable until the early 20th century.

In 1940, Oskar Süß developed a positive photoresist using diazonaphthoquinone. This photoresist functioned in a contrasting manner: the initial coating was not soluble but became soluble in areas that were exposed to light⁶⁵. In 1954, Louis Plambeck Jr. introduced the Dycryl polymeric letterpress plate, which significantly accelerated the platemaking procedure. In the past, photoresist development was done by immersing a group of wafers in a developer bath. However, current processes now develop one wafer at a time to enhance process control⁶⁶.

Photolithography is a technique used to create detailed patterns on the surface of polymer-based photoresists, achieving structures as small as nanoscale. Photolithography utilizes light to deposit a precise geometric pattern onto a photoresist by causing chemical reactions that enable the photoresist to be later removed or etched. The replication of relief patterns can be achieved through either direct laser writing or by exposing the photoresist to ultraviolet (UV) light or X-rays using a photomask. To achieve high-quality relief patterns, photolithography relies on the use of appropriate photoresists and carefully adjusted processing conditions. Failure to do so can result in compromised photoresists⁶⁷, leading to surface degradation and carbonization⁶⁸.

UV lithography (UVL) is a precise method of creating patterns by transferring different designs onto photoresists made of polymers. It is achieved by exposing the photoresists to UV light using photomasks. UV light exposure causes chemical reactions that promote the removal of both exposed and non-exposed areas of photoresist through subsequent chemical etching. Using photomasks, UVL has the ability to create desired patterns that have a periodicity as small as 50–100 nm⁶⁹. Due to the limited usability of many photomasks for only one patterning procedure, there is a current trend to avoid their use by utilizing digital mirrors⁷⁰ or by creating reusable polydimethylsiloxane (PDMS) photomasks⁷¹. Highly focused and consistent light sources emitting extreme ultraviolet (EUV) wavelengths can be utilized for specialized applications that demand photoresists with higher energy requirements for precise patterning. The technique used in this process is known as extreme ultraviolet lithography (EUVL). It has the capability to produce surface patterns with lateral periodicities smaller than 30 nm, such as grooves and circular patterns⁷².

X-ray lithography (XRL) is a technique that complements UVL and EUVL by utilizing synchrotron-generated wavelengths instead of UV light. X-ray lithography may produce relief patterns with a periodicity as small as around 50 nm⁷³ due to its utilization of short wavelengths, which are less than 1 nm. Regrettably, XRL necessitates the utilization of costly instruments⁷⁴, resulting in a limited availability of relief patterns obtained using XRL^{73,74}.

Direct laser writing (DLW) is a maskless process that uses laser modulation to form relief patterns with a lateral periodicity of a few hundred nanometers schematically shown on Figure [4.2](#). This modulation triggers a chemical reaction, such as polymerization, in a small focal volume on the photoresist⁷⁵. Periodic relief patterns are achieved by moving the laser across the photoresist surface, causing a considerable change in the solubility of the photoresist in the exposed areas. This is then followed by film development. To achieve patterns of superior quality, factors such as laser intensity, spot size, and writing speed must be adjusted⁷⁶. For example, the movement of the focus spot position caused by mechanical drifting in relation to the sample could lead to undesired effects on the generated patterns compared to the original model⁷⁷, necessitating the development of new and creative solutions⁷⁸. Improper utilization of

processing parameters, such as the time of exposure, power of the laser, or dose, can result in harm to the photoresist⁷⁹ and cause the pattern to become discolored⁸⁰.

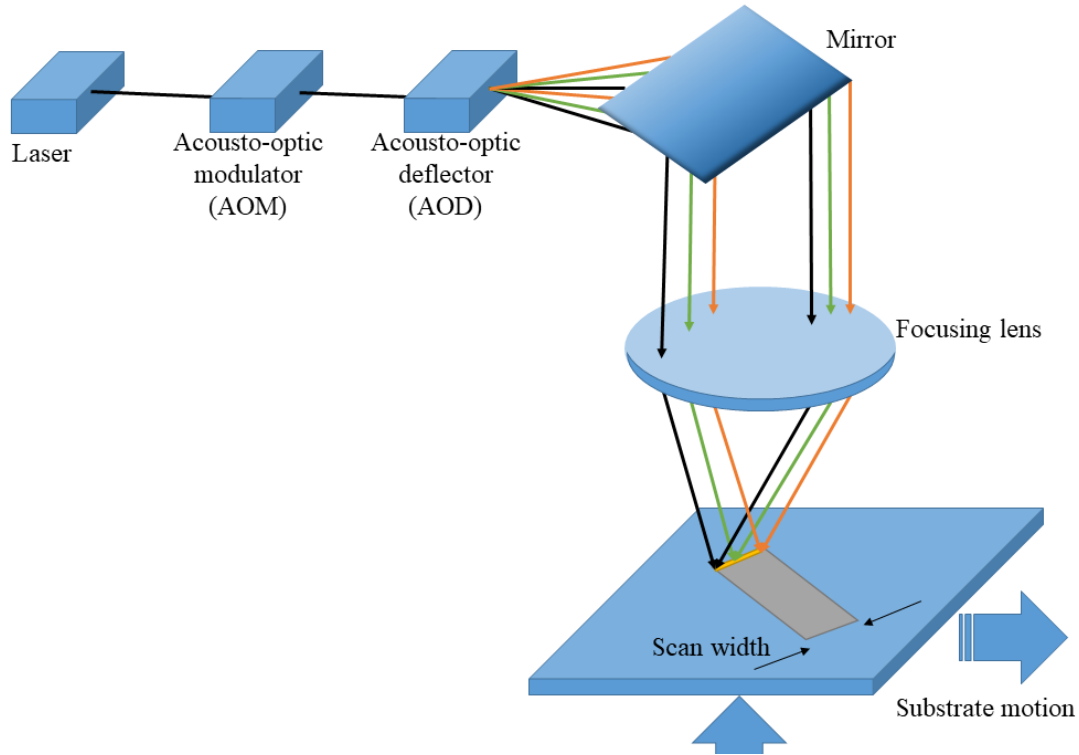


Figure 4.2: Schematic of laser direct writing system

4.1.2. Electron beam lithography

Electron beam lithography (EBL) is a crucial method for fabricating patterns at the nanoscale. The creation of EBL tools commenced in the late 1960s⁸¹ with the adjustment of scanning electron microscopes design. The working principle of EBL is rather straightforward and closely resembles photolithography: An electron beam is directed towards a substrate coated with an electron-sensitive substance called resist. The resist undergoes changes in its solubility properties based on the amount of energy transferred by the electron beam. Areas that are either exposed or not exposed, depending on the tone of the resist, are eliminated during the development process. Ever since Hatzakis discovered polymethylmethacrylate (PMMA) as an electron resist in 1969⁸², EBL has been utilized for creating a diverse range of devices. These devices include

integrated circuits^{83–85}, photonic crystals^{86–89}, and channels for nanofluidics investigations^{90,91}.

EBL is considered to have the best resolution among the different types of lithography commonly used. This is especially true when using primary electrons with energy between 50 and 100 keV. Researchers have utilized e-beam lithography to generate features with diameters as small as 5 nm and below⁹². Although e-beam lithography provides more resolution than current production deep ultraviolet (DUV) instruments, its throughput is significantly slower, limiting its use in high-volume commercial manufacturing. A modern optical lithography scanner can process over one hundred wafers per hour. A conventional electron beam instrument typically requires several hours to expose a single wafer, and more complex masks or templates can take several days. Reducing the optimal spot size will result in a prolonged time to improve resolution. E-beam patterning is more time-consuming because it uses nonchemically amplified resists with higher resolution, which require much higher doses compared to the chemically amplified resists (CARs) commonly used in optical lithography. In the past, the low capacity of e-beam lithography had limited its application to mask production, research, and development. Nevertheless, continuous efforts have been made to improve the rate at which data may be processed by implementing techniques and designs such as projection e-beam^{93–96}, multiple-beam^{97,98}, shape-variable beam⁹⁹, and reflecting beam¹⁰⁰. At present, multiple-beam e-beam lithography is regarded as the most advanced technique. It increases efficiency by dividing the beams that create the wafer on a large scale¹⁰¹. Many forms of EBL, particularly in nanotechnology, are considered viable options for creating patterns on a surface Figure [4.3](#).

Despite the complexity of modern electron beam lithography systems, they all have a common set of essential components that enable them to attain exceptional levels of resolution, precision, and reproducibility. Figure [4.4](#) depicts the diagram of a standard EBL system, illustrating its key equipment components.

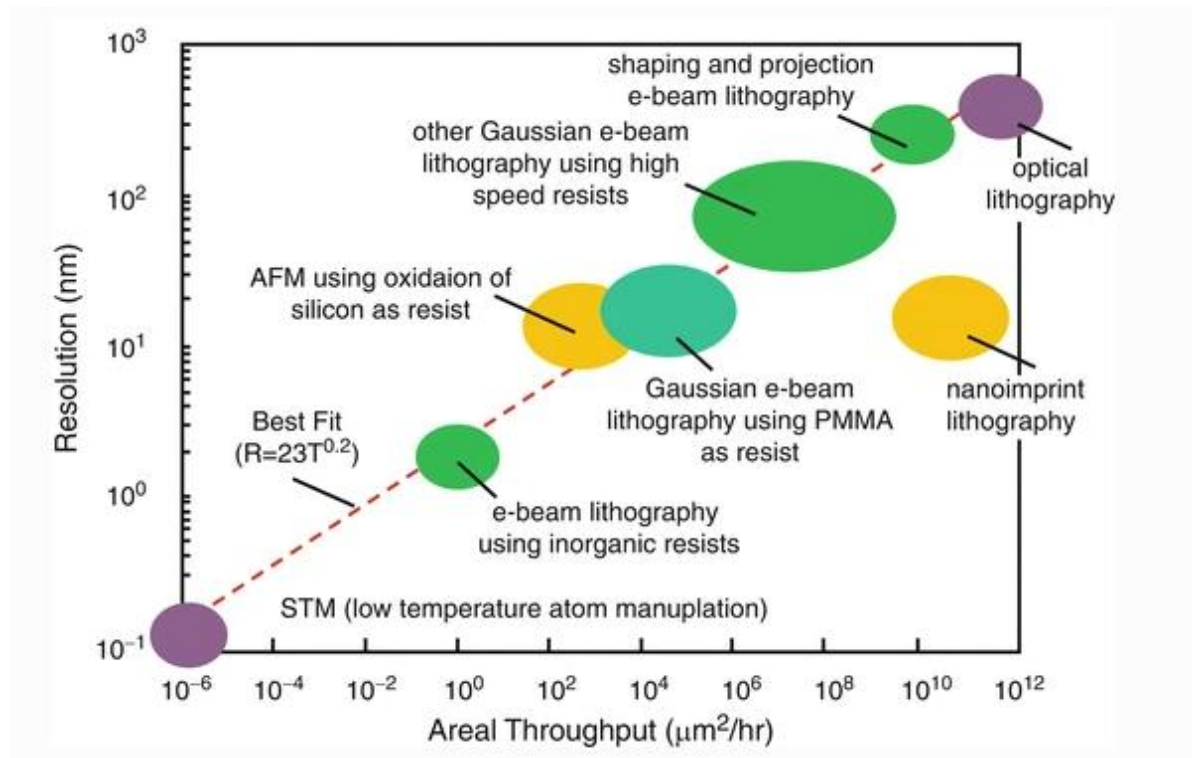


Figure 4.3: Resolution of different lithographic techniques as a function of throughput¹⁰²

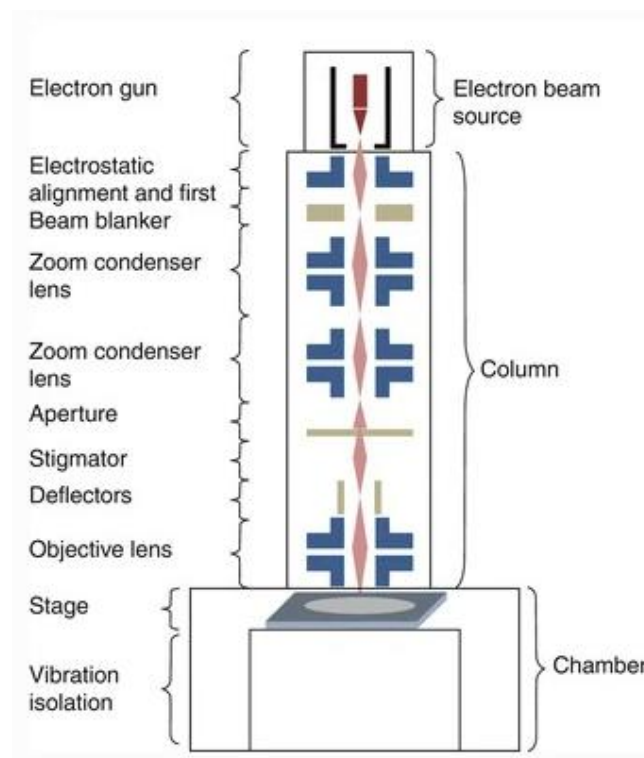


Figure 4.4: Schematic of a typical electron beam lithography system¹⁰²

Table 2 shows a comparison among UVL, XRL, and EBL, with a focus on the preparation of graphene quantum dot bolometers.

Table 2: comparison among UVL, XRL and EBL

Property	UVL (Ultraviolet Lithography)	XRL (X-ray Lithography)	EBL (Electron Beam Lithography)
Resolution	Moderate (~200 nm)	High (~50 nm)	Very High (~1 nm)
Fabrication Speed	Fast (large-area patterning)	Moderate (slower than UVL)	Slow (point-by-point writing)
Mask Requirement	Requires photomasks	Requires X-ray masks	No mask required
Cost	Lower (due to mask usage and high throughput)	Higher (X-ray source and masks are expensive)	High (expensive equipment, slower throughput)
Material Compatibility	Works on various materials, including polymers and semiconductors	Best for thick substrates, harder materials	Works well with a wide range of materials including thin films, metals, and semiconductors
Resolution for Quantum Dots	Limited precision for small-scale structures	Capable but not as precise as EBL	Excellent precision for nanoscale patterns and small quantum dots
Advantages for Graphene Quantum Dot Bolometers	Less suitable for fine-scale patterning of graphene structures	Can be used for precise fabrication, but expensive for high-throughput processes	EBL is particularly beneficial for creating precise graphene quantum dots, as it offers extremely high resolution and the ability to define intricate nanoscale patterns necessary for high-performance bolometers.
Need and Benefit for Graphene Quantum Dot Bolometer Preparation	Typically less advantageous due to its limited resolution for small-scale and highly precise patterning required in graphene quantum dot structures	While XRL is capable of creating precise patterns, it is not as commonly used due to high costs and slower throughput compared to EBL	EBL's ability to directly write nanoscale patterns on graphene allows for the fabrication of precise quantum dots, critical for enhancing the sensitivity and performance of graphene-based bolometers. Its high resolution is essential to define the tiny, highly controlled graphene quantum dots needed for optimal sensor function.

EBL is the preferred choice for graphene quantum dot bolometer preparation because of its high resolution and direct writing capability, making it ideal for fabricating the tiny, precise structures needed in bolometer sensors. Despite being slower and more expensive than UVL or XRL, its ability to create highly controlled quantum dot patterns justifies its use for graphene-based bolometers, where accuracy and performance are critical.

4.1.3 Deposition technique

There are generally two methods for thin film deposition. These approaches are categorized based on the processes involved in the procedure, specifically whether they are physical or chemical in nature.

Physical Vapor Deposition (PVD) encompasses a variety of vacuum deposition techniques used to create thin coatings and films. During the PVD process, a substance undergoes a transformation from a condensed state to a vapor phase and subsequently returns to its original state as thin films. Figure 4.5 illustrates the PVD procedure. The primary procedures involved in PVD are evaporation and puttering.

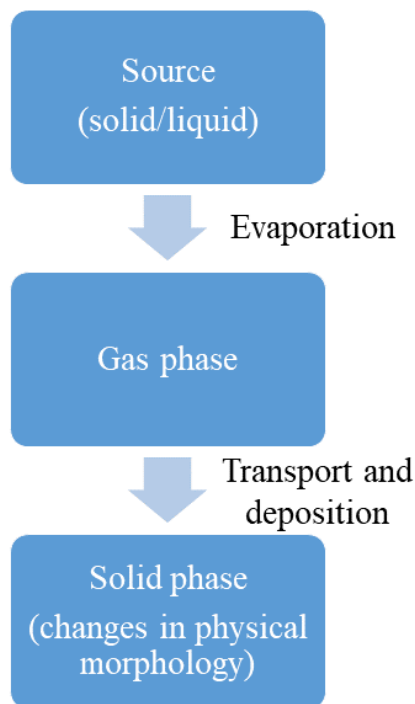


Figure 4.5: The physical vapor deposition process.

It is utilized in the manufacturing of objects that demand thin coatings for optical, mechanical, electrical, or chemical processes. These coatings have a long lifespan because they are resistant to corrosion, have high level of hardness, and possess strong impact resistance. PVD offers a variety of methods for depositing films. However, each technology has its limitations, with some only functioning at high temperatures and others requiring a vacuum to operate. In addition, they require water-based cooling systems to manage substantial heat loads. The uses of this technology cover various fields, such as semiconductor devices and solar panels that utilize thin films to generate energy.

Electron beam evaporation is a process that involves using of an electron beam to vaporize a material for deposition on a substrate. Electron beam evaporation entails using a concentrated beam of high-energy electrons to vaporize the source material. Thermionic emission is the process by which a hot filament releases electrons. These electrons can be accelerated to generate enough energy to vaporize any substance. When 1A of emission is accelerated through a voltage drop of 10 kV, the impact results in the delivery of 10 kW of power¹⁰³. In order to prevent the filament from melting due to the evaporant, it is positioned away from the evaporant, as depicted in Figure 3.5. Additionally, a magnetic field, denoted as B , is used to pull the electron beam towards the surface. The direction of this magnetic field is indicated in the picture. The Lorentz force, denoted as F , refers to the combined force acting on an electron in the presence of both an electric field (E) and a magnetic field. This force is mathematically expressed as described in reference¹⁰⁴:

$$F = F_E + F_B = q_e E + q_e (\mathbf{v} \times \mathbf{B}) \quad (4.1)$$

where $\mathbf{F}$ is in N, q_e is in C, $\mathbf{E}$ is in V/m, $\mathbf{B}$ is webbers/m² or Tesla (T), and the electron velocity $\mathbf{v}$ is in m/s. The cross-product vector, $\mathbf{F}_B$, is oriented orthogonally to both vector $\mathbf{v}$ and vector $\mathbf{B}$, as indicated in Figure 4.6. In Equation (4.1), the initial force term propels the electrons in the opposite direction of the filament, or cathode. The gained velocity leads the electrons to be diverted laterally when they traverse the magnetic field lines, in accordance with the second force term. The electrons' centrifugal force, as they curve at a radius of r , counteracts the second force.

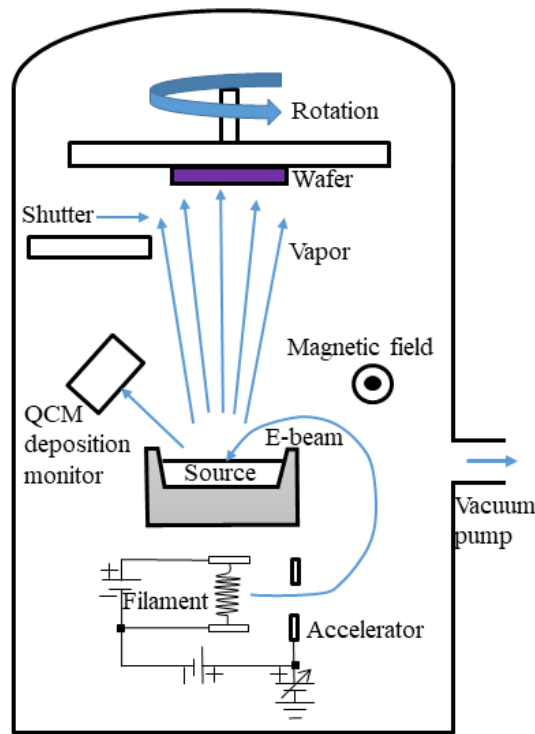


Figure 4.6: The phenomenon of the electron beam evaporation system in a schematic.

4.1.4. Dry and wet etching

Etching is a process that modifies the surface of a material by dissolving it using chemically aggressive liquids or gases (known as etchants) or through electrochemical reactions in the case of metals. The etchant is prevented from attacking certain areas by a protective layer, typically made of photoresist in micro- and nanofabrication but sometimes made of inorganic materials. This protective layer is usually removed after the etching process is finished, enabling the use of etching to create patterns in micro- and nanostructures.

Etching of solid surfaces can be achieved by wet procedures, such as wet-chemical etching or electrochemical methods¹⁰⁵, as well as dry treatments, which can involve physical, chemical, or a combination of both techniques¹⁰³. Special applications may utilize mechanical techniques, either with or without a chemical component.

For a wet-chemical etch process to be viable, the resulting product of the target material must be able to dissolve in the etchant medium, or alternatively, the etchant medium must be able to remove the etched target material from the surface. For dry

etching to occur, it is necessary for the reactant to possess a high level of volatility. Nevertheless, in wet-chemical etching and dry etching, if only the top layer reacts without being eliminated, the resulting reaction products will ultimately create a passivation layer, which halts the etching process.

The etching process can be categorized based on different parameters. The etchant's aggregate state refers to its physical state, such as being a solid, liquid, or gas. The etching process can be carried out using either liquid methods, such as wet-chemical etching or electrochemical etching, or gaseous methods, such as dry etching. Dry etching involves the use of either vapor (vapor phase etching) or plasma state gas as the etchant. The plasma can be used to separate the chemical species of the etchant in order to intensify the chemical attack (known as plasma etching), generate charged particles that physically bombard the substrate to etch it (known as ion beam etching), or both (employed by a few alternative techniques).

Another criterion for classification is the direction of the etch attack and the resulting etch profile. Figure 4.7 shows various options for etching a masked region Figure 4.7 (a). Etching can occur in different ways, such as isotropic etching Figure 4.7 (b). It can also follow the crystal directions of single-crystal materials, known as anisotropic etching. This is specifically seen in the wet-chemical etching process for single-crystal silicon Figure 4.7 (c-d). Additionally, etching can have a preference for a certain direction, known as directional etching Figure 4.7 (e). This preference can be induced by the direction of ion bombardment¹⁰³. Isotropic etching is the fundamental process used for bulk micromachining of silicon, which is a crucial technology in the fields of Micro Electromechanical Systems (MEMS) and Nano Electromechanical Systems (NEMS).

A glow discharge can be used to achieve directional ion bombardment and chemical reactions. This can be done, for example, by creating a glow discharge between parallel plate electrodes, with the substrate placed directly on one of the electrodes¹⁰⁶. The term used to describe this procedure is reactive ion etching. The system configuration is analogous to sputtering, with parallel plates functioning as the substrate table (anode) and the target (cathode). An radio-frequency (RF)-induced direct current (DC) bias generates a plasma that ionizes the gaseous species, dissociating the reactive gas. Because

of this, the substrate can be damaged chemically by radicals (the isotropic chemical aspect of RIE) and physically by ions hitting it from the side (the directional etching aspect of RIE).

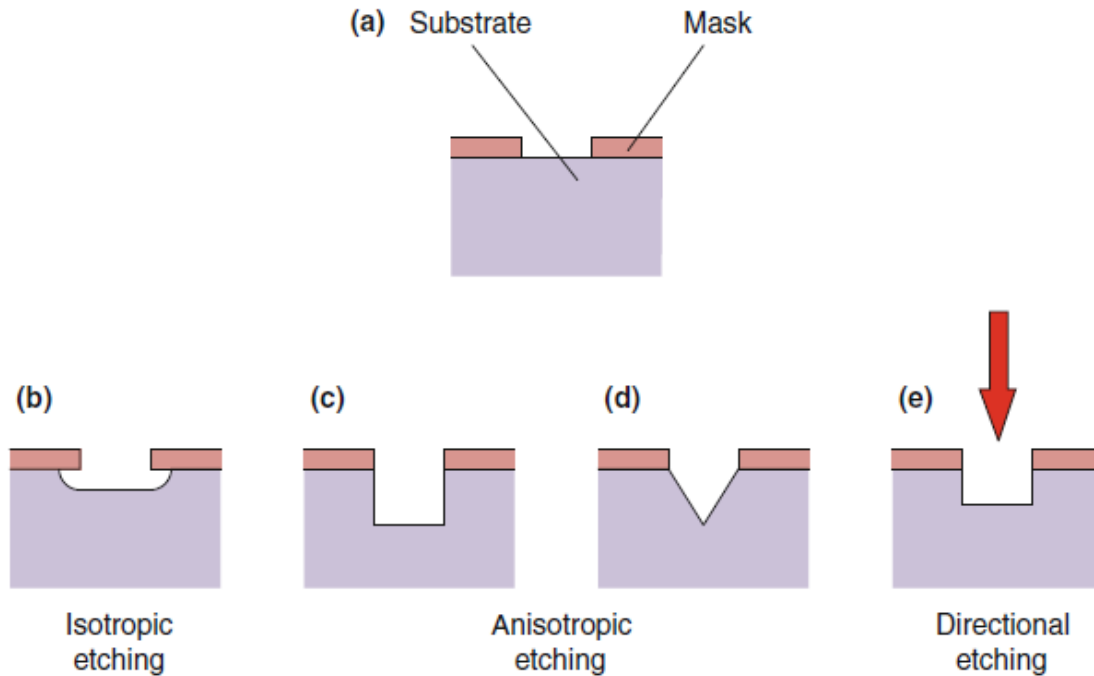


Figure 4.7 Etch profiles adapted from¹⁰³: (a) Masked area. (b) Isotropic etching. (c–d) Anisotropic etching of single crystal material with crystallographic planes serving as etch stops. (e) Directional etching by an ion beam

The parallel plate reactor is the predominant tool configuration used for reactive ion etching^{103,106}. This configuration can be traced back to Reinberg's 1973 patent, which described a mostly physical etching technique¹⁰⁷. Figure 4.8 illustrates the schematic design. Within the confines of a vacuum chamber, there exists a superior electrode equipped with a built-in gas intake resembling a "shower head.". In parallel to this, there is a lower electrode that functions as a platform for the substrate. The upper electrode is maintained at a reference potential of zero volts, while the lower electrode is linked to a RF source, resulting in the bombardment of ions onto the substrate. The substrate is securely fastened to the energized electrode, which can be shielded by a quartz or graphite coverplate to prevent erosion of the electrode and can also be cooled. The ion density and energy are determined by the RF plasma source¹⁰⁶.

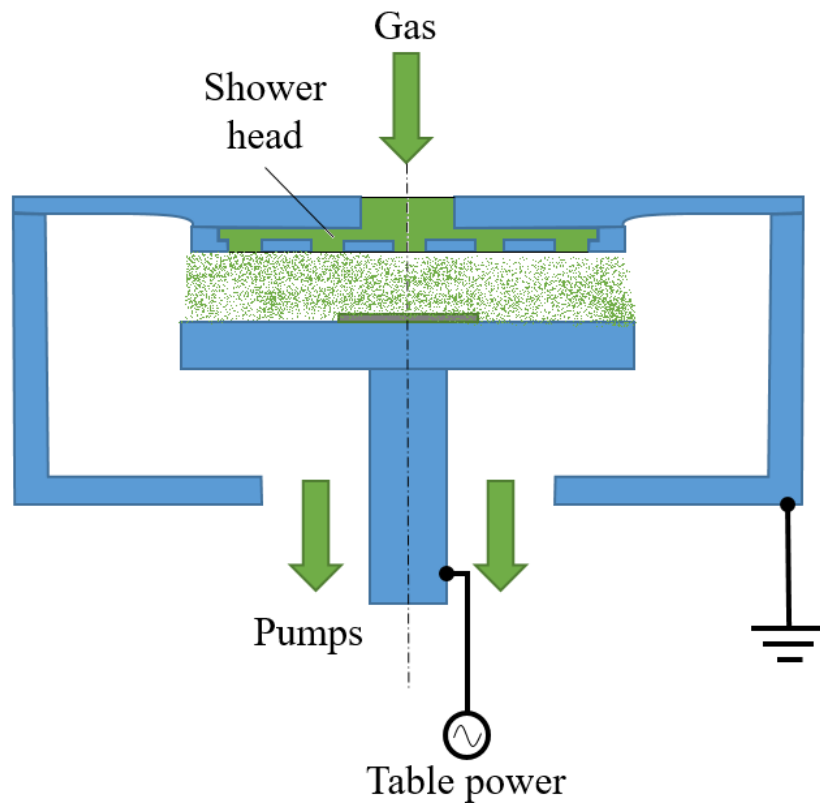


Figure 4.8 Schematic representation of a parallel plate reactive ion etching (RIE) tool adapted from Oxford Instruments¹⁰⁶

4.2. Nanofabrication of device

Dose test

In e-beam lithography, the dose refers to the amount of electron beam exposure a resist receives during the patterning process. It is typically measured in microcoulombs per square centimeter ($\mu\text{C}/\text{cm}^2$). The dose determines how much energy is delivered to the resist, affecting its chemical structure and solubility. An appropriate dose is crucial for achieving the desired resolution and feature size in the resist material. The underexposure leads to incomplete patterning and overexposure causes excessive resist removal or blurring of features. Though the dose can vary depending on the prior parameters for spin coating and soft bake (SB), as well as on the shape of the desired pattern. As so, dose tests are done in advance for every used resist and pattern.

The first approach of fabrication involved covering sample with thin layer of metal such as Au, to protect our CVD graphene from being contaminated from the chemicals of resist. As such, the first dose tests were done on samples covered with thin layer of Au. For nanodevices such as CVD graphene quantum dots arrays, we tested an e-beam resist SX AR-N 8200 (Medusa 82) from Allresist Agency. During the tests, it was found out that Medusa 82 performs bad adhesion with Au. Several tests were made with Medusa 82 and we received substandard results in each case for this resist. All lithography was done in RAITH 150 TWO at 20 kV, with working distance focused on 10 mm and an aperture size of 15 μm . The first test was done with spin coating Medusa 82 at 3000 revolutions per minute (RPM) for 60 seconds, then soft bake was done on hot plate at 150 $^{\circ}\text{C}$ for 10 minutes. The lithography was performed in the range of doses from 60 $\mu\text{C}/\text{cm}^2$ to 100 $\mu\text{C}/\text{cm}^2$ with the step of 5 $\mu\text{C}/\text{cm}^2$. The developing process was done with the use of developer AZ 726 MIF. Figure 4.9 shows the result after developing process.

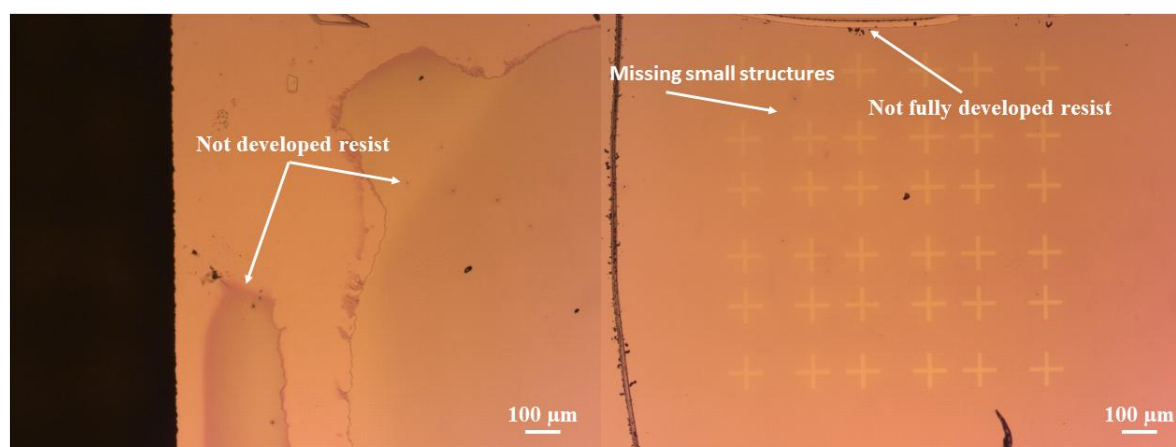


Figure 4.9 (left) Still remaining resist after development process. (right) Big structures in the view of crosses which were used for easier finding of the smaller structures between them, but small structures were not found, by lightly the scratching the surface, were found out that resist is not developed.

For the next test we prepared a new sample with Medusa 82 spin coated at 3000 RPM for 60 seconds, before being soft bake on a hot-plate at 150 $^{\circ}\text{C}$ for 10 minutes. The lithography was performed in the range of doses from 60 $\mu\text{C}/\text{cm}^2$ to 100 $\mu\text{C}/\text{cm}^2$ with the step of 5 $\mu\text{C}/\text{cm}^2$. The developing process was done with the use of another solution of NaOH 1% + NaCl 4% as a developer. The result is shown in Figure 4.10.

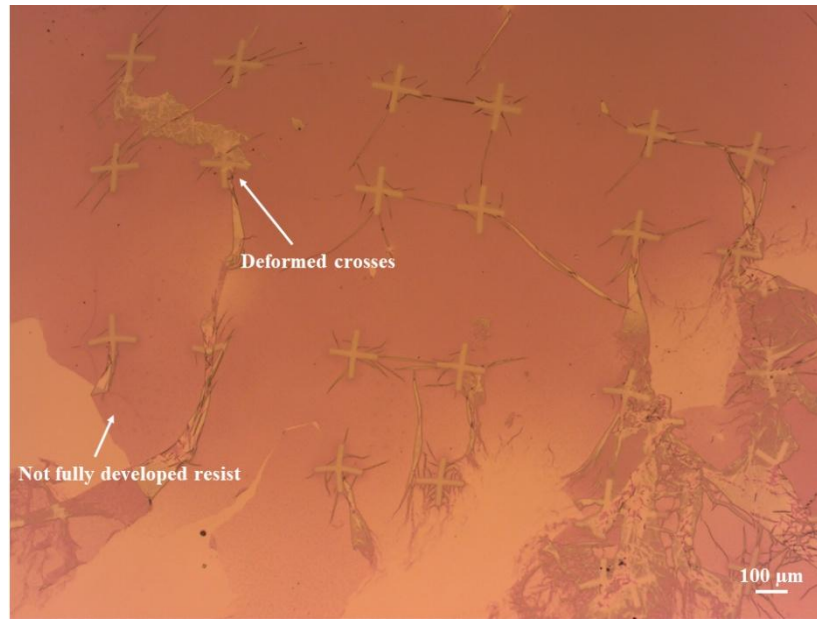


Figure 4.10 Shows the result of dose test with the usage NaOH 1% + NaCl 4% solution as the developer. As visible from the image, the structures were deformed during development process and bad development result.

Next attempt was done with the usage of polymer layer AR 300-80 which act as the primer, before spin coating Medusa 82 at 3000 RPM for 60 seconds, then soft bake was done on hot-plate at 150 °C for 10 minutes. The lithography was performed this time in a wider range of doses from $30 \mu\text{C}/\text{cm}^2$ to $150 \mu\text{C}/\text{cm}^2$ with a step of $15 \mu\text{C}/\text{cm}^2$. The developing process was done with the use of the solution NaOH 1% + NaCl 4% as a developer. There was improvement in developing and stitching bigger structures to the surface, but small structures were not found either by optical microscopes or by atomic force microscope (AFM). The result is shown on Figure 4.11.

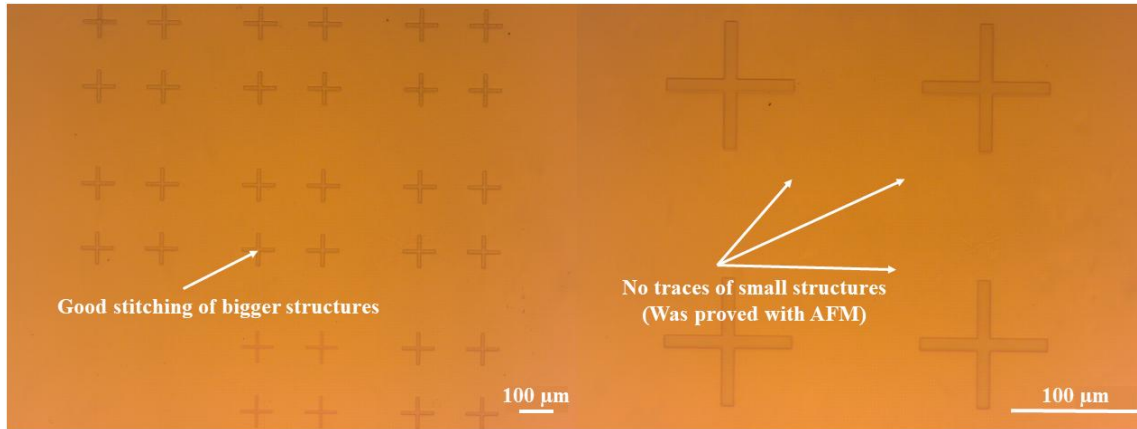


Figure 4.11 (left) Good development, bigger structures are remaining on the sample without deforming. (right) Small structures are missing, was proved by using AFM.

As lithography and development with prior use of polymer layer AR 300-80 seems to get improved, another test was done with same parameters for preparing sample spin coating Medusa 82 at 3000 RPM for 60 seconds, then soft bake was done on hot-plate at 150 °C for 10 minutes. The lithography was performed this time in a wider range of doses from $30 \mu\text{C}/\text{cm}^2$ to $150 \mu\text{C}/\text{cm}^2$ with the step of $15 \mu\text{C}/\text{cm}^2$. The difference was made only by using the developer AZ 726 MIF. The result was not satisfying as even big structures were deformed and moved. The result is shown in Figure 4.12.

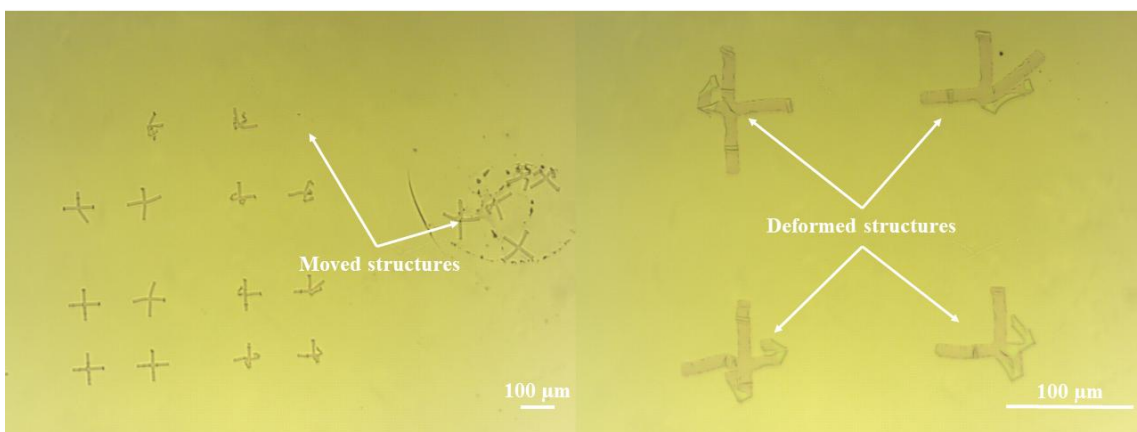


Figure 4.12 (left) Good development no residue remaining, but bigger structures moved due to bad stitching to the surface. (right) Deformed big structures due to bad stitching of resist to the surface.

The last test of Medusa 82 was done with adding on top of Au layer a thin layer (5 nm) of Ti and slightly changing the pattern for the dose test by adding bigger structures in the

shape of a dot with contacts, comparing to the previous tests. After that sample was spin coated with Medusa 82 at 3000 RPM for 60 seconds, then soft bake was done on hot-plate at 150 °C for 10 minutes. The lithography was performed this time range of doses from $40 \mu\text{C}/\text{cm}^2$ to $120 \mu\text{C}/\text{cm}^2$ with the step of $10 \mu\text{C}/\text{cm}^2$. The developer which was used is AZ 726 MIF. The result was much better but the smallest structure which stayed on Ti was around 500 nm (originally 250 nm in pattern with huge overdose), smaller structures (100 nm in pattern) were not found at all (was proved by AFM). The result is shown on Figure 4.13.

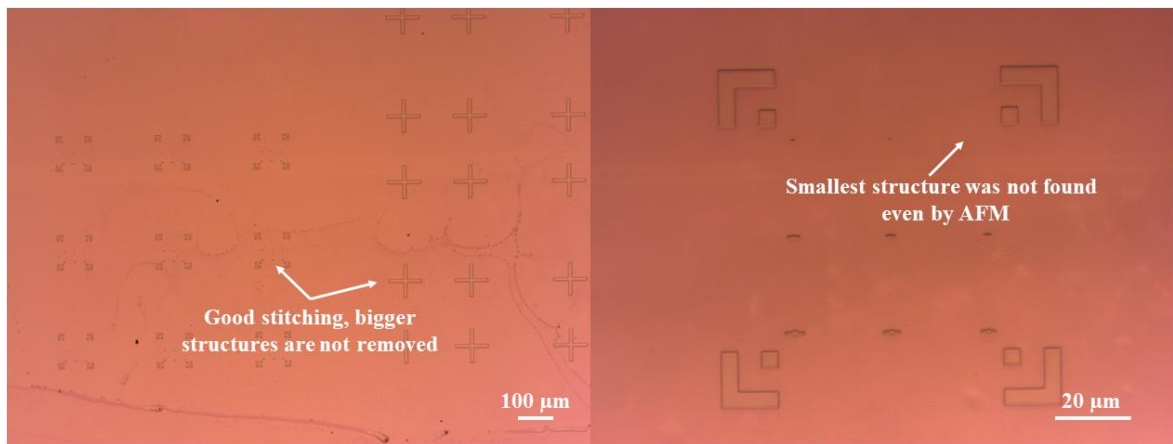


Figure 4.13 (left) Good development no resist residue remaining, bigger structures have good stitching to the surface. (right) smallest structure which stayed on Ti was around 500 nm (originally 250 nm in pattern with huge overdose), smaller structures (100 nm in pattern) were not found at all (was proved by AFM).

Another e-beam resist named AR-N 7520 was tested for the desired device features. All lithography was done in RAITH 150 TWO at 20 kV, with working distance focused on 10 mm and aperture size 15 μm. The first test was done with spin coating AR-N 7520.17 and diluted AR-N 7520.17 to match the properties of AR-N 7520.07 at 4000 RPM for 60 seconds, then soft bake was done on hot-plate at 85 °C for 60 seconds. The lithography was performed in the range of doses from $45 \mu\text{C}/\text{cm}^2$ to $85 \mu\text{C}/\text{cm}^2$ with the step of $5 \mu\text{C}/\text{cm}^2$. The developing process was done with the use of developer AR 300-46. After the development process and examination of the results in AFM, it was found out that the bottles with resist was most probably contaminated as lots of small particles was found out on surface and on the patterned structures. Figure 4.14 shows the

result after developing process for AR-N 7520.17 and Figure 4.15 shows the result after developing process for AR-N 7520.07.

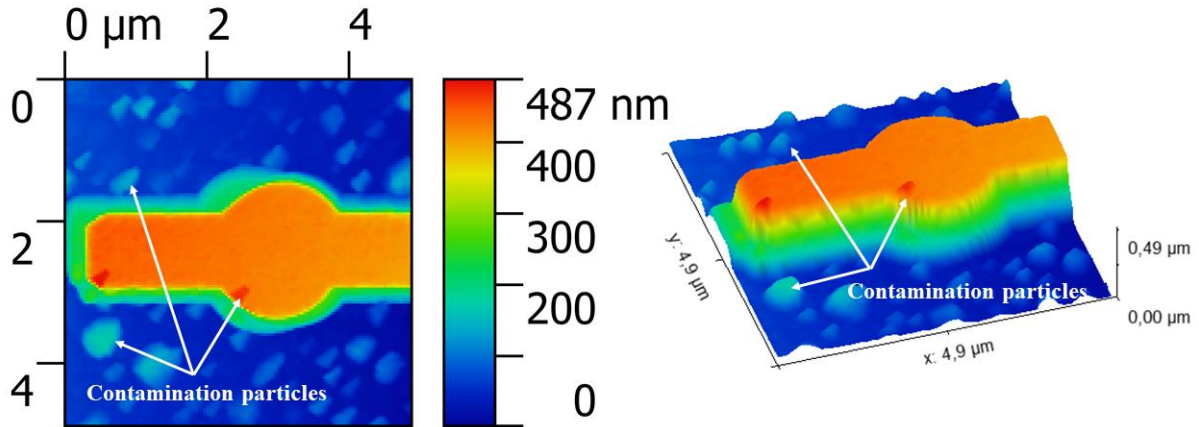


Figure 4.14 (left) shows the result after developing process for AR-N 7520.17 for the dose of $80 \mu\text{C}/\text{cm}^2$ measured by AFM. (right) 3D view of measured area.

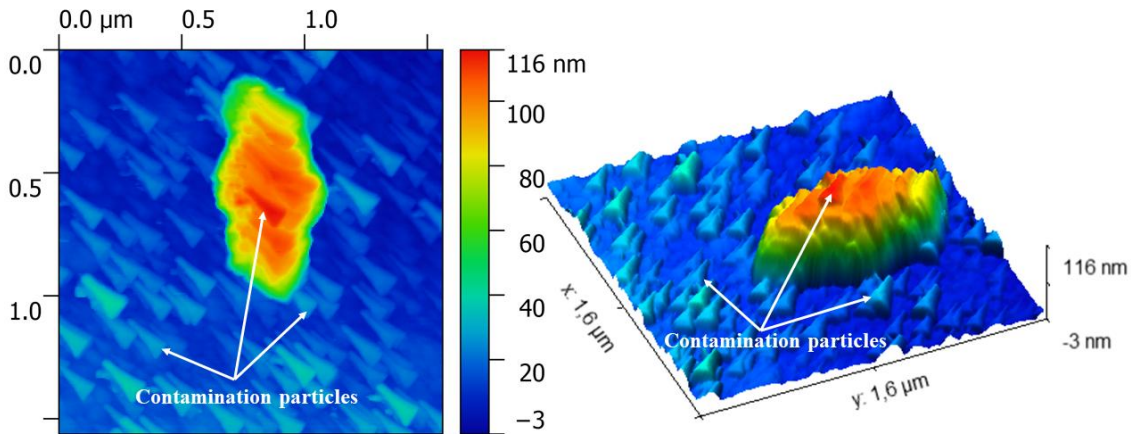


Figure 4.15 (left) shows the result after developing process for AR-N 7520.07 for the dose of $80 \mu\text{C}/\text{cm}^2$ measured by AFM. (right) 3D view of measured area.

As the e-beam resist was contaminated and it was not possible to make a conclusion if this resist is suitable for fabricating our structures from the previous test we requested for the filtration of e-beam resists and after repeating the dose test for both variation of e-beam resist AR-N 7520 with the same parameters. The results were much better as it is shown on Figure 4.16 for e-beam resist AR-N 7520.17 and on Figure 4.17 for e-beam resist AR-N 7520.07. It is visible that filtration of e-beam resists greatly helped in removing particles from contamination. Only some small roughness could be

detected on the sample with AR-N 7520.07, but it did not ruin the pattern of the structure as it was seen previously.

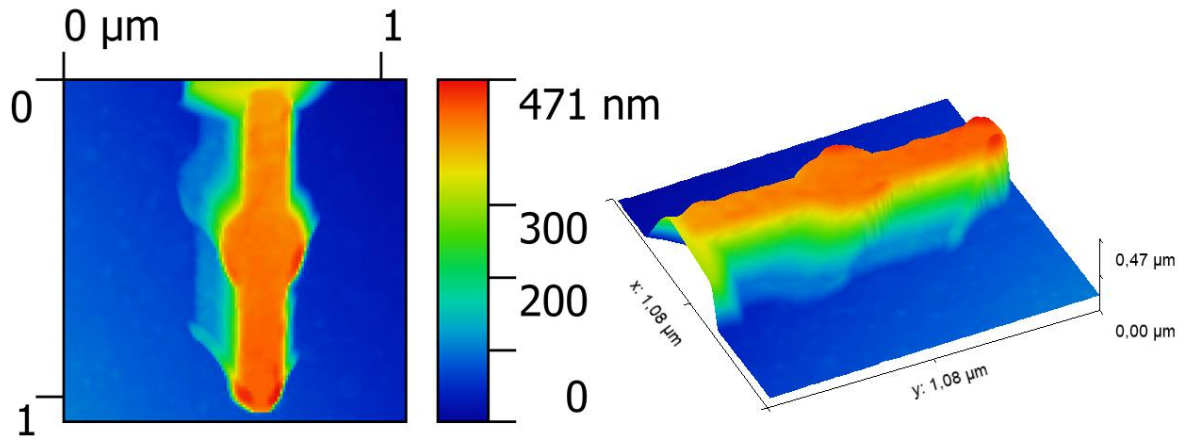


Figure 4.16 (left) shows the result after developing process for AR-N 7520.17 for the dose of $80 \mu\text{C}/\text{cm}^2$ measured by AFM. (right) 3D view of measured area.

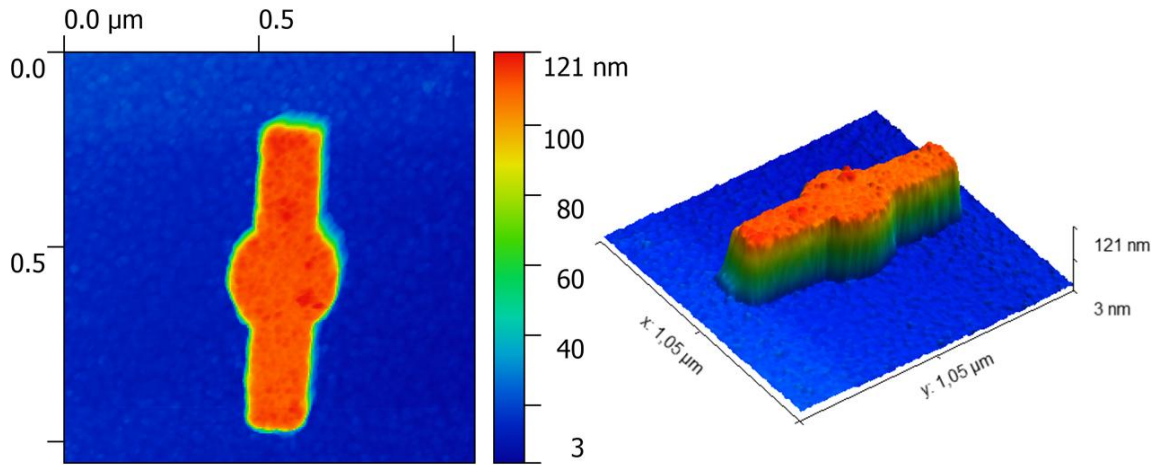


Figure 4.17 (left) shows the result after developing process for AR-N 7520.07 for the dose of $80 \mu\text{C}/\text{cm}^2$ measured by AFM. (right) 3D view of measured area.

Further dose tests were carried out using only e-beam resist AR-N 7520.07 as after spin coating at 4000 *RPM* the thickness of the resist is roughly around 100 nm which leads to more controllable process of e-beam lithography. Any difference in preparation process can lead to the change in the required dose for lithography. Previously we were getting our structures bigger than they were originally in the pattern, so it was decided to adapt the preparation process and use same process for the future tests. The sample was

spin coated with e-beam resist AR-N 7520.07 at 4000 RPM and SB was done at 85 °C on hot plate for 90 seconds. The lithography was performed in the range of doses from $45 \mu\text{C}/\text{cm}^2$ to $85 \mu\text{C}/\text{cm}^2$ with the step of $5 \mu\text{C}/\text{cm}^2$. The pattern was also adapted to make the dose test on the array quantum dots Figure 4.18.

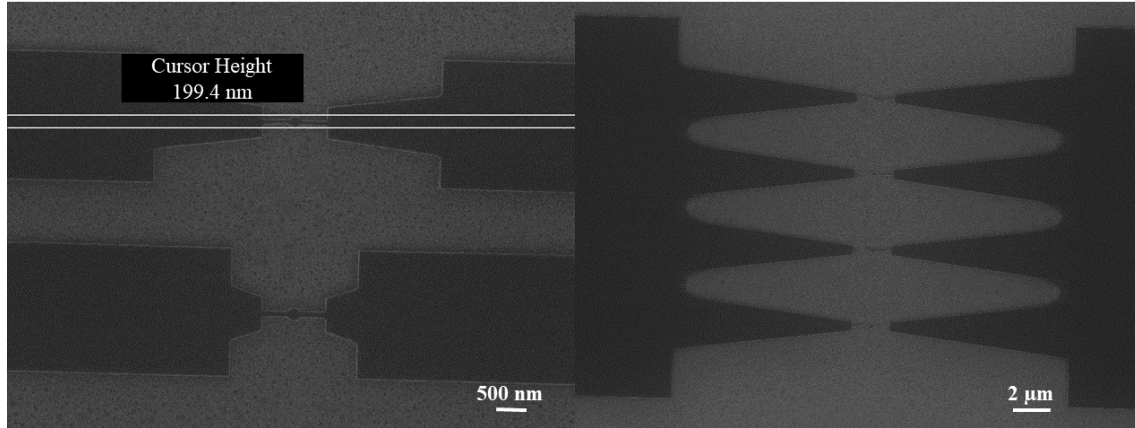


Figure 4.18 (left) SEM image of the quantum dot device made from negative resist AR-N 7520.07 with different sizes of bow-tie shape connected to the quantum dot. The Dose is $60 \mu\text{C}/\text{cm}^2$ (right) SEM image of the array of quantum dots device made from negative resist AR-N 7520.07 at the dose of $60 \mu\text{C}/\text{cm}^2$.

We attempted to employ hydrogen silsesquioxane (HSQ) negative resist for e-beam lithography, but, due to its intricate handling and the numerous challenges encountered, we stopped our attempts to utilize HSQ.

The dose experiments performed and outlined above were carried out for the nanofabrication process, which entails applying a thin layer of Au onto the sample beforehand. As a result, we encountered an issue during the fabrication process on CVD graphene already transferred onto a SiO_2/Si wafer obtained from Graphenea (Spain). The low adhesion between the CVD graphene layer and the metal layer caused the metal layer to detach after only one minute in the solution, leading to its loss during the lithography step and subsequent development procedure. In order to address this problem, CVD graphene was employed on Cu foil and subsequently transferred onto the chips during the final stages of nanofabrication. The doses obtained from previous studies on the Au layer were also appropriate for SiO_2/Si samples without a metal covering. The procedure of covering with an Au layer prior to manufacturing is still suitable for samples with epitaxial graphene on SiC.

Sample preparation

The 4" wafer SiO_2/Si was covered with protective layer of resist AR-P 679.04 (PMMA 950 K) which was spin coated for 60 s at 4000 *RPM* and left for drying overnight without soft bake (SB) to prevent contamination from dust and small particles during laser cutting Figure 4.19. The wafer was precut for small samples with dimensions of $8 \times 8 \text{ mm}$ by using Oxford Lasers A-Series Laser dicer. Precut was done at 10 *kHz* using 35% of Power with speed 6 *mm/s* repeating 3 passes in total.

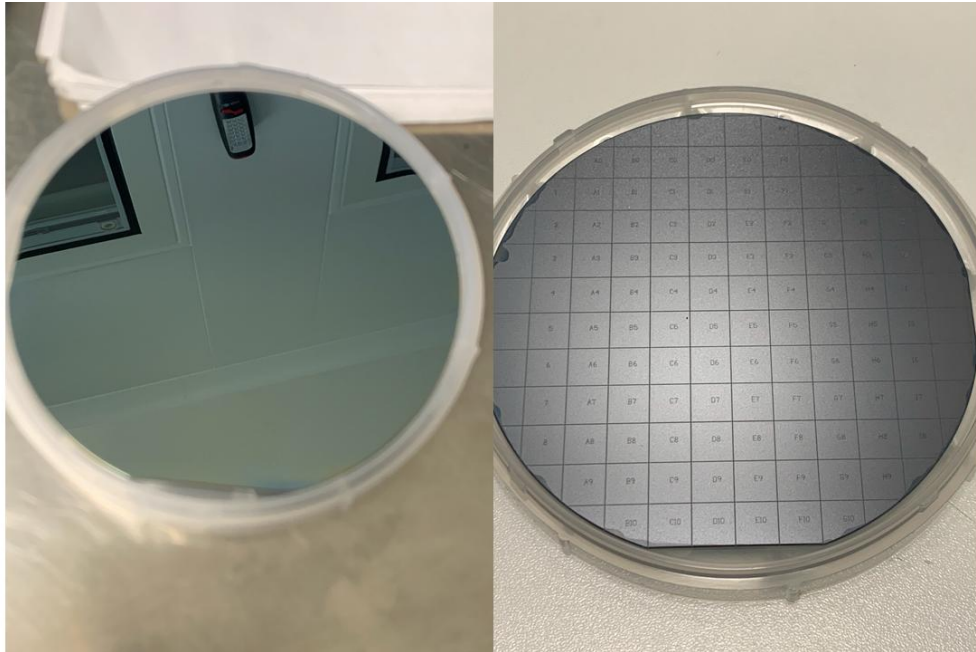


Figure 4.19: (left) 4" SiO_2/Si wafer covered with AR-P 679.04 resist. (right) Backside of the 4" SiO_2/Si wafer after precut and engraving was done.

After dividing wafer into smaller samples, cleaning procedure was done. The cleaning involved 5 min in acetone, 5 min in methanol, 5 min in isopropanol (IPA), 10 min in Deionized water (DI) (AMIW cleaning). For better result, during the cleaning procedure ultrasonic bath was included. And in the end, O_2 plasma cleaning was used in RIE-FLUORINE for 5 *min* at 50 *W* power with an O_2 flow of 20 *sccm* at 40 *mTorr* pressure.

Spin-coating

After the cleaning procedure, for the first step of lithography the samples were spin coated with a $\sim 80\text{--}145\text{ nm}$ thick films of double layer polymers (AR-P 639.04 and AR-P 649.04 PMMA) resists by spinning at 4000 RPM 60 s and then SB at $180\text{ }^{\circ}\text{C}$ for 60 s for both on a hot-plate. For the second step of lithography samples were spin coated with $\sim 1.4\text{ }\mu\text{m}$ thick film of photoresist (AZ 1514 H) by spinning at 4000 RPM 60 s and the SB at $100\text{ }^{\circ}\text{C}$ for 90 s on a hot-plate. Third step lithography was done with a $\sim 80\text{--}100\text{ nm}$ thick films of double layer resists, involving positive resist on the bottom and neqgative resist on the top (AR-P 639.04 and AR-N 7520.07) by spinning at 4000 RPM 60 s and then SB at $180\text{ }^{\circ}\text{C}$ for 60 s on a hot-plate for the bottom layer and by spinning at 4000 RPM 60 s and then SB at $85\text{ }^{\circ}\text{C}$ for 60 s on a hot-plate for the bottom layer accordingly. There was no post-baking involved in any of three steps.

Electron-beam lithography and photolithography

Electron beam lithography is used to pattern the devices. In this process, the double layer of PMMA is exposed with an electron-beam at a dose of $\sim 300\text{ }\mu\text{C}/\text{cm}^2$ for the first step of lithography.

The chip is placed in RAITH 150 TWO the high-resolution low voltage electron beam lithography system. The chip is then patterned with metal contacts on which later would be transferred CVD graphene, as well as alignment marks and marks for next steps of lithography. All the devices are designed to be closer to the center of the chip where the resist layer is the flattest, if compared with the corners. The $15\text{ }\mu\text{m}$ aperture is used and must be optimally focused. After writing the patterns, the chip is developed by placing it in developer AR 600-56 for 60 seconds . It is then placed in IPA for 30 seconds to stop the development and dried with nitrogen spray. It is inspected under an optical microscope to verify there were no major issues with the pattern writing Figure [4.20](#).

Following the completion of procedures such as metal deposition, lift-off and new resist spin coating and SB the sample is ready for the second step of lithography. This step is done by photolithography to speed up the process as bigger structures are prepared.

The photoresist AZ 1514 H undergoes exposure through direct laser writing, with a dosage of around $200 \mu\text{C}/\text{cm}^2$

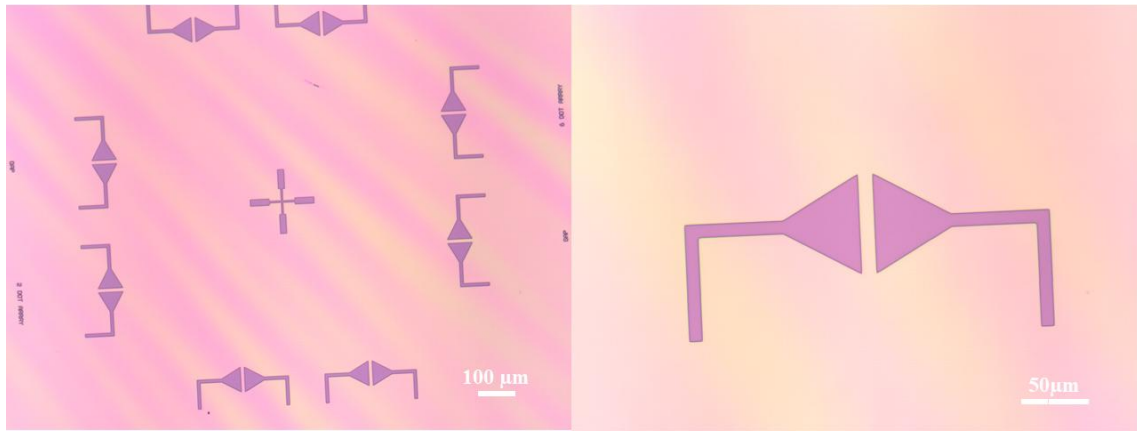


Figure 4.20: (left) Shows the sample after the first step of lithography and development, before metal deposition. (right) Increased view of the fingers which were done by e-beam lithography and developed.

The chip is inserted into the ML3 Baby MicroWriter a photolithography machine designed for rapid prototyping and small-volume manufacturing in R&D laboratories and clean rooms. Utilizing the previously created structures for the second step lithography, we establish the precise location for the placement of our metal pads. After writing the patterns, the chip is developed by placing it in developer AZ 726 MIF for 60 seconds. It is then placed in DI water for 30 seconds to stop the development and dried with nitrogen spray. It is inspected under an optical microscope to verify there were no major issues with the pattern writing Figure 4.21. Based on the photos, there are apparent remnants of resist residue in certain regions after the development process. To ensure proper bonding of metal to the surface during further fabrication steps, it is necessary to clean the surface using O_2 plasma.

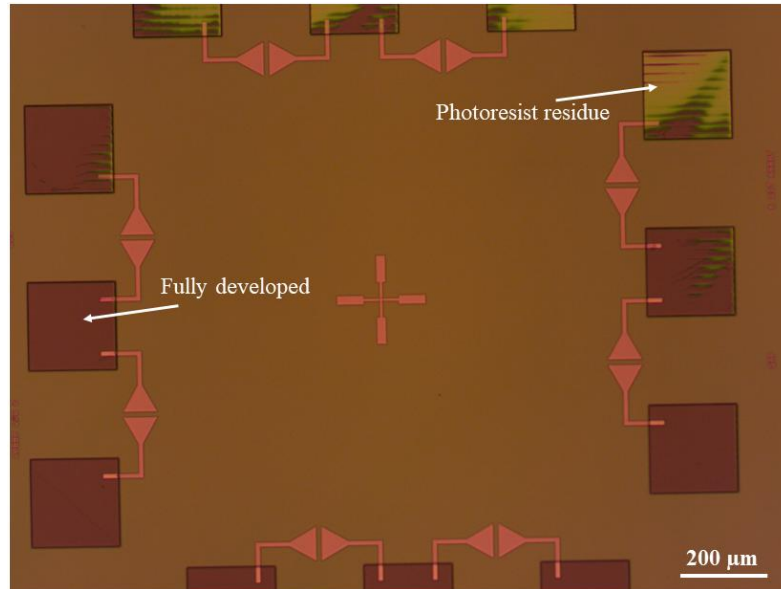


Figure 4.21: Shows the sample after the second step of lithography and development, before metal deposition, with developed areas and with areas with photoresist residue.

The third step of lithography is done by RAITH 150 TWO. In this step, the double layer of PMMA on bottom and AR-N 7520.07 is exposed with an electron-beam at a dose of $\sim 60 \mu\text{C}/\text{cm}^2$.

The chip is then patterned with the bow-tie shapes that will form the graphene quantum dots arrays, between the two metal contacts. The $15 \mu\text{m}$ aperture is used and must be optimally focused to achieve the small features of the quantum dot. After the lithography is done, the chip is developed by placing it in developer AZ 726 MIF for 60 seconds and then placed in DI water for 30 seconds to stop the development and lightly dried with nitrogen spray to not break the tiny parts which connects the quantum dots with bow-tie shapes. Later it is inspected under an optical microscope to verify there were no major issues with the pattern writing. However, the optical microscope cannot see the small features, which are more likely to have problems. The chip can be imaged under the SEM at this point to see the small features written in the resist, but even then, what appears under the SEM to be a well-defined feature in the surface of the resist may result in badly defined feature once the shaping by dry etching is done as shown in Figure 4.22. As such, this inspection is typically skipped.

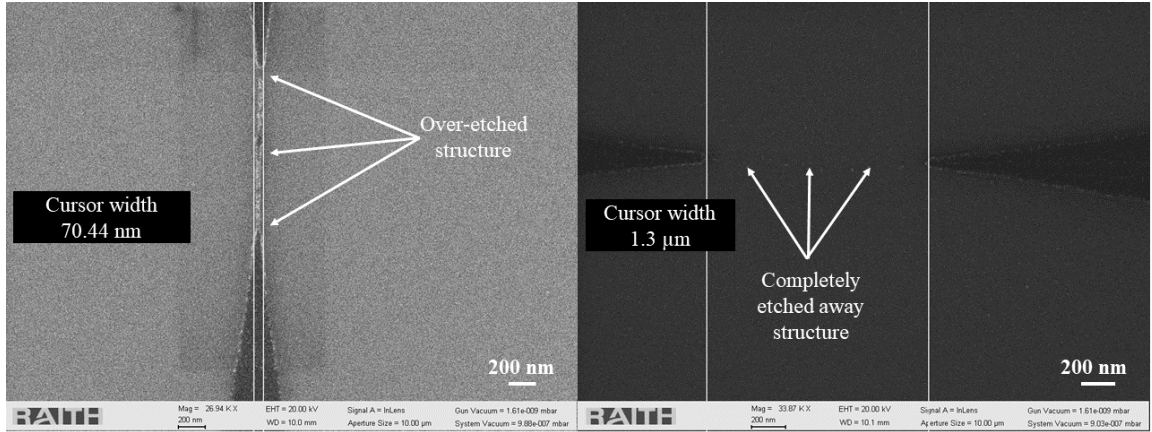


Figure 4.22: (left) Shows the over-etched structure, the connection between the quantum dot and bow-tie shapes of CVD graphene was damaged. (right) Completely etched away quantum dot with stripes which connected quantum dot to bow-tie shape CVD graphene.

Electron-beam evaporation

Devices are loaded into the metallization chamber after patterning contacts and with prior use of O_2 plasma etching in RIE-FLUORINE for 15 s to burn any possible residue of resist to guarantee good stitching between metal and substrate for following lift-off process. The physical vapor deposition technique of electron-beam evaporation is used after the first and second steps of lithography. In electron beam evaporation, a crucible containing metal is heated using an electron-beam to eject metal in gaseous form. This assembly sits in a high vacuum chamber, and the substrate located directly in-sight of the crucible gets coated by the precipitated solid metal film. After the first step of lithography, a thin layer of titanium (Ti) of 3 nm thickness was evaporated with following 20 nm of gold (Au) layer with a growth rate of $\sim 0.7 \text{ \AA/s}$ and $\sim 1 \text{ \AA/s}$ accordingly. After the second step of lithography, the layers of Ti\Cu\Au were deposited with the thickness of 5\200\20 nm accordingly. The growth rate was $\sim 0.7 \text{ \AA/s}$ for Ti, $\sim 1 \text{ \AA/s}$ for copper (Cu) and $\sim 1 \text{ \AA/s}$ for Au. Figure 4.23 shows the sample after the first step of lithography with deposited thin layer of metal before lift-off processes was done.

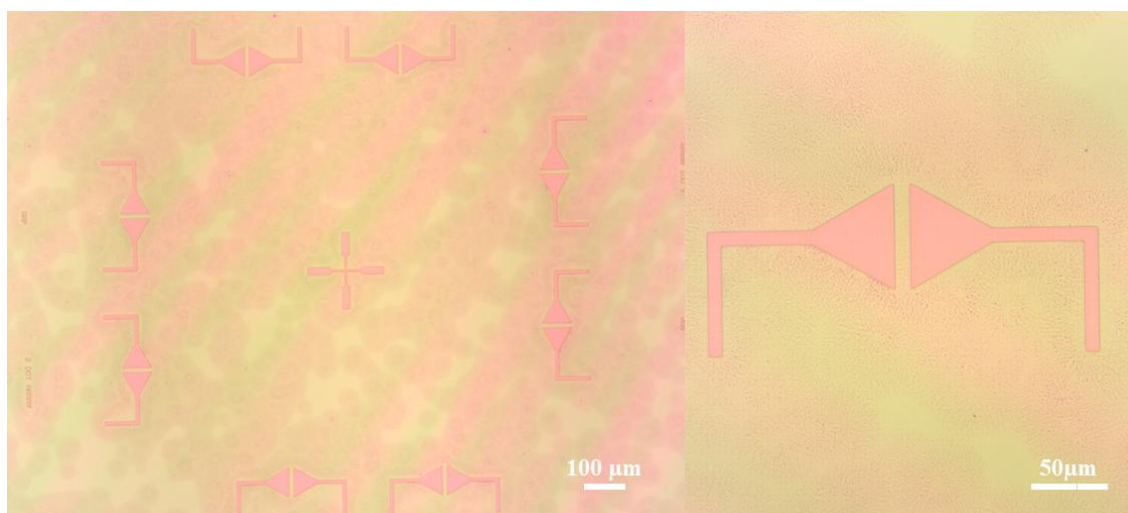


Figure 4.23: (left) Shows the sample after first step of lithography with deposited thin layer of metal ($3\sqrt{20\text{ nm}}$) before lift-off processes was done. (right) Increased view of the fingers which were done by e-beam lithography with deposited metal ($3\sqrt{20\text{ nm}}$) before lift-off process.

Lift-off process

Metal lift-off is a microfabrication technique used to create a pattern by applying a thin metal film onto a resist that has been designed with a certain overcut profile. The resist is then dissolved using a solvent, leaving behind only the metal in the desired pattern on the substrate. The lift-off method was used to selectively remove the metal that had evaporated onto the resist on the sample, leaving it solely in the regions where patterns were created using lithography. The sample was immersed in acetone for a minimum of 3 hours. Subsequently, it was subjected to ultrasonic treatment for 1 minute and finally rinsed with IPA to eliminate any metal residues. The sample was then dried using a stream of nitrogen. Figure 4.24 depicts the sample following the lift-off operation in the initial and subsequent stages of lithography.

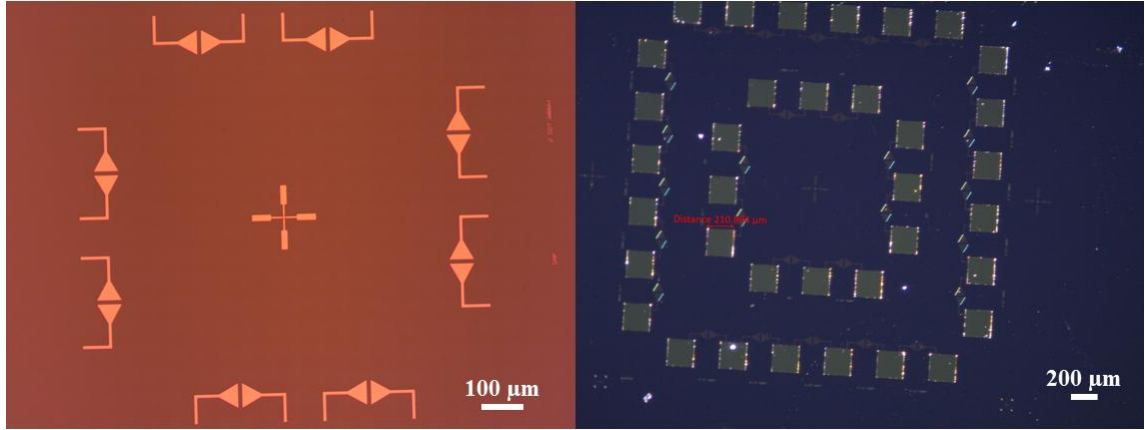


Figure 4.24: (left) Shows the sample after lift-off procedure for the first step of lithography. (right) Shows the sample after lift-off procedure for the second step of lithography.

Transfer of CVD graphene

We utilized CVD graphene on a copper substrate, which was acquired from Graphenea (Spain), for the production of our nanodevices. The CVD graphene on a copper substrate was coated with PMMA 950K at a speed of 2000 *RPM* without the use of a SB and allowed to dry for a period of 24 hours. Once the PMMA layer had dried, the substrate was placed into a RIE-FLUORINE system, with the Cu layer positioned on top. The substrate was then subjected to O₂ plasma etching at a power of 50 *W* with an O₂ flow rate of 20 *sccm* and a pressure of 40 *mTorr* for a duration of 2 minutes. This process was carried out to eliminate any resist material that may have come into contact with the bottom of the Cu layer during the spin coating process. After completing the cleaning procedure, we used sharp scissors to cut the Cu substrate to the dimensions that are necessary for us. The sliced substrates were immersed in a solution of $Fe(NO_3)_3 \cdot H_2O$ to remove the copper from the graphene and PMMA. The substrates were left in the solution for a duration of 20 minutes. After etching the Cu, the substrates are immersed in DI water. This procedure is repeated three times, with each repetition involving the use of fresh DI water, to guarantee complete removal of the etchant solution. The subsequent approach involves immersing our substrates in hydrochloric acid (HCl) for a duration of 10 minutes and then repeating the same process with deionized water as done previously. It should be noted that distinct clean SiO₂/Si samples were utilized for transferring substrates in HCl solution and in water. Following the cleaning process in deionized

water, our substrates were transferred to the samples that had undergone lithography stages. CVD graphene was then placed in the center of the sample, directly on top of the prepared metal contacts. Subsequently, the samples were placed on a hot plate and allowed to dry for a duration of 2 minutes at a temperature of 100 °C. A few drops of PMMA 50K were applied over the CVD graphene, which was already covered with PMMA 950K, in order to push it against the substrate. Spin coating was not used in this process. In order to eliminate all PMMA layers, our samples were immersed in acetone for a duration of 90 minutes. Subsequently, they were transferred to IPA and then to ethanol. The samples were held in both solutions for a period of 1 minute each. Following the completion of all the necessary procedures, we now possess samples containing CVD graphene that are prepared for examination using Raman spectroscopy. This examination is crucial in order to verify the outcome and proceed with the third stage of lithography. Figure 4.25 displays the sample containing CVD graphene that has been placed onto metal contacts. Graphene in certain regions experienced damage during the transfer process, but it remains intact in the areas where the lithography phase would be performed to shape our devices.

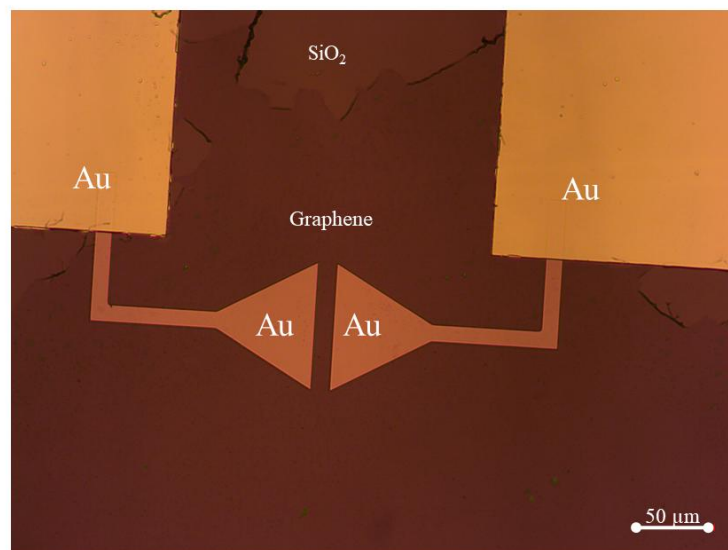


Figure. 4.25: shows the sample with transferred CVD graphene on metal contacts.

Plasma etching

After transferring the CVD graphene onto the sample and structuring the devices by the third step of lithography, an additional stage of reactive oxygen plasma etching is carried out for the CVD graphene devices. This is done in order to obtain from transferred CVD graphene area from the large flakes to the shape of our nanodevices. Typical plasma etching is done at 20 W power with an O₂ flow rate of 20 sccm at 40 mTorr pressure for 70 s. We selectively etch the PMMA layer and graphene layer around the sample, excluding our graphene devices, which are safeguarded by a negative resist AR-N 7520.07 layer on top of the PMMA. Figure 4.26 shows images taken from optical microscope and SEM of our nanodevices.

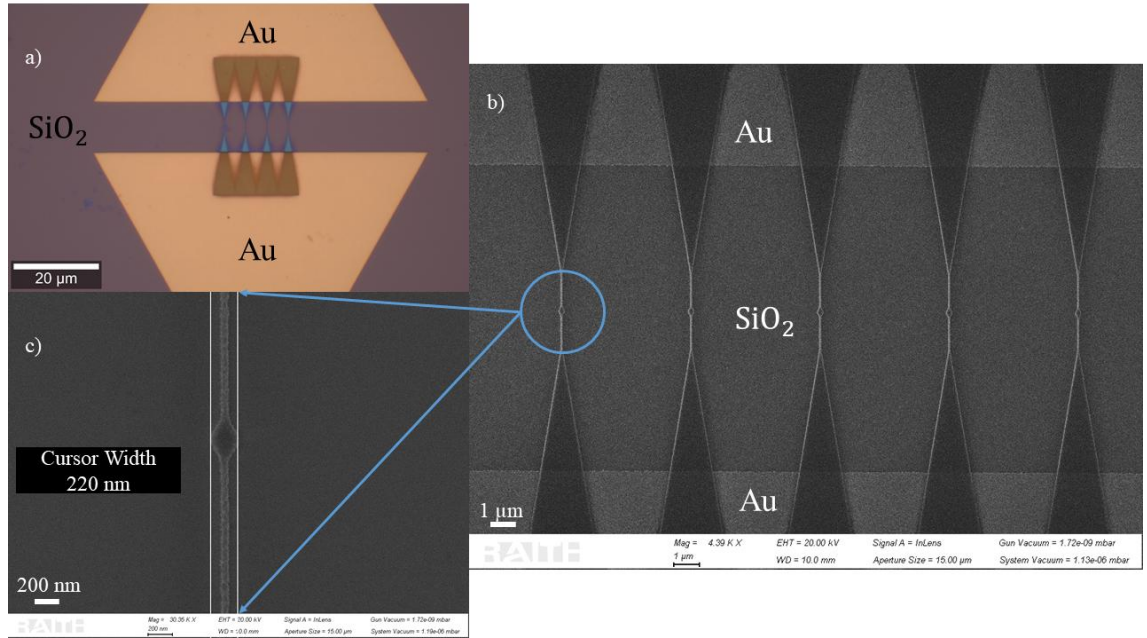


Figure 4.26: (a) Image from optical microscope of the sample with 4 dots array bolometers device shaped by e-beam lithography and after reactive oxygen plasma etching. (b) Image from SEM of the sample with 5 dots array bolometers device shaped by e-beam lithography and after reactive oxygen plasma etching. (c) Image from SEM with increased magnification showing one dot from the 5 dots array bolometers device.

Final steps

Once graphene has been shaped by the process of dry etching, the array of quantum dot bolometers is prepared. Prior to use, the objects need to be mounted in order to establish a connection with the instruments employed for measuring purposes. A chip expander is created by mounting a SiO₂/Si chip containing graphene devices onto a circuit

board using silver paste. The gold pads on the chip are connected to the pads on the chip expander using wire bonding, which allows for electrical connection between the devices through the pins on the chip holder when the chip expander is placed on top of it. Figure 4.27 shows a SiO₂/Si chip with a graphene array of bolometers that have been installed and wire bonded on a chip expander. The chip expander is then positioned on a chip holder. The chip is now prepared for insertion into the probe and connection to the electrical transport measurement devices via pin connectors.

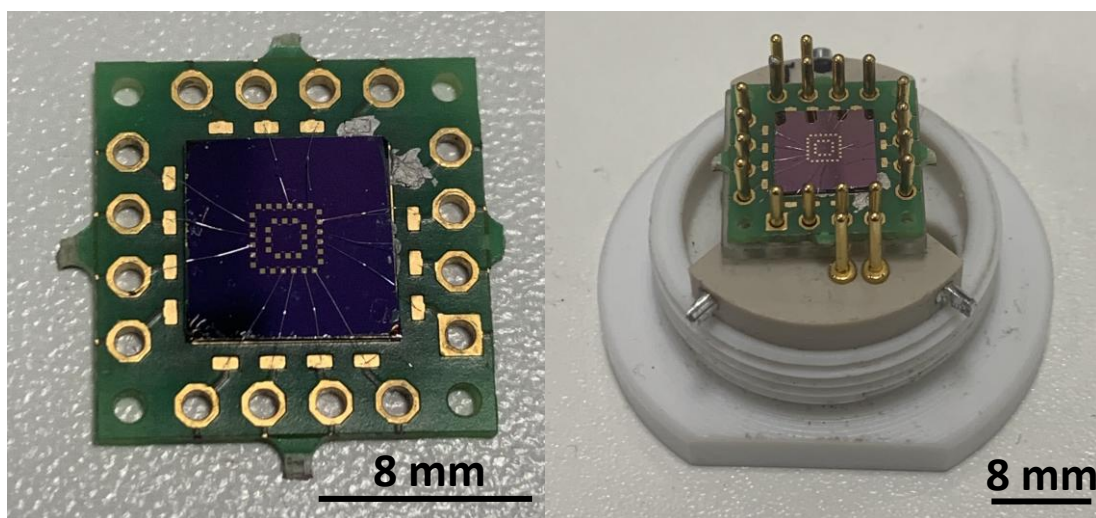


Figure 4.27: (left) SiO₂/Si chip mounted on chip expander. The graphene devices are too small to see, but gold contact pads are visible on the chip, with thin wires connecting them to connectors on the chip expander. (right) Expander with SiO₂/Si chip placed on chip holder.

4.3 Conclusion

This chapter presents a comprehensive overview of the fabrication process for CVD graphene-based quantum dot bolometers, focusing on advanced nanolithography techniques, material deposition, and etching protocols. The fabrication flow begins with substrate preparation, including spin-coating of protective resists and laser dicing, followed by sequential lithographic steps integrating both electron beam lithography (EBL) and photolithography. Detailed characterization and optimization of e-beam resists, such as Medusa 82 and AR-N 7520, are discussed through systematic dose testing. The chapter highlights the critical role of resist adhesion, developer chemistry, and the underlying substrate in achieving nanoscale feature resolution.

Special attention is given to the nanofabrication of multi-dot quantum architectures, including challenges encountered during the dose optimization phase and resist residue elimination. The patterning of quantum dot arrays is achieved using high-resolution EBL and optimized development processes. Subsequent steps involve precise electron-beam evaporation of multilayer metal contacts, lift-off, and transfer of CVD graphene using PMMA-assisted wet transfer. Reactive ion etching (RIE) is employed to shape the transferred graphene into nanoscale devices. The final integration includes wire bonding to chip expanders for electrical measurement readiness.

5. Characterization techniques

5.1. Raman spectroscopy

Raman spectroscopy is a powerful technique for investigating a wide range of materials¹⁰⁸. This spectroscopy was described by C. V. Raman and his colleague K. S. Krishnan in 1928¹⁰⁹. The sample is subjected to photon illumination using a focused laser beam, and the photons that are scattered inelastically are gathered and examined. The difference in wavelength between the photons that are transmitted and the photons that are scattered offers information about the phonon modes that exist in the sample. The Raman spectrum depicts the intensity of photons that have been scattered inelastically, in relation to the change in their wavelength (known as Raman shift).

Graphene has a Raman spectrum with three distinct peaks as shown in Figure [5.1](#). The G peak, which represents the zone's core mode, is also present in other carbon-based materials. The 2D peak is caused by the scattering of phonons at the edge of the zone [ref]. The D peak arises from single-phonon scattering events and corresponds to the same zone border phonons as the 2D peak. The pristine graphene lattice does not exhibit single-phonon scattering. However, in the presence of defects or along the edges of graphene, the disruption of symmetry allows for the occurrence of single-phonon scattering.

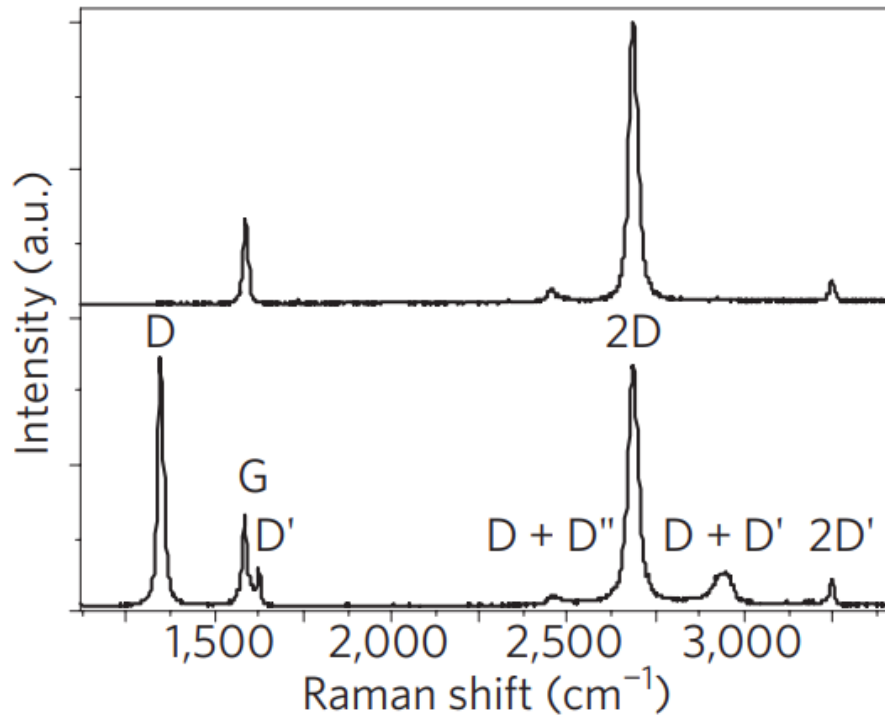


Figure 5.1 Raman spectra of pristine (top) and defected (bottom) graphene. The main peaks are labelled¹¹⁰

Raman spectroscopy is quite useful for characterizing graphene samples. The D peak's intensity serves as an indicator of the density of faults in the lattice. Mechanical strain causes a displacement of the G peak from its initial position, enabling the estimation of potential deformations in the sample. In the case of multilayer graphene, the 2D peak undergoes a splitting phenomenon, resulting in several components that collectively resemble a single asymmetric peak. This allows for the differentiation between monolayer graphene and multilayer graphene without the need to create electrical devices.

As CVD graphene was bought from Graphenea (Spain), we were ensured that it was monolayer graphene on Cu foil before the transfer. But after the transfer of graphene, we have to check the result by Raman spectroscopy, Figure 5.2 black line. Second Raman spectroscopy was performed after all fabrication steps to check the presence and quality of GQDs between the contact pads, as presented in Figure 5.2 with red line. These measurements are performed with a WiTec Alpha 300R combination microscope using a 532 nm wavelength laser, situated at the Central European Institute of Technology (CEITEC) in CEITEC Nano cleanrooms.

Spectra for single-layer graphene are shown in Figure 5.2, the identifying characteristic being the 2D peak at $\sim 2700 \text{ cm}^{-1}$ wavelength. The 2D peak in a single layer graphene is sharper and of higher intensity than the G peak at $\sim 1580 \text{ cm}^{-1}$. The G peak corresponds to a first-order Raman scattering process involving the doubly degenerate in-plane longitudinal and transverse optical phonon modes at the Γ point. The 2D peak is a result of a second-order process involving two transverse optical phonons at the K point of the first Brillouin zone. The strong Raman signals and the peak ratio $I_{2D}/I_G \sim 2$, as shown in Figure 5.2 with red line, demonstrate that the quality of graphene remains intact after all fabrication steps.

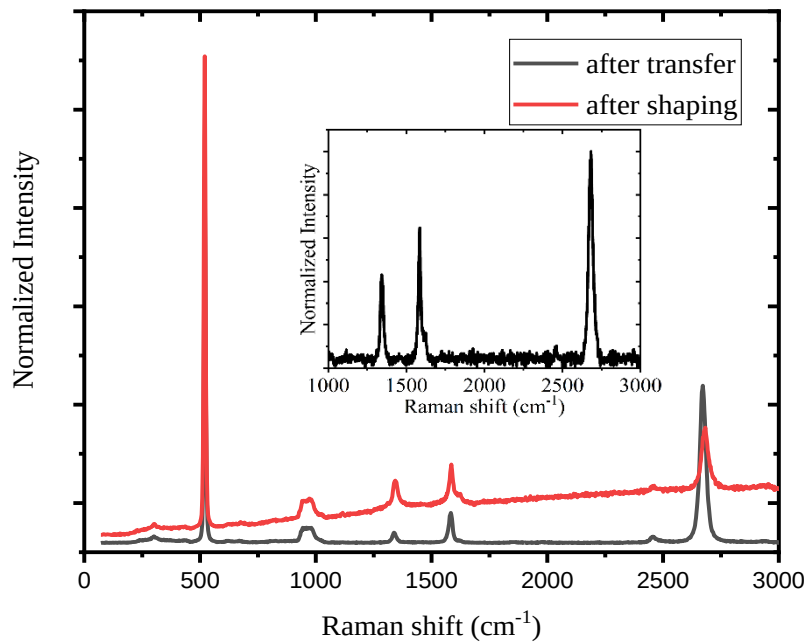


Figure 5.2: shows the Raman spectra of CVD graphene after transfer process with black line and the Raman spectra of CVD graphene after covering with resist and shaping by dry etching process with red line. Input shows the same Raman spectra of CVD graphene as with red line just normalized and with corrected background.

5.2. Scanning electron microscopy

Scanning electron microscopy (SEM) is an analytical technique that utilizes a concentrated stream of high-energy electrons to produce various signals on the surface of the solid specimens it investigates.

The signals generated from the electron-sample interactions provide insights on several characteristics of the sample, including its exterior shape, chemical composition, crystalline structure, and material orientation. Typically, data is collected from a specific area of the sample's surface, and then a two-dimensional image is generated to depict the spatial differences in the sample's characteristics.

Electrons possess significant levels of kinetic energy when they are accelerated in a SEM process. The energy dissipates through a variety of signals generated by the interactions between electrons and the sample as the incident electrons slow down within the solid sample. The signals comprise secondary electrons (which provide SEM images), backscattered electrons (BSE), diffracted backscattered electrons (EBSD), photons (specifically X-rays used for elemental analysis and continuum X-rays), visible light, and heat. The signals are utilized to ascertain various details regarding the surface of the specimen. In SEM, the primary focus is on utilizing secondary electrons and backscattered electrons to generate the image of the samples. Secondary electrons primarily contribute to the production of shape and surface features, whereas backscattered electrons are utilized to analyze the variations in the composition of samples with several phases. Figure [5.3](#) shows a schematic depiction of the operational mechanism of the SEM.

SEM allows for a straightforward examination of the topographical properties of any material specimen through image processing and data analysis. The backscattered electron beam technique and diffracted backscattered electron techniques can be utilized to gain information about the crystal structure orientation and chemical compositions of specimens. SEM is a highly used method for analyzing the surfaces of materials.

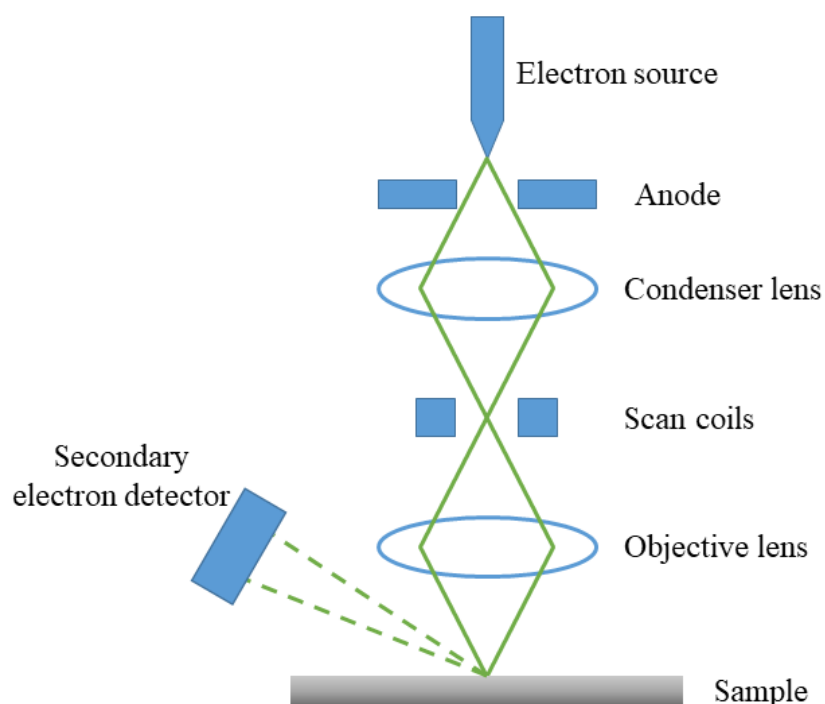


Figure 5.3 Schematic image of SEM working principle.

One drawback of SEM is that the samples must be appropriately sized to fit inside the chamber. In cases where this technique cannot identify low-pressure oxidizing samples or moist samples, such as organic compounds, sample compositions are crucial. Moreover, to enhance data analysis, the materials need to exhibit electrical conductivity or have conductive coatings.

5.3. THz FraScan Spectrometer

Figure 5.4 presents a comprehensive summary of the THz FraScan spectrometer situated at the research group 'Magneto-optical and THz Spectroscopy' at the Central European Institute of Technology (CEITEC), Brno University of Technology, in Brno, Czech Republic.

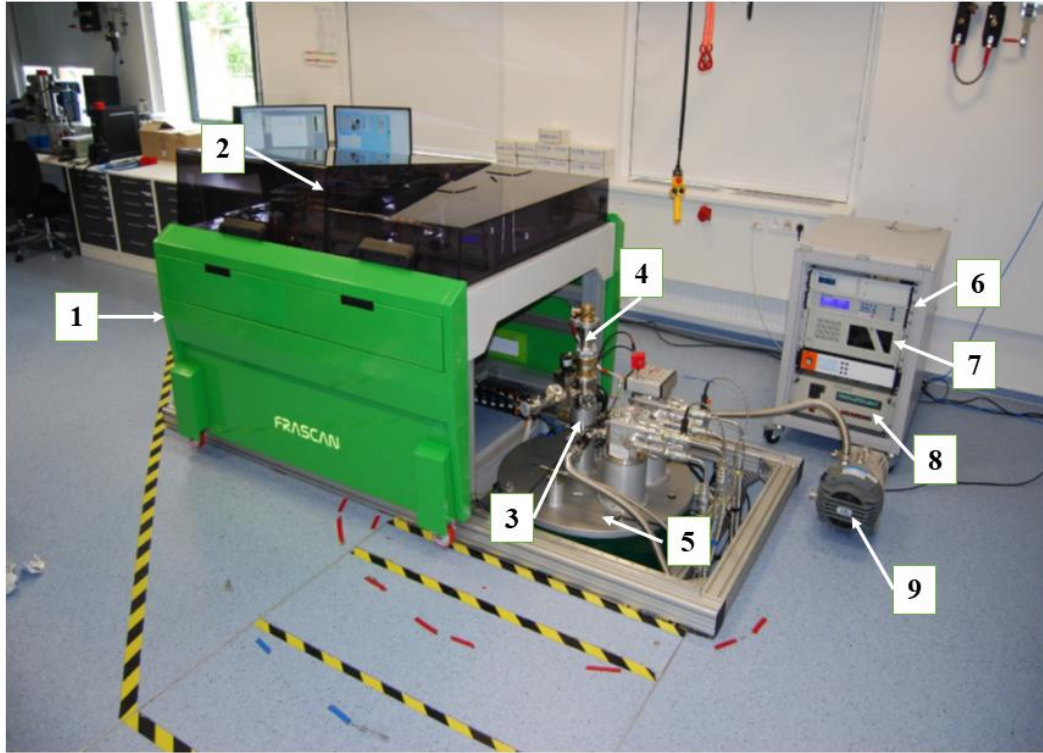


Figure 5.4: The photo shows the THz FraScan spectrometer situated at CEITEC, Brno University of Technology, Czech Republic. (1) Moving table. (2) QO components are enclosed under the protective shell. (3) The home-built airlock system of the variable temperature insert (VTI). (4) The electron paramagnetic resonance (EPR) probe loaded into VTI. (5) Superconductive cryogen-free magnet. (9) The VTI pump. The rack on the right side consists of a temperature control unit (6), the spectrometer's PC (7), and the magnet power supply (8).

The spectrometer contains a mobile table (1) that transitions into operational mode by sliding along the magnet frame rails. A protective Plexiglas cover sits on top of the table, concealing the quasi-optical (QO) components (2), along with the microwave (m.w.) sources and detectors. The configuration includes a microwave synthesizer that generates a fundamental frequency between 9 and 14 GHz. This signal can be multiplied to attain microwave frequencies of up to 1125 GHz, providing flexibility in selecting radiation parameters based on experimental needs. In operational mode, the magnet frame shifts to a specific position. The magnet frame moves until it connects the electron paramagnetic resonance (EPR) probe (4) with the microwave window to the QO table. To prevent air contamination in the pure helium environment, the home-built airlock system (3) places the EPR probe into the variable temperature insert (VTI) of the superconductive cryogen-free magnet. This magnet may generate magnetic fields of up

to 16 Tesla (5). A dry scroll pump (9) generates a continuous flow of helium in the closed-cycle VTI, maintaining a pressure of approximately 10 mbar in the sample region. The spectrometer's rack is opposite the magnet frame, housing a personal computer (PC) (7) responsible for overall operation of the spectrometer, the temperature control unit which offers accurate temperature control from 2 K to 320 K, guaranteeing thermal stability throughout the measuring process (6), the magnet power supply (8), and other equipment.

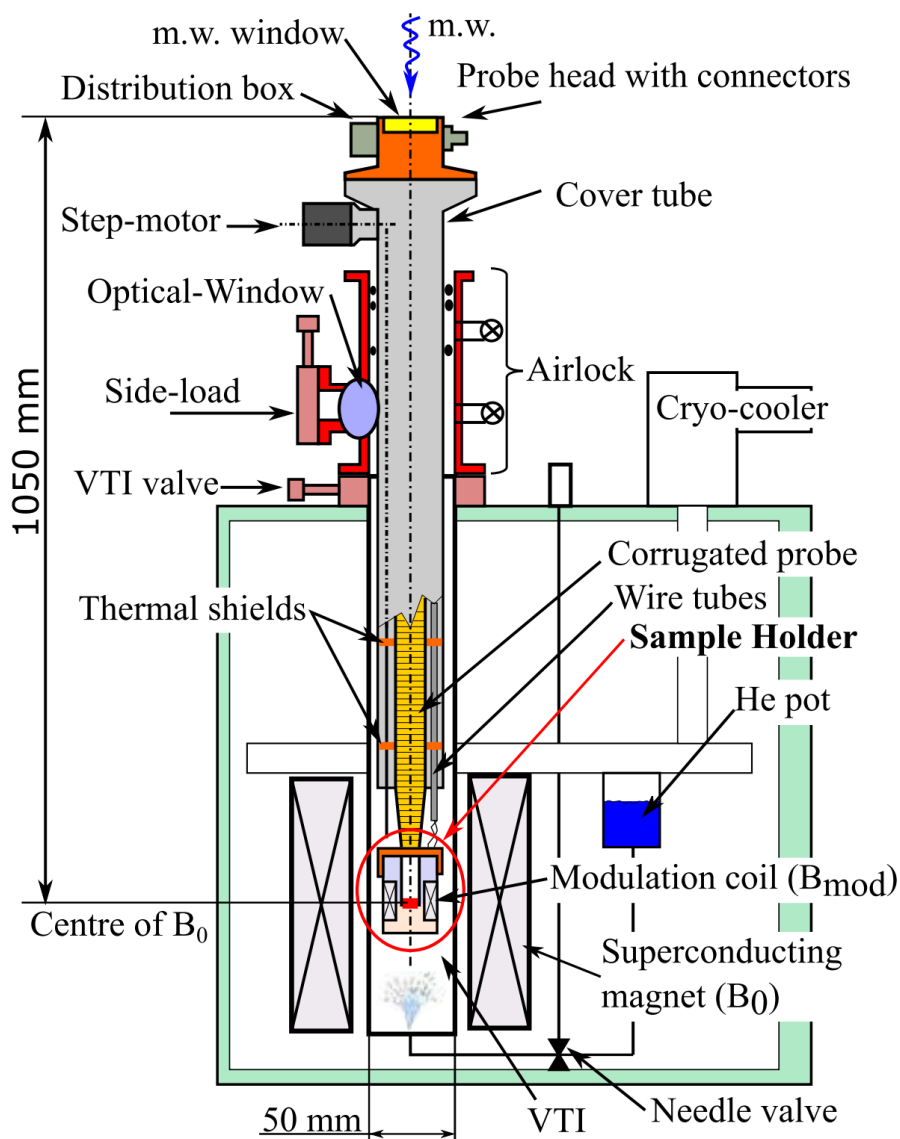


Figure 5.5: Schematic drawing of the ESR probe with an SH located in a cryogen-free superconducting magnet equipped with a variable temperature insert¹¹¹

Figure 5.5 shows schematic part of the FRaSCAN ESR spectrometer where sample holder (SH) is placed. The sample holder is positioned at the end of the measurement probe, approximately 1 meter in length, which is inserted into a cryogen-free superconducting solenoid magnet with a VTI with a sample space diameter of 50 mm (Cryogenics Ltd., London, U.K.). A homemade airlock port enables probe insertion to prevent contamination of the closed-cycle helium environment by evacuating and purging the probe area prior to its installation into the operational position through the subsequently opened VTI valve.

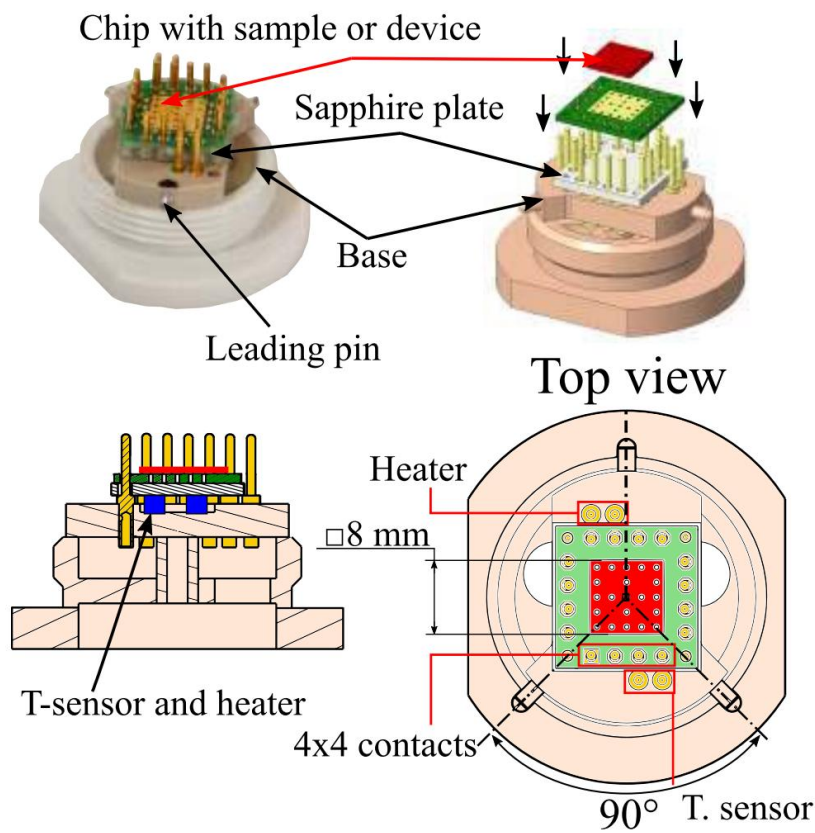


Figure 5.6 Picture and drawings of the Chip Sample Holder functional part. The T-sensor and the heater are under the sapphire plate, which works as a heat buffer. The sample is glued onto the chip that is inserted into the male connectors of the functional part. The interspace between the contacts is slightly bigger than the interspace between the holes in the chip, ensuring good electrical contact at any temperature¹¹¹.

The chip sample holder enables the characterization of electrical and electronic devices under microwave irradiation or enables magnetotransport studies. The functional component has 20 connectors, 16 of which fit a chip expander, while the remaining four

link the T-sensor and the heater. The chip expander is a compact printed circuit board (PCB) featuring 16 gold-plated holes and contacts, designed for wire-bonding of samples. The maximum sample size that can be wire bonded is $8\text{ mm} \times 8\text{ mm}$. A slight misalignment between the electrical connectors and the chip expander's apertures ensures stress for a dependable connection. Any device that is produced and wire-bonded to the chip expander can be effortlessly loaded with minimal user intervention (Figure 5.6). A sapphire heat sink is positioned beneath the chip expander to efficiently dissipate heat to the sample. The heat sink is nonconductive to avert short circuits between contacts and eddy currents generated by the modulated magnetic field. A sapphire plate was selected due to its non-conductive properties and excellent thermal conductivity at low temperatures. The T-sensor and heater are fixed to the underside of the sapphire plate, enabling accurate temperature regulation of the sample.

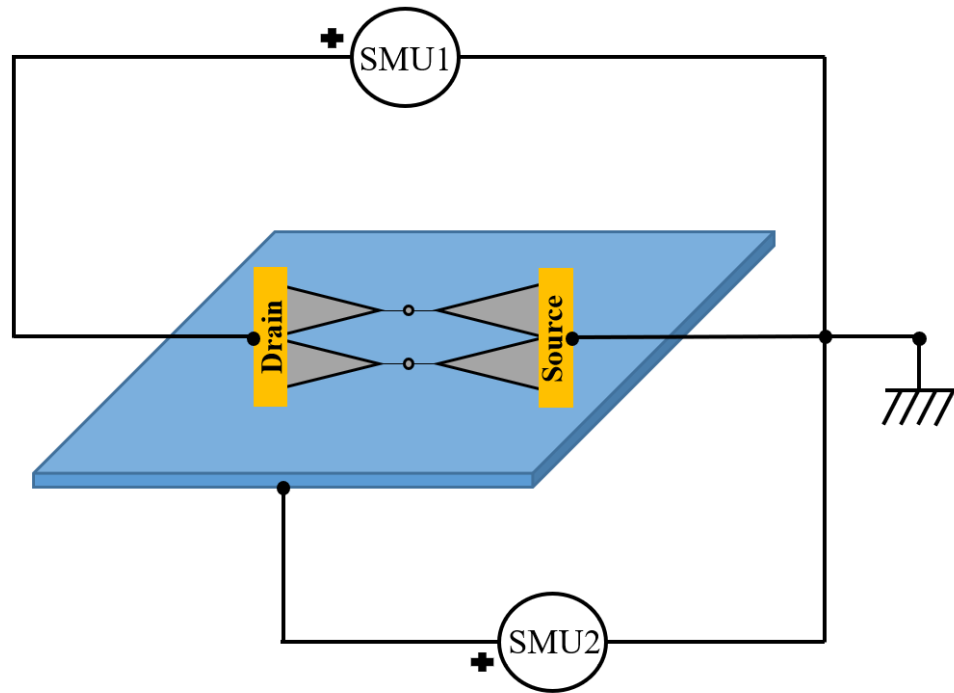


Figure 5.7 Schematic view of the connection of two Keithley source measure units to the sample for measurements.

We conducted all electrical measurements using two Keithley source-measure units connected to the sample holder via probe head with connectors schematically shown on Figure 5.7. One SMU was connected to the source and drain, while second SMU was used for applying back gate voltage. This layout enabled precise current-voltage (I–V)

characterization of the devices under study. Also, we used a VTI in conjunction with a temperature control unit to maintain constant thermal conditions throughout all measurements. For studies involving microwave radiation, we used microwave source (Virginia Diodes, USA). And in experiments requiring the utilization of an external magnetic field, a superconducting cryogen-free magnet (Cryogenics, UK) was used.

5.4 Conclusion

In this chapter, a comprehensive set of characterization techniques was employed to assess the structural, morphological, and electronic properties of graphene-based quantum dot bolometers at various stages of the fabrication process. Raman spectroscopy proved to be a critical tool in confirming the monolayer quality of CVD graphene both before and after lithographic patterning and plasma etching. The presence of a strong and symmetric 2D peak, indicated minimal introduction of defects and preservation of graphene's structural integrity. Scanning electron microscopy (SEM) enabled high-resolution visualization of nanostructured features, allowing for the inspection of device geometry, edge definition, and overall pattern fidelity. For functional characterization, a custom THz FraScan spectrometer was utilized, incorporating a wide-frequency microwave source, variable temperature control (2–320 K), and a superconducting cryogen-free magnet capable of generating magnetic fields up to 16 T. This setup allowed for detailed electrical and magnetotransport measurements under precisely controlled environmental conditions. The implementation of a chip sample holder with integrated thermal regulation and a sapphire heat sink ensured stable operation during low-temperature measurements. Electrical transport characterization was achieved using dual Keithley source-measure units.

6. Results obtained

Room Temperature Measurements

Fabricating graphene quantum dot bolometers was not always successful. Due to the complexity of producing nanometer-scale quantum dots, not all attempts at fabrication were successful. While certain fabrication flaws, including lift-off failures resulting in the presence of a metal layer over significant areas, were clearly visible, other issues were not easily detectable during the manufacturing process. The small sizes of the quantum dots resulted in significant impacts on the device's functionality due to slight variations in the nanostructure's configuration. Therefore, even if many bolometers were produced at the same time on a single chip, the devices would display various performance characteristics, despite having the same design.

Following completion of the fabrication process, the chips and devices can undergo preliminary verification using SEM before proceeding to wire bonding for further analysis. The completion of the nanofabrication stages, which involve the nanofabrication of the devices, enables this process. A larger number of devices were fabricated on a single chip that could be connected using wire bonding. Specifically, around 20 to 30 devices were fabricated on each chip, but the chip mount only had enough pins to establish wire bonded connections for approximately 10 devices at a time. Therefore, it was crucial to determine which devices showed the most potential before proceeding with wire bonding. Following the wire bonding process, the devices underwent initial characterization, including room temperature measurements.

Room temperature measurements were conducted using a probe without inserting it into the VTI. A Keithley source measuring unit was utilized and operated through a customized LabVIEW program. The channel resistance measurement was one of the crucial characterizations used to determine whether a device is working and suitable for further characterization. Devices that exhibited satisfactory performance generally had a resistance at room temperature ranging from 200 k Ω and 1 M Ω , which varied based on the number of dots in the array.

Figure 6.1 shows the relationship between I_d mapping and V_d and V_g for 2 and 8-GQDs devices, which were measured at room temperature. The devices showed higher current values for negative V_g and significantly reduced current values for positive V_g , indicating that our device is of p-type with holes as the dominant carriers, and its hole density is considerably larger than the electron density.

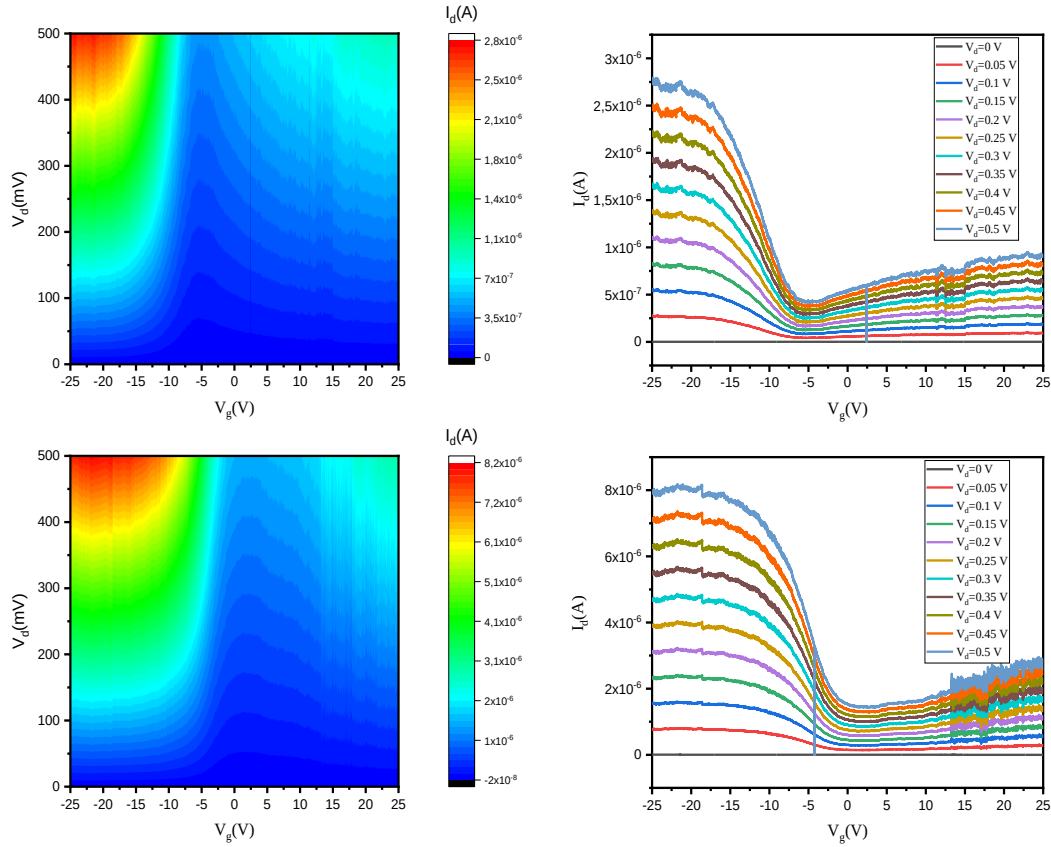


Figure 6.1 (a, c) The I_d mapping as a function of V_d and V_g for 2 and 8-GQDs devices, respectively. (b, d) The I_d - V_g curves at different V_d values, extracted from the current map for 2 and 8-GQDs devices, respectively. All the data has been recorded at the temperature of 300 K.

Temperature Dependent Resistance Measurements

After wire bonding, devices can be characterized by connecting the chip holder to the probe and inserting it inside the VTI in the magnet in HF FraScan EPR. The electrical properties of the devices were characterized, starting with the temperature dependence of the resistance. The electrical measurements are taken using two Keithley source measure units (SMUs) and Labview application. To probe the transport behavior of the GQDs devices on SiO₂/Si substrate, the variation of resistance as a function of temperature has

been measured with respect to back gate voltage at drain voltage $V_d = 5$ mV. This voltage is low enough to prevent joule heating from substantially affecting the bolometer temperature. The resistance of the device is recorded as the VTI cools the device from 50 K to approximately 2 K. Figure 6.2 (a) presents the variation of resistance versus temperature for 2-dots and 8-dots devices at zero gate bias. It shows that the room temperature resistance of the 2-dot devices is 3.5 times higher than that of 8-dot devices, which agrees with the fact that parallelly assembled resistances reduce the overall impedance. However, the resistance of the 8-dot device abruptly increases at 60 K (~ 5.1 meV) and becomes higher than that of 2-dot devices. This could be understood by the fact that the transport at low temperatures is dominated by activation energy, which is higher for the 8-dot device as shown in Figure 6.2 (d) at zero gate voltage. The number of parallelly assembled GQDs plays a crucial role in the device's total impedance while increasing the device's active area. The transport behavior also demonstrates that the gate voltage can be used to control the devices' total impedance rather than the number of parallelly assembled dots. At a temperature of 2 K, dR/dT goes as high as $76.1 \text{ M}\Omega \text{ K}^{-1}$ and $5.4 \text{ G}\Omega \text{ K}^{-1}$, respectively, for the 2-dots and 8-dots devices at zero back gate voltage. Also, it has been observed that the device impedance can easily be tuned just by applying the back gate voltage, as depicted in Figure 6.2. For example, Figure 6.2 (b) shows the variation of resistance versus temperature concerning different gate voltages for the 2-dot device and provides $25.1 \text{ M}\Omega \text{ K}^{-1}$ and $3.1 \text{ M}\Omega \text{ K}^{-1}$ variation in dR/dT at 2 K for a back gate voltage of -2 V and 2 V. Figure 6.2 (c) show the gate dependence of the R versus T curves has a similar behavior as observed for the 2-dots device. The activation energy has also been estimated from the resistance versus temperature curve using $R = R_0 \exp\left(\frac{E_c}{k_B T}\right)$, which turns out to be 0.96 meV and 3.11 meV, respectively, for 2-dots and 8-dots devices at zero gate voltage. The variation of activation energy with respect to the applied gate voltage has been estimated for all the devices at each gate voltage and is presented in the inset of Figure 6.2 (d).

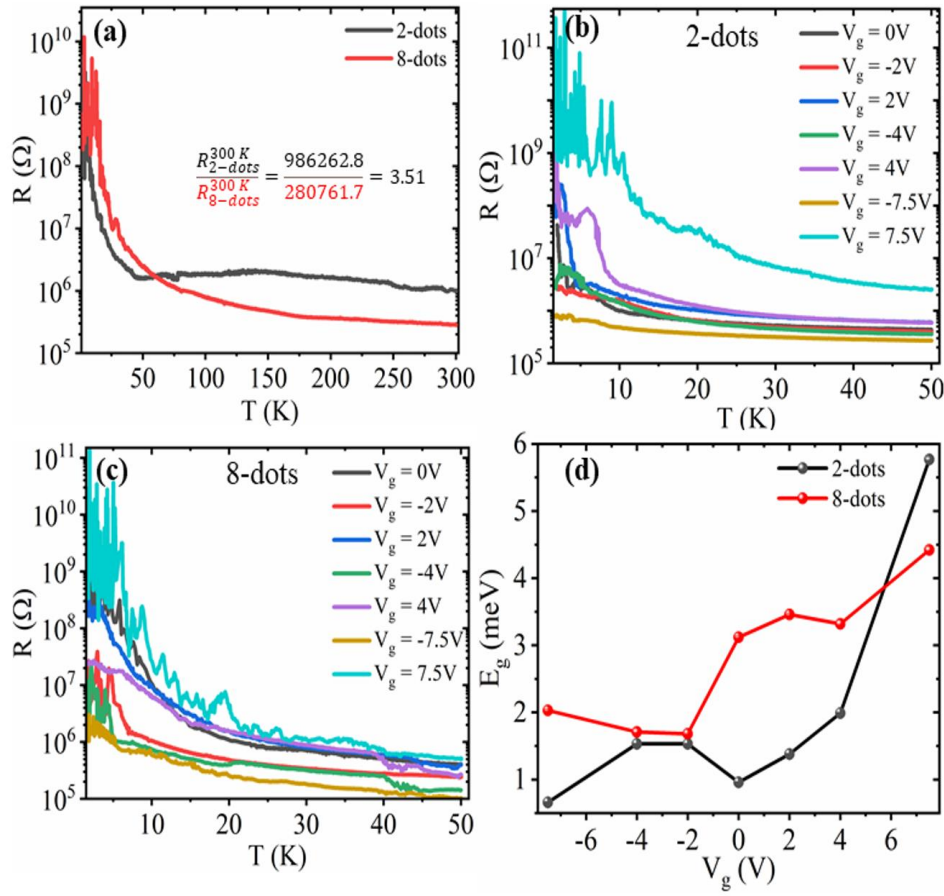


Figure 6.2 (a) The temperature dependence of the resistance for 2-dot and 8-dot GQDs devices at zero back gate voltage. The data has been recorded by applying 5 mV across the source and drain. The variation of resistance versus temperature with respect to different back gate voltages (b) 2-dots, (c) 8-dots. (d) The variation of the activation energies with respect to back gate voltage and the number of parallelly assembled GQDs.

Low Temperature Current-Voltage Measurements

The evolution of the R versus T curves in the experimental data (Figure 6.2 (b,c)) can be followed from the corresponding I_d - V_g plots depicted in Figure 6.3 (a,d). For negative V_g values, the devices are more conductive, resulting in a lower temperature-dependent resistance; conversely, for positive voltages, the current is very low, and the curves shift towards higher resistance. The transport behavior of GQD devices infers that the energy gap, formed by quantum confinement and Coulomb blockade, along with the energy levels of the GQDs, shifts dynamically with the application of V_g . Figure 6.3 (a, d) demonstrates the low bias ($V_d = 26$ mV $\sim k_B T$) I_d - V_g characteristics of the 2-dot and 8-dot devices. The I_d - V_g characteristics of all the GQDs devices resemble that of

mesoscale graphene devices like nature at higher back gate bias windows.

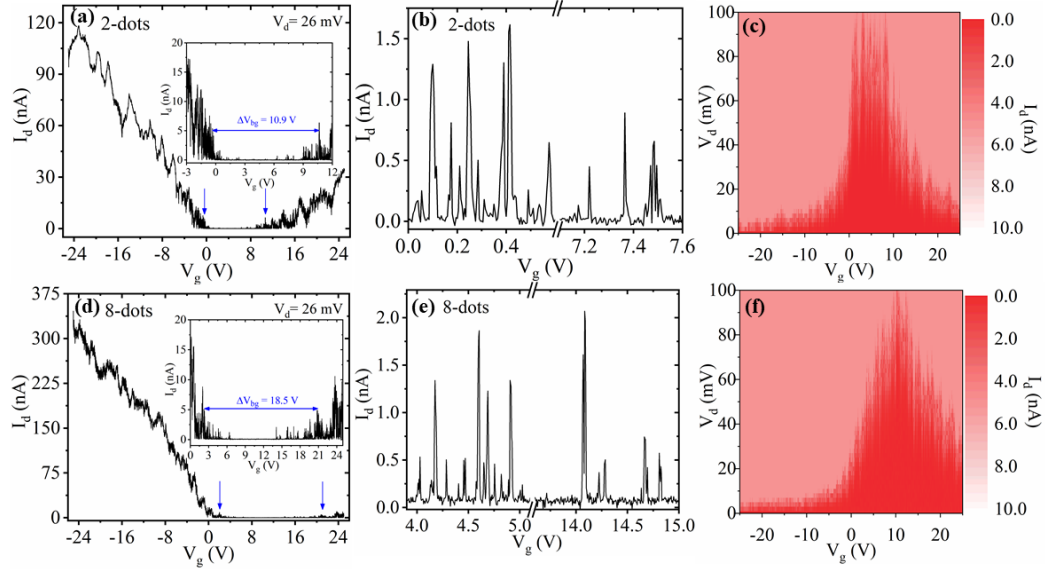


Figure 6.3. The I_d - V_g characteristics of GQD devices at $V_d = 40$ mV (a) 2-dot device, (d) 8-dot device. The inset shows the enlarged view of the transport gap indicated by the blue arrows. The Coulombic resonance peaks inside the transport gap (b) 2-dot, (e) 8-dot device. The I_d mapping as a function of V_d and V_g for (c) 2-dot and (f) 8-dot devices. All the data has been recorded at a temperature of 2 K..

Both the devices show a suppressed region of conductivity (indicated by blue vertical arrows) in the applied back gate bias window, either side of which the conduction could be tuned as electron or hole dominant as visualized in the insets of Figure 6.3a, d. This region of the suppressed conductivity is the so-called transport gap (ΔV_{bg}), which is found to be 10.9 V and 18.5 V, respectively, for 2-dot and 8-dot devices. Furthermore, a detailed examination of the I_d - V_g characteristics in the transport gap reveals Coulomb peaks in both electron/hole dominant regions on either side for both 2-dot and 8-dot devices, as described in Figure 6.3b, e. These Coulombic peaks are indicative of the Coulomb blockade effect at low bias induced via quantum confinement. Minor distortions in the form of smooth fluctuations are present in each curve arising from quantum interference^{112,113}. A close observation of these fluctuations reveals an inhomogeneity in the peak height, which could be understood in terms of quantum interference-induced effects that could effectively alter the barrier height^{114–116}. The transport gap narrows (Figure 6.3 c, f) with increase in the bias voltage for both configurations as presented in the I_d mapping. Previous works revealed similar behavior¹¹⁷ which can explain the data

observed in Figure 6.3c,f as the transport is mainly controlled by the two graphene nano constrictions on both sides of the quantum dot.

Low Temperature Bolometric Response Measurements

The final characterization measurement entails determining the device's bolometric response. Device characteristics such as responsivity and noise equivalent power (NEP) can be determined from measurements like these. One way for measuring the bolometric response involves doing current-voltage measurements both with and without applied THz radiation. We expose our devices, consisting of 2 and 8 graphene quantum dots (GQDs), to radiation at a frequency of 100 GHz. This radiation is applied by measuring the current at various gate bias voltages ranging from -25V to +25V, as well as by sweeping the source and drain voltages from 0V to 500mV. Figure 6.4 shows an example of the extracted values.

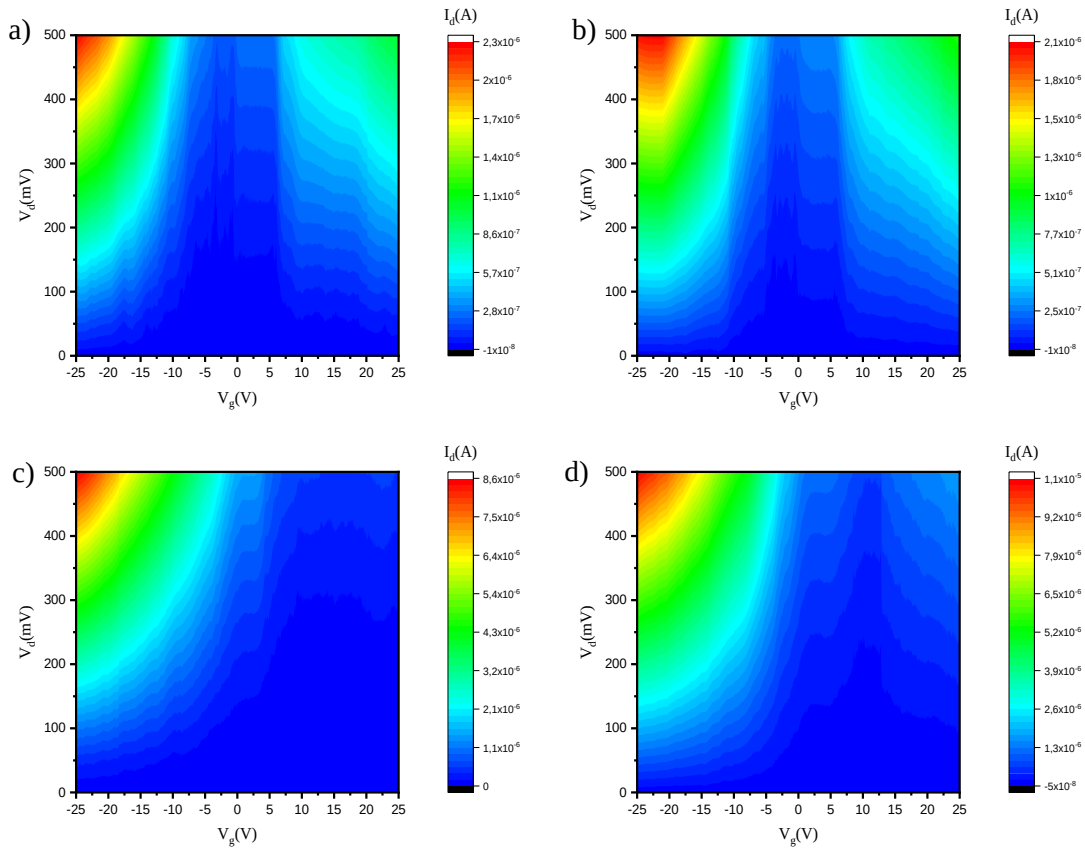


Figure 6.4. (a, c) The I_d mapping as a function of V_d and V_g for 2 and 8-GQDs devices, respectively without applied radiation. (b, d) The I_d mapping as a function of V_d and V_g for 2 and 8-GQDs devices, respectively with applied radiation of 100 GHz. All the data has been recorded at the base temperature of 4.5 K.

Figure 6.5 shows a representation of the numbers obtained from extracting data with a constant source-drain voltage of 100 mV. The black curve represents the current in the absence of radiation, whereas the red curve represents when exposed to 100 GHz radiation. The bolometer absorbs radiation, leading to an increase in electron temperature. This rise in temperature causes an increase in current as electrons become thermally activated across the quantum dots. This behavior serves as evidence that our devices are functioning as detectors. Due to the lack of data the further investigation for CVD graphene devices is planned for the future after the remeasuring devices microwave response.

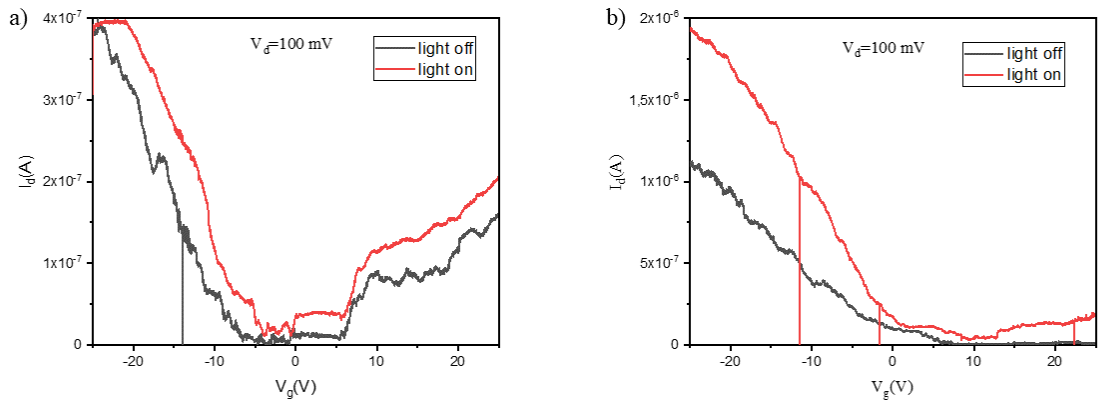


Figure 6.5 (a, b) The I_d - V_g curves at $V_d = 100$ mV, extracted from the maps of Figure 6.6 for 2 and 8-QDs devices, respectively. The black curve represents the current in the absence of radiation, whereas the red curve represents when exposed to 100 GHz radiation.

While for CVD graphene devices there is a need of remeasure of the data for microwave response, similar measurements were provided for the GQDs devices made from epitaxial graphene on SiC.

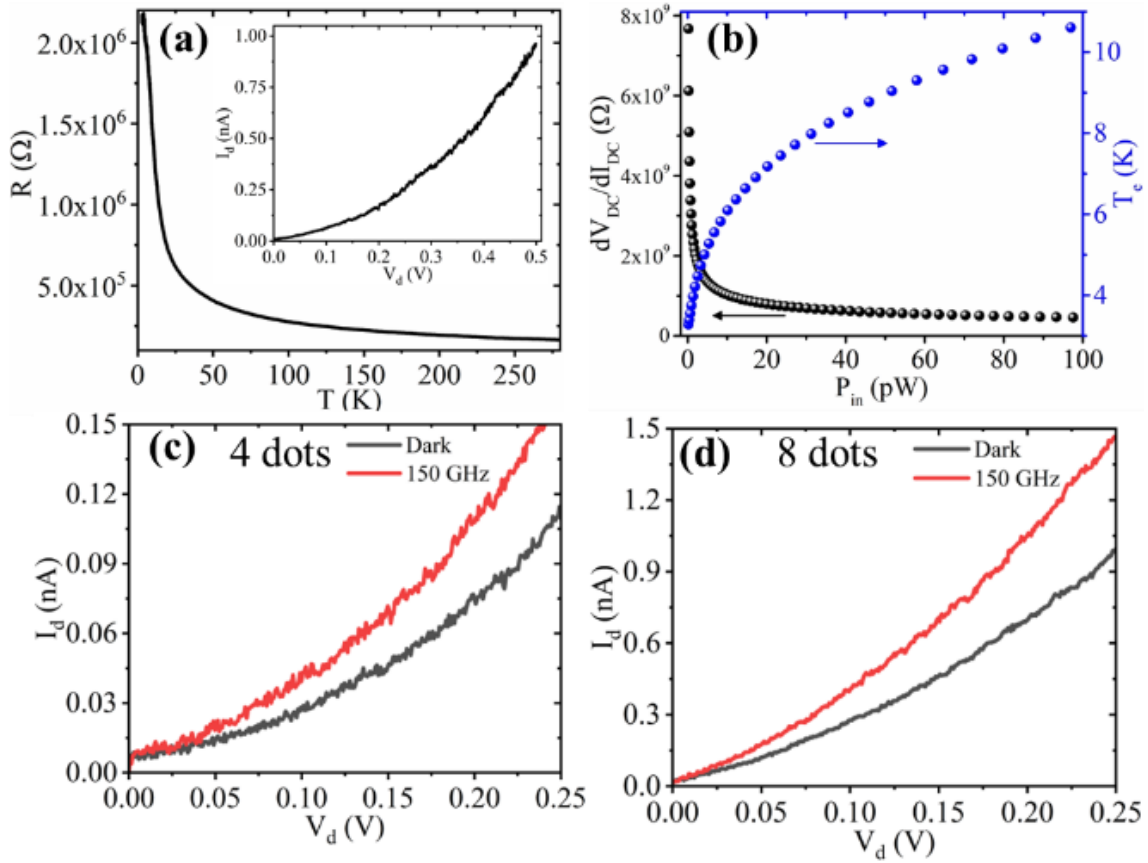


Figure 6.6 (a) Temperature dependence of resistance for a single 200 nm GQD bolometer device fabricated on epitaxially grown graphene on SiC substrate. The inset shows the I_d - V_d characteristics of the same bolometer device at a base temperature of 3 K under dark conditions. (b) Differential resistance and electron temperature versus Joule power at base temperature of 3 K. The I_d - V_d data for a single GQD device (as in the inset of Figure 6.8 (a)) was used to calculate differential resistance and Joule power. T_e is obtained from differential resistance using R - T data. (c) 4-GQDs array bolometer device and (d) 8-GQDs array bolometer device. The diameter of GQDs is 200 nm in each case. The data is recorded at 3 K, under 150 GHz ON and OFF states.

Figure 6.6a presents the resistance variation as a function of temperature for epitaxial graphene GQD on SiC substrate. The resistance versus temperature response is measured for a single GQD bolometer device. At 3 K, dR/dT goes as high as $4.7 \text{ M}\Omega \text{ K}^{-1}$. The activation energy has also been estimated from the resistance versus temperature curve, which turns out to be 1.19 meV. The current-voltage (I_d - V_d) characteristics of the single GQD bolometer device have been depicted in the inset of Figure 6.6a at a base temperature of 3 K without any radiation. The nonlinear behavior in the GQD device arises from the Joule heating, i.e., when the bias (Joule power) increases, the electron temperature (T_e) increases, which decreases the total resistance, as evident

from the strong temperature dependence of resistance shown in Figure 6.6a. Furthermore, assuming the nonlinearity in I_d - V_d measurements is due to only Joule heating, i.e., the electron-phonon scattering is dominant, the T_e dependence on absorbed Joule power ($P_{in} = V_d \times I_d$) can be estimated by coupling differential resistance (dV_d/dI_d) and resistance versus temperature data.

The data can be presented as a single T_e - P_{in} curve by converting the differential resistance to T_e following the R - T dependence and plotting it versus P_{in} . Figure 6.6b demonstrates differential resistance and electron temperature variation versus Joule power for the single GQD bolometer. The differential resistance is obtained from the I_d - V_d data of a 200 nm GQD on SiC substrate bolometer device, as in the inset of Figure 6.6a. The thermal conductance (G_{Th}) can be deduced from this plot as dP_{in}/dT_e , which is ~ 25.0 pW K⁻¹. The expected bolometric electrical responsivity (r) can be estimated from the voltage change across the bolometer relative to absorbed Joule power at a constant bias current and can be calculated as:

$$r = \frac{\Delta V_{DC}}{\Delta P_{in}} = I_{DC} \frac{\Delta R}{\Delta P_{in}} = I_{DC} \frac{\Delta R}{\Delta T} \frac{1}{G_{Th}} \quad (6.1)$$

From the differential resistance versus absorbed power plot in Figure 6.6b, at $P_{in} = 0.5$ pW, corresponding to $I_d \sim 19.9$ pA from Figure 6.6b, the intrinsic responsivity is 0.97×10^9 V W⁻¹ for GQD bolometer device having a single QD of 200 nm.

The changes in the I_d - V_d characteristics of the devices under 150 GHz irradiation are like the Joule heating caused by electrical power. Therefore, the absorbed radiation power is estimated by evaluating the electrical power at the point in I_d - V_d characteristics having the same differential resistance as zero bias differential resistance under radiation OFF and ON conditions. The THz response of all the bolometer devices has been recorded at a base temperature of 3 K under 150 GHz irradiation. Figure 6.6c,d shows the THz response of 4-dot and 8-dot GQDs array devices on SiC at a base temperature of 3 K. The absorbed THz power for the bolometer device with a 4-GQDs array is 0.9 pW (Figure 6.6c). The voltage change (ΔV_d) corresponding to the constant bias current ~ 109 pA due to THz radiation is 48.3 mV, providing electrical responsivity as high as 5.4×10^{10} V W⁻¹. Moreover, the bolometer device having an 8-GQDs array demonstrates an increase in absorbed THz power compared to the former due to increased graphene area. The absorbed THz power for the bolometer device with 8-GQDs is 16.6 pW. Under THz irradiation at 3 K, the 8-GQDs array device demonstrates the voltage change of 57.9 mV

at a fixed bias current of 0.99 nA (Figure [6.6d](#)), which results in the electrical responsivity of $3.5 \times 10^9 \text{ V W}^{-1}$. This electrical responsivity value is called absorbed THz power and is consistent with the expected responsivity estimated based on Joule heating only.

7. Conclusions

In this thesis, we have explored the design, fabrication, and characterization of bolometric detectors based on CVD graphene, with a focus on quantum dot architectures. The work addresses both fundamental scientific challenges and practical engineering considerations in developing highly sensitive, scalable bolometers for cryogenic applications.

The first major achievement is the successful fabrication of graphene quantum dot bolometers, where quantum confinement effects enhance the temperature dependence of electrical resistance—crucial for high-responsivity thermal detection. The second key contribution is the development of a multi-parallel quantum dot architecture that significantly improves device scalability and robustness. This configuration not only allows for the optimization of total impedance—making the bolometers suitable for integration with antennas—but also enables an increase in the total active graphene area while preserving high responsivity, overcoming a typical trade-off in miniaturized sensor designs.

A third important finding is the demonstration that back-gate voltage can be used to tune the temperature dependence of the resistance in graphene quantum dots. This tunability adds a valuable degree of control over bolometer performance, enabling device optimization for specific operating conditions or target applications.

Despite challenges such as nanoscale lithography precision, thermal isolation control, and process uniformity, the results clearly show that CVD graphene is a viable platform for fabricating quantum dot-based bolometers with high sensitivity and tunability. The multi-parallel architecture demonstrated here represents a promising route toward large-scale, antenna-coupled, graphene-based thermal detectors.

These findings open up new directions for the development of advanced bolometers in a variety of fields, including terahertz sensing, molecular magnet detection, and biomolecular analysis such as DNA sequencing. Future work may explore integration with RF antennas, system-level packaging, and enhanced fabrication techniques to further push the performance and application range of these novel devices.

8. References

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9. Author publications and outputs

Articles

- **Martyniuk, O.**, Chaudhary, V., Bartos, M., Laguta, O., Myers-Ward, R., Gaskill, D. K., Barbara, P., El Fatimy, A. & Neugebauer, P. Graphene Quantum Dot Bolometer Camera: Practical Approaches and Preliminary Results. *International Conference on Infrared, Millimeter, and Terahertz Waves, IRMMW-THz* 3–4 (2023). doi:10.1109/IRMMW-THz57677.2023.10298959
- **Martyniuk, O.**, Chaudhary, V., Amine Rhanbouri, M., Laguta, O., Tahsin, M., Kurt Gaskill, D., El Fatimy, A. & Neugebauer, P. Quantum dots array: an approach to multipixel devices. *J Phys D Appl Phys* **58**, 135103 (2025).
- Kamnev, K., Bendova, M., Fohlerova, Z., Fialova, T., **Martyniuk, O.**, Prasek, J., Cihalova, K. & Mozalev, A. Arrays of ultra-thin selenium-doped zirconium-anodic-oxide nanorods as potential antibacterial coatings. *Mater Chem Front* (2025). doi:10.1039/D4QM01081G

Previous Articles

- Evtukh, A. A., Pylypova, O. V., **Martyniuk, O.** & Mimura, H. Resonant tunneling at electron field emission from Si tips coated with SiO₂(Si) films. *Applied Nanoscience (Switzerland)* **8**, 931–935 (2018).

Conferences and Posters

- 06/2024 – Immobilization of Molecular Quantum Bits workshop, Kleinwalsertal, Austria. – Oral contribution.
- 05/2022 – French-German TeraHertz Conference 2022, La Grande Motte, France. – Poster contribution.
- 06/2019 – Magneto-Optical and THz Spectroscopy conference, Masłowski, Poland. – Oral contribution.

Internships

- 13.06.2019 – 13.07.2019 - Ecola Centrale Casablanca, Morocco.
- 15.05.2022 – 18.06.2022 - Charles Coulomb laboratory, Montpellier, France.
- 06.07.2024 – 16.08.2024 - Mohammed VI Polytechnic University, Ben Guerir, Morocco.

List of abbreviations

2D	Two-dimensional
AFM	Atomic Force Microscopy
BSE	Backscattered Electrons
BUT	Brno University of Technology
CAR	Chemically Amplified Resist
CEITEC	Central European Institute of Technology
CNP	Charge Neutrality Points
CVD	Chemical vapor deposition
DC	Direct Current
DI	Deionized Water
DLW	Direct Laser Writing
DNA	Deoxyribonucleic Acid
DUV	Deep Ultraviolet
EBL	Electron Beam Lithography
EBS	Diffacted Backscattered Electrons
EPR	Electron Paramagnetic Resonance
EUV	Extreme Ultraviolet
EUVL	Extreme Ultraviolet Lithography
FWHM	Full-Width-Half-Max
GQD	Graphene Quantum Dot
HCl	Hydrochloric Acid
HEB	Hot Electron Bolometer
HF-ESR	High-Frequency Electron Paramagnetic Resonance
HSQ	Hydrogen Silsesquioxane
IPA	Isopropanol
KID	Kinetic Inductance Detector
MEMS	Micro Electromechanical Systems
MOTES	Magneto-Optical and THz Spectroscopy
NEMS	Nano Electromechanical Systems

NEP	Noise Equivalent Power
PC	Personal Computer
PCB	Printed Circuit Board
PDMS	Polydimethylsiloxane
PMMA	Polymethylmethacrylate
PVD	Physical Vapor Deposition
QO	Quasi-Optical
RF	Radio-Frequency
RIE	Reactive-Ion Etching
RPM	Revolutions Per Minute
RS	Raman Spectroscopy
SB	Soft bake
SEM	Scanning Electron Microscope
SH	Sample Holder
SIS	Superconductor-Insulator-Superconductor
SMU	Source Measure Unit
SNSPD	Superconducting nano-wire single photon detector
UHV	Ultra High Vacuum
UV	Ultraviolet
UVL	Ultraviolet Lithography
VDI	Virginia Diode
VTI	Variable Temperature Insert
XRL	X-ray Lithography

Appendices

Appendix A: Pattern for e-beam and photolithography

The pattern for all fabrication steps is shown in Figure [A.1](#).

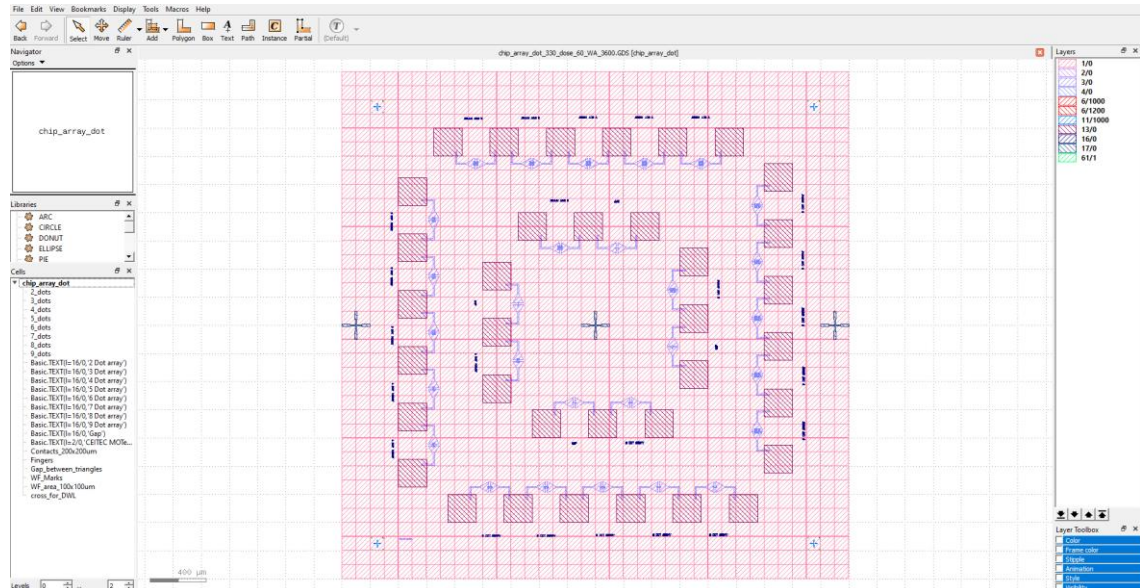


Figure [A.1](#): The printscreen of the pattern with all layers shown at once in the Klayout program.

The pattern contains all parts for lithography as separate layers and with using cell hierarchy which allows easily to modify the dimensions of all separate layers according to the need. Also, pattern was prepared to be used for writefield $100 \times 100 \mu m$ and working area $3600 \times 3600 \mu m$.

For the first step e-beam lithography the pattern shown in Figure [A.2](#). The layers used for this step of lithography consist of the patterns of the marks for the next steps of lithography, contacts and navigation marks for easier navigation.

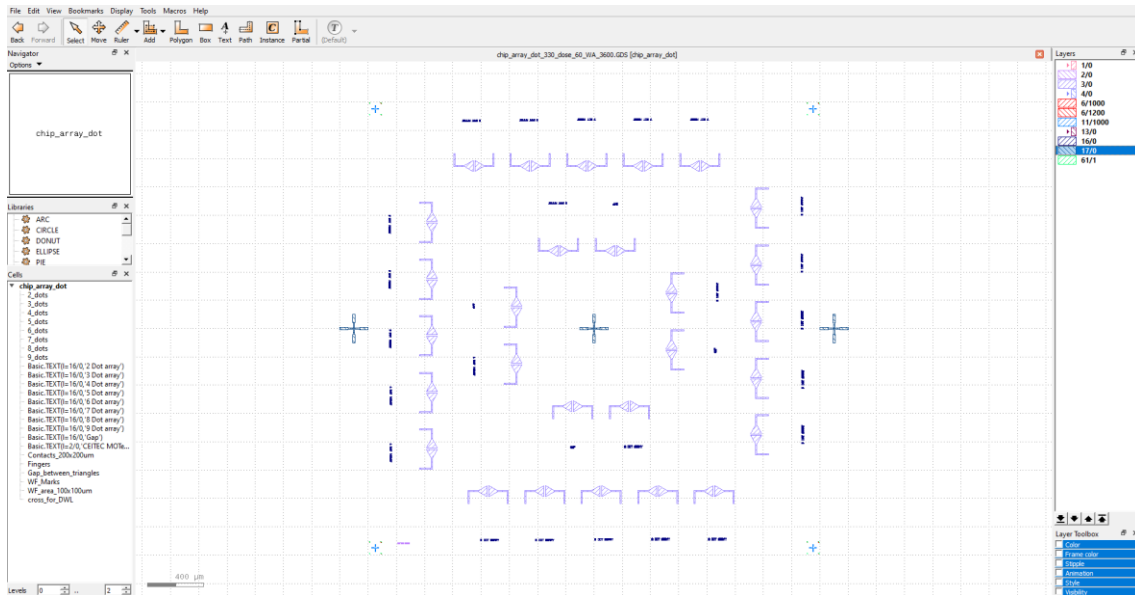


Figure A.2: The printscreen of the pattern with layers used for the first step e-beam lithography in the Klayout program.

Second step of photolithography consist only from the layer for pads and shown on Figure A.3.

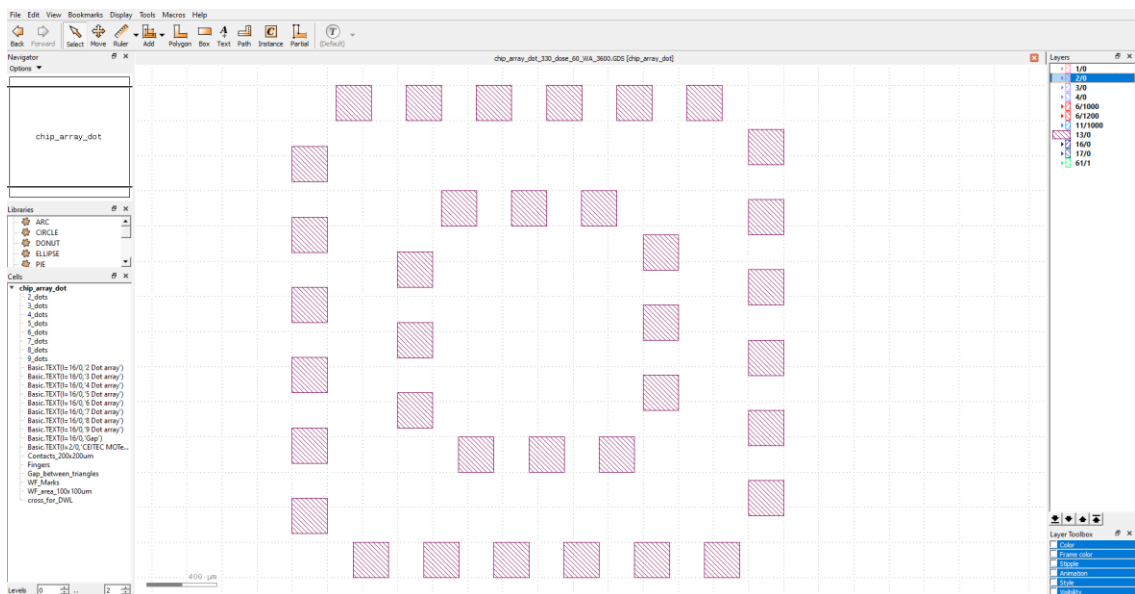


Figure A.3: The printscreen of the pattern with layer used for the second step photolithography in the Klayout program.

For the last third step of e-beam lithography the pattern consists of the structures which are used for shaping our transferred CVD graphene in our GQDs arrays and shown on Figure A.4.

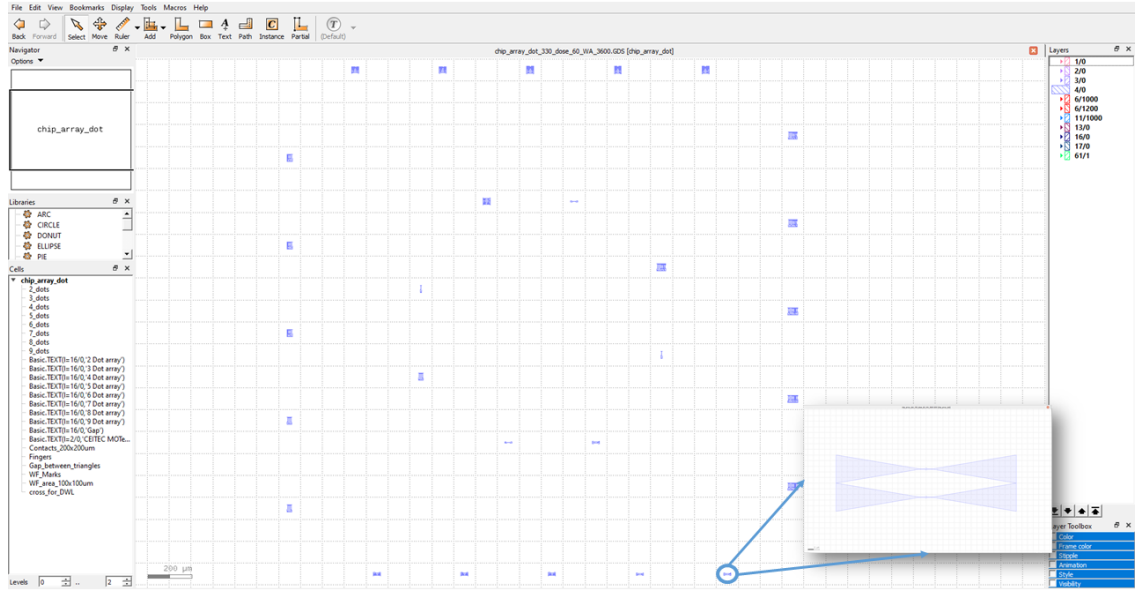


Figure A.4: The printscreen of the pattern with layer used for the third step e-mean lithography in the Klayout program. The inset shows the increased view for 2 GQDs array.

Appendix B: Measurements with an applied magnetic field

To examine the behavior of devices at low temperatures with applied magnetic field, current-voltage (IV) curves are generated. The sweep of V_g was done for 2 and 8 GQDs devices with applied different magnetic field as shown on Figure A.5. We can observe the increase of current with applying and increasing the magnetic field. Further and more detailed investigation of such behavior was decided to leave for the future work.

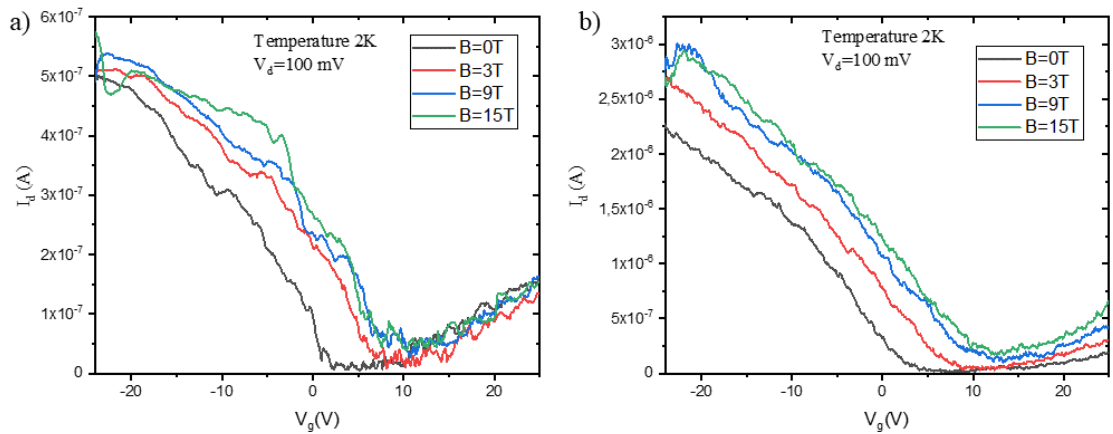


Figure A.5 (a, b) The I_d - V_g curves at $V_d = 100$ mV with applied magnetic field for 2 and 8-GQDs devices, respectively.