Towards a versatile gas sensing platform with epitaxial graphene

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ABSTRACT

The work presented in this thesis focuses on how to utilize epitaxially grown graphene on SiC as a basis for ultra-sensitive gas sensor. Several approaches have been tested and evaluated to increase the sensitivity, selectivity, speed of response and stability and of the graphene based gas sensors with a focus on air quality monitoring applications. The graphene surfaces have been functionalized with different metal oxide nanoparticles and nanolayers using hollow-cathode sputtering and pulsed laser deposition. The modified surface was investigated towards its topography, integrity and chemical composition with characterization methods such as AFM, Raman and XPS. Moreover, the binding energy was calculated with density functional theory for benzene and formaldehyde when reacting with pristine epitaxial graphene and iron oxide nanoparticle decorated graphene to verify the usefulness of this approach. The impact of environmental influences such as operating temperature, relative humidity and UV irradiation towards sensing properties was investigated as well. To further decrease time constants, the first-order time-derivative of the sensor's resistance is introduced as an alternative sensor signal and evaluated towards its applicability.

Applying these methods in laboratory conditions, sensors with a quantitative readout of single ppb benzene and formaldehyde were developed and time constants of less than one minute could be achieved with the first-order time-derivative signal. These results show promise to fill the existing gap of low-cost but highly sensitive and fast gas sensors for air quality monitoring.

PREFACE

This thesis is part of my PhD studies in the Applied Sensor Science group, belonging to the Sensors and Actuators division of the department of Physics, Chemistry and Biology (IFM) at Linköping University. It is performed in close collaboration with other divisions at IFM, the department of Microtechnology and Nanoscience at Chalmers University of Technology, and the Laboratory for Measurement Technology at Saarland University, Germany. The goal of my research is to study gas sensors based on epitaxially grown graphene on silicon carbide and methods to turn them into a versatile gas sensing platform for applications with extreme sensitivity. This research is financially supported by the Swedish Foundation for Strategic research (SSF) for financial support through the grants GMT14-0077 and RMA15-024. During the course of research underlying this thesis, Marius Rodner was enrolled in Agora Materiae, a multidisciplinary doctoral program at Linköping University, Sweden. Research results are summarized, brought into context and then presented in the appended papers, preceded by an introduction to the scientific field and used research methods.

Marius Rodner
Linköping, August 2019

APPENDED PAPERS

- Paper 1** M. Rodner, J. Bahonjic, M. Mathisen, R. Gunnarsson, S. Ekeröth, U. Helmersson, I. G. Ivanov, R. Yakimova, J. Eriksson, Performance tuning of gas sensors based on epitaxial graphene on silicon carbide, *Materials and Design*, 153 (2018)
- Paper 2** M. Rodner, D. Puglisi, S. Ekeröth, U. Helmersson, I. Shteplyuk, R. Yakimova, A. Skallberg, K. Uvdal, A. Schütze, J. Eriksson, Graphene Decorated with Iron Oxide Nanoparticles for Highly Sensitive Interaction with Volatile Organic Compounds, *Sensors*, 19 (2019)
- Paper 3** M. Rodner and J. Eriksson, First-order time-derivative readout of epitaxial graphene-based gas sensors for fast determination of toxic air pollutants, *in manuscript* (2019)

Author's contribution to appended papers

- Paper 1** I evaluated and interpreted all measurement data and wrote the manuscript.
- Paper 2** MR conceived and performed all gas and AFM measurements, evaluated and interpreted the data and wrote the main part of the manuscript.
- Paper 3** MR conceived and performed all measurements, evaluated and interpreted the data and wrote the manuscript.

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OTHER RELATED PUBLICATIONS

- Paper A** M. Rodner, D. Puglisi, R. Yakimova, J. Eriksson, A Platform for Extremely Sensitive Gas Sensing: 2D Materials on Silicon Carbide, *TechConnect Briefs*, (2018)
- Paper B** M. Rodner, D. Puglisi, S. Ekeröth, U. Helmersson, I. G. Ivanov, R. Yakimova, K. Uvdal, A. Schütze, J. Eriksson, Iron Oxide Nanoparticle Decorated Graphene for Ultra-Sensitive Detection of Volatile Organic Compounds, *Proceedings*, 2 (2018)
- Paper C** P. Darshni Kaushik, M. Rodner, G. B. V. S. Lakshmi, I. G. Ivanov, G. Greczynski, J. Palisaitis, J. Eriksson, P. Solanki, A. Aziz, A. M. Siddiqui, R. Yakimova, M. Syväjärvi, G. R. Yazdi, Surface Functionalization of epitaxial graphene using ion implantation for sensing and optical applications, *Carbon*, *submitted* (2019)

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1 Motivation

According to the World Health Organization (WHO), several toxic air pollutants exceed the recommended exposure levels in more than 80 % of the monitored urban areas [1]. Bad air quality is linked to various health impacts such as eye and skin irritation but also respiratory problems, cancer, or even death. It was estimated that poor air quality is accountable for more than 8 million deaths per year [2] also inflicting a yearly financial burden to the European region of about 1.6 trillion US dollars [3].

A proper way of detection needs to be established to be able to detect even trace amounts of hazardous gases. When it comes to the detection of carcinogenic volatile organic compounds (VOCs) like benzene (C_6H_6) and formaldehyde (CH_2O) at relevant levels, there are commercial instruments available, which are, however, large, complex, and expensive. Small low-cost sensor systems, on the other hand, suffer from limited sensitivity and selectivity [4], [5]. A portable low-cost sensor capable of detecting VOCs at single digit parts per billion (ppb^1) or even lower would thus be a breakthrough in the field of air quality monitoring (AQM).

Two-dimensional materials like graphene exhibit several outstanding properties which enables the fabrication of sensor devices that can be used for detection of very small gas concentrations.

One way to strongly increase the sensitivity and, potentially, selectivity of a gas sensor is the combination of different materials or the decoration of a sensitive transducer with a selective metal oxide. This was especially studied using graphene as transducer due to its very good sensing properties. For example, it has been shown that decorating the graphene surface with metal or metal oxide nanoparticles can lead to an increased sensitivity and selectivity towards gases like nitrogen dioxide (NO_2), C_6H_6 and CH_2O [6]. Moreover,

¹ ppb refers here to the ratio in volume. Also known as $ppbv$.

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iron oxide decorated multiwall carbon nanotubes, a close relative to graphene, in combination with UV (ultraviolet) irradiation [7], and zinc oxide fibers [8] exhibit promising sensitivity towards C_6H_6 . All these sensors are able to detect C_6H_6 down to tens of ppb, but not reliably lower. High sensitivity alone though is not sufficient to produce a useful gas sensor. Other properties such as stability, selectivity and fast time constants are also necessary. Especially for indoor AQM, a sensor needs to be sensitive, selective, stable and it must have a high enough sampling rate to allow real-time monitoring with high resolution [9], [10]. Another method to increase sensitivity and decrease time constants is the irradiation with UV light which has been shown for many different material/gas combinations [11].

To speed up the sensor response, usually the sensor is irradiated with a light source during the gas measurement or operated at elevated temperatures. A different method is the use of the sensor signal's first-order time-derivative that was shown to drastically decrease the time constants [12].

The creation of a portable low-cost sensor capable of quickly detecting VOCs at concentrations of interest by combining all these approaches would thus be a breakthrough in the field of air quality monitoring.

This thesis summarizes and elaborates upon the work published in Paper 1-3. Paper 1 discusses ways to improve the performance of gas sensors based on graphene epitaxially grown on silicon carbide with metal oxide nanoparticle decoration, UV irradiation and a smart sensor readout utilizing the first-order time-derivative of the sensor's resistance to evaluate them for AQM applications.

Paper 2 focuses on the first described approach, the surface decoration with iron oxide nanoparticles and the implications for gas sensing properties towards C_6H_6 and CH_2O in the concentration range from parts per million down to parts per billion to create ultra-sensitive gas sensors for hazardous VOCs.

Paper 3 then focuses on the utilization of the first-order time-derivative of the sensor's resistance as a new sensor signal, its implications for time constants and its stability towards external influences to enhance speed of response and stability of the tested gas sensors.

2 Theory and Concepts

This chapter discusses the general properties of graphene, its peculiarities if grown on silicon carbide (SiC) and possible surface modifications to tailor it towards an optimized gas sensor.

2.1 Graphene

The existence of graphene was already predicted in 1947, but it took until 2004 to be able to produce a free-standing, monoatomic layer of graphene that could be studied with regards to its special properties [13]. Since then, a lot of research was conducted and graphene became the most studied two-dimensional material until now. Its two-dimensional structure consists of an arrangement of hexagonal covalently bonded carbon atoms forming a honeycomb structure. The planar structure is due to sp^2 hybridization of orbitals between carbon atoms. Three out of four orbitals are sp^2 hybridized, leading to a strong covalent σ -bonds with a high bonding energy of ~ 5.9 eV in the trigonal system. These bonds are responsible for the flat structure of graphene and the exceptional structural strength. Each carbon atom has four valence electrons available. The solitary p-orbital forms aromatic π -bonds with the adjacent carbon atoms [14]. These delocalized electrons form the valence and conduction bands in graphene and give rise to the materials conductivity. A schematic depiction of the honeycomb lattice structure of graphene and its corresponding reciprocal counterpart are shown in Figure 2.1. The lattice vectors of the real space unit cell are described as

$$a_1 = \frac{3a}{2}\hat{x} + \frac{\sqrt{3}a}{2}\hat{y} ; \quad a_2 = \frac{3a}{2}\hat{x} - \frac{\sqrt{3}a}{2}\hat{y} \quad (2.1)$$

where a is the distance between adjacent carbon atoms ($1.42 \text{ \AA}$). The hexagonal lattice of graphene can be described as a combination of two triangular sublattices, A and B. The primitive cell contains two atoms in total, one from each sublattice.

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Figure 2.1: Left: Real space honeycomb lattice of graphene, consisting of two overlapping triangular sublattices A (black atoms) and B (grey atoms). The lattice vectors a_1 and a_2 form the primitive cell together with the dotted lines. Right: Reciprocal lattice with the 1st Brillouin zone. Adapted from [15].

The 1st Brillouin zone (BZ) is shown in the reciprocal lattice, which is defined by the reciprocal lattice vectors b_1 and b_2 . The corners of the hexagonal 1st BZ are marked by six points, with only two non-equivalent points K and K' , due to the two sublattices A and B. These six points are called Dirac points. The reciprocal vectors and the Dirac points can be calculated using

$$b_i a_j = 2\pi \delta_{ij} \quad (2.2)$$

where δ_{ij} is the Kronecker delta leading to

$$b_1 = \frac{2\pi}{3a} \hat{x} + \frac{2\pi}{\sqrt{3}a} \hat{y} ; \quad b_2 = \frac{2\pi}{3a} \hat{x} - \frac{2\pi}{\sqrt{3}a} \hat{y} \quad (2.3)$$

$$K = \frac{2\pi}{3a} \hat{x} + \frac{2\pi}{\sqrt{3} \cdot 3a} \hat{y} ; \quad K' = \frac{2\pi}{3a} \hat{x} - \frac{2\pi}{\sqrt{3} \cdot 3a} \hat{y} \quad (2.4)$$

2D graphene can also be the starting point for other interesting carbon allotropes (see Figure 2.2). It can be wrapped into 0D fullerenes (also referred to as ‘Buckyball’), rolled into 1D nanotubes (also

Figure 2.2: Different structures formed out of graphene [16].

referred to as ‘CNTs’) or stacked into 3D graphite (also referred to as ‘Multilayer graphene’ if only a low number of layers is used). Each structure with its peculiar properties is used in different fields of research and applications.

2.1.1 Electronic properties

Graphene has some outstanding properties like high electrical conductivity ($\sim 10^8$ S/m), high melting point (4510 K), high thermal conductivity (2000–5000 W/(m K)), high current density ($\sim 1.6 \cdot 10^9$ A/cm²) and a high electron mobility ($2 \cdot 10^5$ cm²/(V s) at electron density $\sim 2 \cdot 10^{11}$ cm⁻²) [17]. Figure 2.3 shows the low energy band structure for graphene with the Dirac points. At the six Dirac points, valence and conduction band meet in the reciprocal space. The energy dispersion is linear close to the Dirac points at low energies $|E| < 3$ eV and is similar to that of ultra-relativistic particles with zero rest mass like photons. For such particles, the Schrödinger equation can be simplified into the 2D Dirac equation which describes the behavior of massless Dirac fermions. This is also the reason why the K and K’ points are called Dirac points. The linear

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dispersion creates a conical shape in reciprocal space, the so-called Dirac cone. The density of states (DOS) can then be calculated as

$$\text{DOS}(E) = \frac{2|E|}{\pi(\hbar v_F)^2} \quad (2.5)$$

$\hbar$ is the so-called Planck constant and v_F is the Fermi velocity. Electron hopping is the dominating charge transfer mechanism in graphene and therefore the charge carriers move at the Fermi velocity ($\sim 10^6 \text{ m}^{-1}$)[15]. The DOS is linear with energy and vanishes at the Dirac point. In theory this means that, at absolute zero, graphene is an electrically insulating material with infinite resistance at the Dirac point. Since there is no band gap, graphene is often referred to as a zero-bandgap semi-metal. In practice, there are other factors such as spatial charge disorder which complicate this relation though. Experiments at the Dirac point show not infinite, but finite resistance, with the maximum resistance of graphene being controversial with different theories predicting different values [18].

It is important to note that multilayer graphene can exist in the AB (Bernal) or the AA stacked form. In the AA stacked form, all layers are perfectly aligned, whereas in the Bernal stacked form, half of the atoms lie directly over the center of a hexagon in the lower graphene sheet, and half of the atoms lie over an atom. This

Figure 2.3: Dirac points in graphene with the electronic dispersion of the honeycomb lattice in terms of (zoomed in) the energy spectrum of finite values.

is very important for electrical properties of the graphene sheets [15]. Moreover, the binding energy between AB stacked layers is higher compared to AA stacked layers, leading to a more stable structure [19].

2.1.2 Epitaxial graphene on SiC

SiC is a crystal comprised of layers of tetrahedrally bonded Si-C atom pairs. The most commonly used polytypes of SiC for graphene growth are 6H-SiC and 4H-SiC. The letter H indicates the hexagonal crystal structure and the numbers 6 and 4 define the number of Si-C pairs stacked per unit cell. SiC has two different surface terminations: Si-face (Si atoms) or C-face (C atoms). For the growth of monolayer graphene, the Si-terminated surface state (0001) is usually used, as it exhibits a slower and more controlled growth process [20]. C-terminated SiC ($000\bar{1}$) leads to multi-layered and more inhomogeneous growth of graphene instead [21]. Therefore, the Si-face is used for applications where high quality graphene is needed, such as Quantum Hall Effect (QHE) devices [22], [23] or gas sensors.

If SiC is heated to sufficiently high temperatures, Si-atoms sublimate and leave a carbon-rich layer beneath which eventually forms graphene. The growth is explained in more detail in section 3.3.1. The very first layer of graphene forms the so-called buffer layer, where around 30 % of the carbon atoms are still covalently bond to the SiC bulk, turning it into an insulating layer. It is also often referred to as zero-layer graphene. The second layer then forms the freestanding conducting monolayer of graphene. Figure 2.4 shows a schematic of the grown graphene lattice on top of SiC with the buffer layer in between. Nevertheless, the graphene layer is still influenced electrically by the buffer layer and the SiC bulk. The buffer layer has a distance of only $< 4 \text{ \AA}$ to the graphene layer and acts as an electron donor leading to intrinsic n-doping in the order of $n \approx 10^{13} \text{ cm}^{-2}$ [24]. Moreover, it has a high density of states.

Figure 2.4: Schematic of epitaxial graphene on SiC.

The SiC bulk also affects the doping of graphene in the same direction as the buffer layer [21]. The buffer layer reduces the mobility in epitaxial graphene (EG) compared to exfoliated graphene due to the introduction of charges and scattering centers. To eliminate the influence of the buffer layer, the covalent bonds between buffer and SiC can be removed through the intercalation of, for example, hydrogen which will decouple the buffer layer into a freestanding graphene layer [21]. To produce monolayer graphene in this manner it is necessary to perform the intercalation step on SiC that has been processed to have just the buffer layer with no graphene on top.

2.2 Graphene as gas sensor

Besides the already mentioned properties, its exceptionally low electronic noise makes graphene very promising for sensing applications, such as strain sensors, electrical sensors and chemical sensors including gas sensors [17]. Fluctuations due to thermal motion of charges and defects lead to intrinsic noise, limiting the detection resolution of gas sensors. Schedin et al. demonstrated already in 2007 that graphene can be used to detect single atoms/molecules [25]. Adsorbates can attach to a graphene surface, alter the local carrier concentration and, thus, change the resistance accordingly. Since then, a lot of research has been conducted to utilize graphene as ‘the ultimate gas sensor’. It was found that when using graphene

as a sensitive layer, the amount of layers does greatly affect the sensor performance [26]. This is especially true for EG on SiC, as the sensitivity depends on the band structure which in turn depends on the number of layers, as SiC exhibits Bernal stacking of graphene layers. Moreover, graphene has been found to be very sensitive towards some gases like ammonia (NH_3) or NO_2 , but needs functionalization to fully exploit its potential [27]. Due to its high sensitivity towards many gases, graphene suffers from poor selectivity. At the same time, graphene exhibits poor interaction with several gases of interests in AQM, such as VOCs and also exhibits slow adsorption and desorption, leading to long response and recovery times. Moreover, its low number of dangling bonds on the surface limits the chemisorption of the target gases, thus limiting the sensitivity [28].

2.2.1 Sensor performance tuning

There are many different ways to overcome the limitations of pure graphene gas sensors. Usually, the surface is functionalized with doping, decorated with other materials, combined into a compound material, defects are generated through etching or ion irradiation to generate adsorption sites or UV irradiation is applied to increase the surface energy of the sensing layer.

The enhancement of sensitivity and decrease of time constants using UV irradiation was shown for many different material/gas combinations [11]. The irradiation with light allows energized photons to interact with the target gas or sensing material. This interaction highly depends on the possibility to adsorb energized photons. Thus the photon energy level has to be compatible. This in turn means that the interaction depends on the wavelength of the irradiation source and might be enhanced for one wavelength, but has no effect at all for other wavelengths. The photon interaction can help to split up gas molecules into detectable gas atoms or it can help to clean the sensor surface from the adsorbed gas and ac-

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tivate adsorption sites. For example, it was reported that UV irradiation can be attributed to cleaning of the graphene surface, thus freeing active sites for target gas adsorption [29]. Unfortunately, this method does not work for all material/gas combinations, making it a useful, but not very versatile add-on.

The most common and extensively studied approach is to work with graphene itself and turn it into a hybrid structure with metal oxides. Metal oxides are very well studied in the gas sensor community and are dominating in industrial applications due to their advantages like low cost and controlled production. Having the optimal metal oxide and target gas combination already leads to a very good sensor performance. The sensitivity towards a certain gas can drastically be increased by increasing the surface-to-volume ratio of the sensing layer as a larger detection area per unit volume results in a higher adsorption of gas molecules per volume, thus leading to more material gas interaction. Therefore, nano-sized structures are often used in combination with highly sensitive materials. Combining the advantages of sensitive and more selective metal oxides with sensitive and low noise graphene, can lead to very promising new sensor hybrids [30], [31], where the surface chemistry is controlled by the metal oxide nanostructure, whereas the graphene is utilized as a highly sensitive transducer. Moreover, graphene can be turned into graphene oxide or wrapped into CNTs. This new material is then again p as a transducer and functionalized with different sensitive materials. In this work, graphene was decorated with different metal oxide nanoparticles (NPs) and nanolayers (NLs).

It was also shown that the sensitivity of graphene can be optimized by introducing vacancies or doping impurities into the lattice [32]. This can lead to higher sensitivities but normally entails a higher noise level, due to local disruptions of the sp^2 hybridization.

One option where no additional equipment or actual functionalization is needed is the use of transient or secondary data, generated during the measurement. A common approach, usually applied for metal oxide semiconductor (MOS) or field effect transistor (FET)

devices, is the operation mode called temperature cycled operation (TCO) [33], [34]. A high operation temperature is often desirable, as it accelerates reactions on the sensor like ad- and desorption, influences speed and repeatability, and can change the catalytic activity of the sensor surface. Even more information can be gained by quickly cycling between different temperatures to create non-equilibrium states that can be used to enhance sensitivity and selectivity [35]. If the sensor does not support high temperatures or the system should exhibit a low power consumption, other methods have to be applied. To substantially decrease the sensor's time constants, the first-order time-derivative of the static signal can be calculated and used. This approach focuses on the change in signal during ad- and desorption phases and can be extracted from almost any sensor signal. It is discussed in more detail in section 4.3.

2.2.2 Sensing mechanism

A change in the sensor's resistance follows from a change in charge carrier concentration or mobility. The resistivity ρ is proportional to the product of the charge carrier concentration and the mobility [36].

$$\rho = \frac{1}{ne\mu_e + pe\mu_h} \quad (2.6)$$

e is the elementary charge, whereas n and p , and μ_e and μ_h are the electron and carrier concentration, and mobility, respectively.

Adsorption of gas molecules on the graphene lattice can result in charge transfer, thus changing the sensor's resistivity. Moreover, the Fermi level E_F is modified as well since the adsorbents act as chemical dopants [37]. Adsorption of electron-accepting molecules introduces extra holes, resulting in p-type doping, shifting the Fermi level down and increasing the resistivity for n-doped graphene, such as EG on SiC. Adsorption of electron-donating molecules, on the other hand, results in extra electrons, leading to n-type

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Figure 2.5: Schematic of Fermi-level dependence on doping in graphene.

doping, shifting the Fermi level up and decreasing the resistivity. The effects of doping on the Fermi level are shown in Figure 2.5.

In free-standing graphene the Fermi level is located at the charge neutrality point, the Dirac point. In as-grown epitaxial graphene the Fermi level is shifted to ≈ 0.4 eV above the Dirac point, due to the n-type doping from the buffer and substrate [38]. The sensing mechanism of graphene decorated with metal oxide NPs can be modeled by a receptor and a transducer process. Physisorption and chemisorption occurs at the metal oxide surface, forming the receptor process. The transport of electrons between metal oxide NPs and graphene as well as establishing the electrical signal belongs to the transducer process. [31]. It is believed that the change in resistivity is due to trapping of electrons by adsorbed gas molecules and additional scattering points induced by such. For example, adsorbed oxygen (O_2) on the sensing material withdraws electrons from the metal oxide NPs as shown in Equation (2.7).

This negatively charged, adsorbed oxygen molecule causes a depletion region at the interface between the metal oxide NPs and the graphene lattice, leading to an decreased resistivity of the graphene lattice [31]. Reactions with oxidizing molecules will further increase the depletion region, whereas reactions with reducing molecules result in the trapped electrons being returned to the metal oxide NPs, thus increasing the resistivity of the graphene lattice again [39].

3 Experimental Methods

The research and development from ideation to realization of a novel sensing material involves several different fabrication and characterization techniques and systems. This chapter gives an overview of what is needed to end up with a functioning epitaxially grown and functionalized graphene gas sensor. It starts with the different deposition techniques and material characterization methods. Thereafter, the process of sensor fabrication itself is addressed and, finally, the gas mixing systems with utilized test gases are discussed.

3.1 Deposition techniques

Depending on the application in mind, several different deposition techniques may be used to grow a thin film on an already existing substrate. One distinguishes usually between physical vapor deposition (PVD) and chemical vapor deposition (CVD) techniques. In the case of CVD, a liquid or gaseous precursor undergoes a chemical change at a solid surface, resulting in the growth of a new solid film on top. PVD, on the other hand, uses thermal, mechanical or electromechanical processes to produce a thin solid film on top of a substrate. All techniques applied in this work belong to the family of PVD and are described in the following subchapters.

3.1.1 Thermal evaporation

Thermal evaporation is a very easy concept, where a target material, normally pure metals, gets evaporated using thermal energy and recondenses on a sample substrate mounted above it. A schematic of this process is shown in Figure 3.1. Small pieces of the target material are put into a metal ‘boat’ (holder), which is mounted below in parallel to the sample substrate. The heating occurs due to a high current of approximately several tens of amperes,

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which first melts the target metal and then slowly evaporates it. The evaporation rate is rather slow and depends on the supplied power and the material density. The deposited thickness is measured with a quartz crystal microbalance. This crystal is oscillating and changes its resonance frequency depending on its mass. With known evaporation material properties (density and Z-ratio) and the detected mass, the thickness of the deposited layer can be calculated. The Z-ratio describes the correction of the frequency-change-to-thickness transfer function for effects of acoustic-impedance mismatch between the deposited material and the crystal.

In this work, a custom built thermal evaporation chamber was used to deposit contacts titanium/gold (Ti/Au) on top of some graphene sensors. The base pressure was $\sim 10^{-6}$ Torr before evaporation in a nitrogen background and the current was adjusted to obtain and keep a deposition rate of ~ 0.1 nm/s. The Z-ratio for Ti is 0.628 and 0.381 for Au.

Figure 3.1: Schematic of thermal evaporation process.

3.1.2 Sputter deposition

Sputter deposition techniques are usually divided into non-reactive and reactive sputtering. For non-reactive sputtering, the background ambient consists only of an inert gas like argon (Ar), whereas for the reactive sputtering a more reactive gas, e.g. oxygen, is present as well, which then can react with the ejected target atoms to form oxides. The main principle though is similar for both techniques: A sputter gas, normally argon, is ionized with a high energy source and directed to the so-called sputter target where it bombards the surface and ejects target atoms from the bulk [40]. Depending on the atomic weight of the sputter atom, the ejection mechanism differs. For the first mechanism, heavy sputter atoms hit the surface, transferring their energy into the surface, which generates a cascade of collision and eventually ejects atoms out of the surface. On the other hand, if a rather light atom hits the surface, it does not produce a cascade of collision. Instead, those ions get reflected from inside the surface layer, colliding with surface atoms from the backside and ejecting them. For argon with its intermediate mass, both mechanisms contribute to the sputter yield [41]. The sputter yield, defined as the ratio between ejected target atoms and incoming ions, is highly dependent on the angle, mass and kinetic energy of the incoming ion as well as the target material. These atoms move to the opposing substrate and grow into a film on it. Figure 3.2 shows a schematic of the general sputter process. Besides the ejection of target atoms, also secondary electrons are ejected. Accelerating these free electrons close to the target surface will further increase the rate of ionization, eventually leading to the forming of a plasma with its origin on the target surface. In this work, we use only “soft” deposition techniques with rather low kinetic energy of the incoming target atoms to maintain the integrity of the graphene surface and to not induce structural damage.

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Figure 3.2: Schematic of sputter process.

3.1.2.1 Magnetron sputtering

As the name suggests, a magnet is utilized in a magnetron sputter system to confine the sputter electrons close to the target. The magnetic field bends the electrons' trajectory back to the target surface. This locally increases the plasma density through ionizing collisions with neutral atoms [42].

A custom built magnetron sputter system was used to deposit contacts (Ti/Au) on top of the sensor chips. For titanium, the base pressure was 1.5 mTorr with a voltage of 350 V and a current of 300 mA, whereas the values were 1.9 mTorr, 400 V and 200 mA for gold. Both depositions were performed with an argon flow of 25 ml/min.

3.1.2.2 Pulsed plasma hollow cathode sputtering

A hollow cathode sputter system traps the electrons inside the cathode cylinder, where it is accelerated and repelled by the opposing cathode sheaths. This will lead to an oscillation of electrons inside the cathode and collisions of gas atoms with these highly energized electrons will form a plasma with a high degree of ionization. High power pulses are applied similar to high power impulse magnetron sputtering, which has been shown to enhance the ionization of the

sputtered species substantially as compared to direct current magnetron sputtering. A schematic view of the experimental arrangement is given in Figure 3.3.

One of the main advantages of hollow cathode sputtering is the control of size, shape and dispersion of the deposited nanoparticles, as well as minimizing agglomeration on the substrate surface by alternating pulse amplitude, length and frequency [43], [44]. The nanoparticles are formed in the gas phase by the sputter vapor and their growth is depending on three main stages: In the first stage, a dimer is formed by nucleation during a three-body collision. This dimer then grows into a small cluster through the addition of more individual metal atoms/ions. If the cluster is large enough, it will get negatively charged in the second stage as the electron mobility will become higher as the mobility of positive ions. This leads to coagulation. When the coagulated cluster reaches sizes of > 10 nm, the built-up negative charge prevents it from further coagulation. In the third stage, the particle grows only due to slow addition of metal atoms/ions [43].

Figure 3.3: Schematic of hollow cathode sputter process based on [44].

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Table 1: Used hollow cathode targets and their deposition parameters.

Sputter material	Deposition time (min)	Substrate bias (V)
Fe ₃ O ₄	0.50	floating
Fe ₃ O ₄	1.00	floating
Fe ₃ O ₄	2.00	floating
Fe ₃ O ₄	4.00	floating
TiO ₂	0.25	+10

In this work, the technique has been leveraged for fabrication and deposition of metal oxide nanoparticles on graphene substrates. Titanium dioxide (TiO₂) and magnetite (Fe₃O₄) nanoparticles were deposited on top of the graphene layer using this technique. The substrates were placed outside the dense plasma region, preventing energetic species from reaching them and damaging the graphene lattice. The discharge parameters for the Fe₃O₄ particles were: a pulse frequency of 1200 Hz, a pulse width of 80 μ s and an average power of 90 W. A substrate bias can be used to attract the particles to the substrate surface. For the Fe₃O₄ particles no bias was applied and the substrates were exposed to nanoparticle deposition ranging from 0.5 to 4 minutes. For the TiO₂ nanoparticles the deposition time was 15 s and the bias was +10 V. Other process parameters are given in reference [44]. Important deposition parameters are summarized in Table 1.

3.1.3 Pulsed Laser Deposition

Pulsed laser deposition (PLD) uses a coupling of photonic energy to a bulk target material through electronic processes for growing a layer on a substrate opposite of the target. Both target and substrate are positioned within a vacuum chamber with an optical quartz glass window and usually with several in- and outlets for

gases. A high energy laser pulse is focused onto the rotating target and is partially absorbed near the surface. Exceeding the ablation threshold of the target, a plasma plume occurs with particles moving perpendicular to the target. The material within the plasma plume can collide and react with background or inlet gases or ion sources. Nevertheless, it will recondense on the substrate, hence a layer will grow. A schematic of the general principle is shown in Figure 3.4.

The PLD process used in this work is described in [45]. Different target materials were ablated using a krypton fluoride (KrF) excimer laser at a wavelength of 248 nm. The oxygen partial pressure was kept at either 0.1 or 0.05 mbar. The laser pulses were adjusted to keep a layer thickness of around 0.5 – 1 nm. The sensor substrates were kept at room temperature during deposition. Copper oxide (CuO), Fe_3O_4 , vanadium pentoxide (V_2O_5) and zirconium dioxide (ZrO_2) have been used as target materials. Their process properties are summarized in Table 2. Unfortunately, the ZrO_2 sample processed at 0.05 mbar was not available for measurements and V_2O_5 (0.1 mbar) physically broke after some measurements.

Figure 3.4: (a) Schematic of the PLD process and (b) picture of occurring plasma plume within the vacuum chamber of the PLD apparatus. Adapted from [46].

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Table 2: Used PLD targets and their deposition parameters.

PLD material	O ₂ pressure (mbar)	Laser fluence (J/cm ²)	Number of laser pulses
CuO	0.05	5	120
CuO	0.10	5	180
Fe ₃ O ₄	0.05	7	150
Fe ₃ O ₄	0.10	7	200
V ₂ O ₅	0.05	5	120
V ₂ O ₅	0.10	3	200
ZrO ₂	0.10	3	220

3.2 Characterization methods

To gain information about the cleanliness, thickness uniformity and induced damages of graphene samples, they are analyzed using atomic force microscopy (AFM), Raman spectroscopy and X-ray photoelectron spectroscopy (XPS) before and after the decoration with NPs or NLs. AFM gives information about the topography, while Raman spectroscopy and XPS is used to acquire information about structural properties. Additionally, XPS provides information about the chemical composition of the investigated material.

3.2.1 Atomic Force Microscopy

Using a very sharp needle attached to a cantilever, the AFM scans the surface of a specimen, where different scanning modes are possible: contact mode, non-contact mode and tapping mode. Here, only the tapping mode is used, where the needle oscillates close to its resonance frequency in z-direction while scanning the whole surface in a raster scan. Depending on the topology, van der Waals forces

will change the oscillation amplitude of the cantilever, which is detected via a laser beam. Resolutions down to an atomic level can be achieved in height, which provides an opportunity to gain topography information of very flat samples such as graphene. In addition to the amplitude, also the phase difference between the excitation signal of the cantilever and its actual oscillation is recorded. The phase provides an insight into mechanical properties and the viscoelasticity of the studied material as it measures energy loss. For EG on SiC, for example, it can reveal whether the surface consists of different graphene domains as different graphene thicknesses, monolayer, bilayer or multilayer exhibit different Young's moduli. Besides topography measurements, AFM measurements can also be adapted to measure, for example, the work function (Kelvin Probe Microscopy) or conductivity using a conductive tip.

In this work, a Quadrex Dimension 3100 with a Nanoscope IVa controller was used with silicon tips (PPP-NCHR-50 from Nanosensors) with a tip radius of curvature below 7 nm exclusively in tapping mode. The overall roughness in height is calculated as the root mean square deviation.

$$R_q = \sqrt{\frac{\sum_{i=1}^N (Z_i - Z_{\text{average}})^2}{N}} \quad (3.1)$$

N is the total number of measurement points, Z_i is the height at measurement point i and Z_{average} is the average height. Note that the roughness in height is calculated for an arbitrary area within the AFM measurement and should only be utilized to compare similar samples with each other.

3.2.2 Raman spectroscopy

With Raman spectroscopy, incoming monochromatic light gets scattered inelastically on the sample surface due to interactions with molecular vibrations or excitations. This inelastic scattering leads to a characteristic energy shift of the outgoing laser light, the so-

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called Raman effect. Raman scattering can be separated into Stoke scattering and Anti-Stoke scattering. The incident radiation has a higher frequency than the scattered radiation for Stoke scattering and vice versa for Anti-Stoke scattering [47]. Narrow optical filters shield the detector from reflected, non-scattered light from the laser.

The quality of graphene can easily be verified using Raman spectroscopy. A typical Raman spectrum of EG on SiC is shown in Figure 3.5. The important modes are D at 1350 cm^{-1} , G at 1580 cm^{-1} , D' at 1610 cm^{-1} (not present here) and G' (also referred to as 2D) at 2700 cm^{-1} . The G and 2D peaks refer to high quality graphene while the D peak arises only when disorder or lattice defects are present.

A micro Raman setup was used to perform Raman spectroscopy and reflectance measurements. A CCD (charge-coupled device) camera coupled to a monochromator (HR460) was utilized along with a $100\times$ magnification objective which were excited at 532 nm using a solid-state laser. The power was kept at 17 mW for PEG and below 1 mW for DEG samples. The focused spot size had a diameter of $\sim 0.9\text{ }\mu\text{m}$ on the sample and a system spectral resolution of approximately 5 cm^{-1} could be achieved. The Raman spectra of Si-face graphene were obtained by subtracting a reference Raman spectrum of 4H-SiC (0001). A more detailed description of this setup can be found in [48].

Figure 3.5: Typical Raman spectra of EG on SiC with important modes. Adapted from [Paper 1].

3.2.3 X-ray photoelectron spectroscopy

XPS is normally utilized to gain information about the surface chemistry of a sample, such as what elements are present and what other elements they are bonded to and the type of bonding. The typical depth that can be analyzed is around 0-20 nm and standard XPS setups are able to detect all elements with atomic numbers above 3. The detection limits for most of the elements are in the parts per thousand range, but it is possible to achieve even ppm under special conditions. An XPS spectrum is the measurement of the kinetic energy and number of electrons that are released from the sample surface while being irradiated with an x-ray beam. To enable this detection, XPS measurements need to be performed in high vacuum ($< 10^{-8}$ mbar).

A Microlab 310-F spectrometer was used to investigate possible alterations to the graphene lattice made to the sample after the decoration with NPs and to establish if the NPs consisted of Fe_3O_4 as expected. More information about the system can be found in [49].

3.2.4 Density functional theory

Density function theory (DFT) is used to calculate and predict material behavior. It is based on quantum mechanical models which in turn are based on the Hohenberg-Kohn theorems [50]. DFT is often put to use in material science to investigate the electronic structure of many-body systems. Here, the adsorption of gas molecules on pristine EG (PEG) and decorated epitaxial graphene (DEG) with Fe_3O_4 NPs was investigated. The calculations are based on hybrid gas-phase DFT and executed with the Gaussian 16 Rev. B.01 program package [51]. PEG has been modeled as one 4×5 graphene layer on top of a 4×5 buffer layer, which is covalently bonded to the 4×4 Si-face surface of hexagonal 4H-SiC. DEG was simulated by full geometrical optimization of Fe_3O_4 located on PEG, where all dangling bonds are passivated by hydrogen atoms. M06-2X level

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theory with consideration of a split basis set was used for all calculations [52]. The dispersion-corrected DFT functional M06-2X implicitly includes modified parameters associated with the Hartree-Fock exchange interaction, allowing the prediction of weak van der Waals interaction [53]. A LANL2DZ (Los Alamos National Laboratory 2 Double-Zeta) basis set was applied for iron (Fe) atoms and a 6-31G basis set for carbon, silicon, oxygen and hydrogen species [54]. All atoms were allowed to fully relax during geometrical optimization and no symmetry restrictions have been used. The adsorption energy of gas molecules (E_{ads}) was calculated as

$$E_{\text{ads}} = (E_{\text{tot}}^{\text{PEG/DEG}} + E_{\text{tot}}^{\text{gas}}) - E_{\text{tot}}^{\text{gas@PEG/DEG}} \quad (3.2)$$

$E_{\text{tot}}^{\text{PEG/DEG}}$ and $E_{\text{tot}}^{\text{gas}}$ are the total energies of isolated PEG or DEG templates and gas molecules, respectively. The total energy of PEG or DEG after the reaction with gas molecules is defined as $E_{\text{tot}}^{\text{gas@PEG/DEG}}$. A compensating correction for basis set superposition error (BSSE) was applied for a more accurate prediction of the adsorption energies [55].

3.3 Sensor fabrication

In this chapter, all the processes involved in the fabrication of the studied sensors are discussed. It starts with the growth of graphene on SiC chips and then elaborates how this chip is mounted to become a free-standing sensor unit and how the sensor readout is done.

3.3.1 Graphene growth

Since it was first experimentally produced in 2003, scientific advances and technology development in graphene have virtually exploded. As such, also the definition of graphene has been expanded to include materials that are not strictly only monoatomic carbon, but also including chemically reduced graphene oxide, composite

materials comprising micrometer-sized graphene flakes, and multi-layer graphene. Clearly, these different types of graphene will have different mechanical, optical, and electrical properties, where the choice of material should depend on the intended use of the graphene. The type of graphene depends on how it was synthesized, and there are many well-established methods for graphene growth [56]. The most common method for production of large area monolayer graphene relies on chemical vapor deposition, where a carbon-rich precursor gas is used to grow graphene on a metallic catalyst substrate. This approach is highly scalable and can produce high quality graphene. However, the necessary transfer of the graphene to an insulating substrate - for electronic devices – adds an additional step which could lead to degradation or contamination of the graphene surface. Another, rather hands-on method is mechanical exfoliation. This method produces the highest quality graphene, but the process is very slow and not scalable. The method employed to grow graphene in this work was epitaxial growth of graphene through thermal decomposition of a SiC substrate. It is referred to as EG since the underlying Si-terminated SiC substrate on which the graphene is grown reconstructs and a supercell of the buffer layer matches quite well with the graphene lattice. Sublimation of silicon occurs at a much faster rate compared to carbon atoms in vacuum at elevated temperatures due to its higher vapor pressure. Usually, an overpressure of argon is applied to enhance the uniformity of the EG layer. Monocrystalline graphene can be grown over an entire wafer with very high quality on insulating or semi conducting SiC, thus allowing the direct fabrication of electronic devices. As mentioned in section 2.1.2, if SiC is heated to sufficiently high temperatures, Si-atoms sublime and leave a carbon-rich layer behind which eventually forms graphene. Figure 3.6 shows a simplified growth process.

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Figure 3.6: Schematic of EG growth on SiC.

In this work, growth was performed on hexagonal polytype 4H-SiC (0001) on-axis Si-terminated substrates. SiC is with a bandgap of 3.26 eV a wide bandgap semiconductor that is either semiconducting or semi-insulating depending on the doping. Its crystal structure matches with the graphene lattice. Moreover, it is available for purchase in very high quality on wafer scale. For the samples in this study, semi-insulating SiC was used. EG was prepared by sublimation of SiC and subsequent graphene formation at 2000 °C in argon and at a pressure of 1 bar [57]. The graphene layer forms on top of a monoatomic carbon buffer layer, which is still covalently bonded to the SiC substrate. As a result, and sensor basis, EG with a monolayer ratio of about 98 % (2 % bilayer) was achieved.

3.3.2 Sensor mounting

The EG-on-SiC-chip is 7×7 mm big and needs to be diced before further processing. To cut the chips, a 30 µm thin diamond blade is used with an automatic dicing saw (DISCO DAD321, Japan) and deionized water cooling during the cutting process. The resulting cut has a width of about 50 µm. To ensure no contamination is induced to the graphene surface, a protective layer of positive photoresist (SU1818) is applied beforehand. The photoresist is applied via spin coating for 30 s at 4000 rpm with an acceleration speed of 2000 rpm/s. The sample is then baked at 100 °C for 20 min in an oven in ambient air for curing. The backside of the fully transparent chips is marked with a diamond pen to exclude using the wrong side. To remove the photoresist after cutting, the chip is put into pure acetone, then into pure ethanol and then blow-dried using a

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nitrogen gun. The samples were either halves or quarters of the initial chip. After successful growth and dicing of the chips, the high quality of the graphene surface is verified. As a first step of transforming the graphene chip into a graphene gas sensor, electrodes are deposited on top. The contacts have either been deposited through thermal evaporation or sputtering of titanium (2 nm) and gold (200 nm) sequentially. The arrangement of electrodes varies, thus influencing the baseline resistance measured in-between two electrodes. In this work, all NP DEG samples had four 0.5 mm squared contacts with a 1 mm gap in between and all NL DEG samples had two 2 mm squared contacts with a 1 mm gap. To enable a closed loop temperature control, each sensor chip is glued using Aremco Ceramabond 571 on top of a ceramic heater substrate (Heraeus GmbH, Germany) with an additional Pt-100 temperature sensor (Heraeus GmbH, Germany). This device was mounted on top of a TO8-socket and connected to its pins using gold-wire bonding and silver glue (Epotek E3081). This setup limits the working temperature to 300 °C, but measurements were only performed up to 200 °C as a safety measure. Figure 3.7 shows a mounted sensor with all necessary parts.

Figure 3.7: Photograph of mounted sensor device. Here Fe_3O_4 NP DEG.

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3.3.3 Data acquisition

The resistance of the graphene layer in-between the deposited contacts is measured over time and used as the sensor signal. As mentioned in section 2.2.2, the charge carrier density will change due to gas interaction, thus altering the sensor's resistance. A schematic of this is shown in Figure 3.8. The resistance is measured with a Sourcemeter (Keithley 2601, USA) and transferred to a custom-made computer program with a sampling rate of 1 Hz. If not specified otherwise, the resistance was calculated from the current measured at 3 V. Some measurements were performed using a specialized board from 3S GmbH, Saarbrücken, Germany, instead. The measurement voltage were kept the same. More information about this system can be found in [58]. A special temperature controller was used to monitor and adjust the sensor temperature. The controller can be programmed to keep the sensor at a given temperature or change it over time to create ramps or plateaus. The ceramic heater heats the sensor and the Pt-100 reads back the actual temperature.

Figure 3.8: Schematic of graphene sensor readout.

3.4 Gas mixing apparatus

To perform gas measurements with well-defined total gas flow and concentrations over the sensor, a gas mixing apparatus (GMA) was used. The GMA can provide different gases whose flows are regulated by mass flow controllers (MFCs). A known gas mixture, usually from a gas cylinder, is connected with a high pressure to the MFCs. Each mass flow controller has a fixed maximum flow of which a range between 5 and 100 % can be reliably set. Zero air out of a zero air generator or pure nitrogen (N_2) can be used with the possibility of varying humidity and oxygen partial pressure as the background or carrier gas for the applied gases. The humidity is produced by splitting the dry carrier gas into two streams, one of which goes through a water bottle, the so-called “bubbler”, which can be assumed having 100 % relative humidity (RH). After this, both streams are reassembled. Humidity can be adjusted by varying the split ratio through MFCs. To ensure that no humidity could leak into the system when performing measurements under dry conditions, the bubbler line was disconnected for those measurements. If not especially mentioned, a total flow of 100 ml/min was applied for all experiments. Test gases are provided via a gas bottle, where the

Figure 3.9: Schematic of gas mixing apparatus.

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test gas is diluted to a specific concentration in the same carrier gas used as background gas, or via a permeation oven. The purity of the test gases is N5.0, which means 99.999 % purity. The sensors are inserted in a flow chamber with a volume of 3 ml. Using specially designed flow chambers, either one sensor, two sensors, or one sensor with a UV-LED (light emitting diode) on the opposite side can be used during a measurement. Figure 3.9 gives an overview of how such a system can look like.

For all measurements performed in Linköping, the carrier gas for the test gas bottles was pure nitrogen. The background and purging gas was applied through two MFCs giving a mixture of 80 % nitrogen and 20 % oxygen. The test gas was added through an additional MFC into the same line. In total, four different test gases can be applied during a single measurement session. The whole gas flow enters a four-way valve which can direct the gas flow either through the sensor chamber or directly to waste. To maintain a constant flow and atmosphere, a second branch with only two MFCs, nitrogen and oxygen, is connected to the four-way valve. When the valve switches one gas flow to waste, the other is automatically lead through the sensor chamber. This system enables sharp steps and time for a new gas mixture to settle. The system is equipped with MFCs from Bronkhorst High-Tech B.V., AK Ruurlo, Netherlands, with maximum flow rates of 20, 50 or 100 ml/min. Nitrogen MFCs had a maximum flow of 100 ml/min whereas all other MFCs had 50 ml/min except for the NH_3 MFC with 20 ml/min. A more detailed description of the system can be found in [59].

Measurements performed in Saarbrücken used zero-air generated by a GT Plus ultra-zero air generator (VICI AG International, Schenkon, Switzerland) as background gas instead. To enable measurements with lower concentrations than what is possible with the standard procedure of injecting the test gas with one MFC, an additional flow line can be connected the predilute the gas. In this case, two additional MFCs (500 ml/min for carrier gas and 10 or 20 ml/min for test gas) are added to predilute the test gas before

the new gas flow is injected into the main gas stream. With this procedure, a dynamic dilution over more than four orders of magnitude can be achieved [60]. This allows the dilution of 100 ppm gas bottles down to one-digit ppb concentrations over the sensor. Another option to prepare rather low concentrations in the gas flow is a permeation oven. Here, a permeation tube is placed in a heated and sealed oven chamber. The permeation tube contains the pure test substance which slowly diffuses through the tube walls made of perfluoroalkoxy alkane (PFA). The rate of diffusion is highly dependent on the oven temperature which therefore is kept constant. The outflow is connected to the main gas flow via an MFC so that the permeation oven is conceptually similar to a gas bottle with a variable test gas concentration. Permeation tubes do not only enable low concentrations, but can also be used for gases with very high vapor pressure, which cannot be kept in gaseous form in pressurized gas bottles. More details about the system can be found in [61], [62].

If UV irradiation is desired during a measurement, a special sensor chamber is used where the UV-LED can be placed opposite of the sensor within the sensor chamber. Two different LEDs with wavelengths of 265 nm (Sensor Electronic Technology Inc, S-T39B-F1-265-01-1-050) and 355 nm (Roithner Lasertechnik GmbH, XSL-355-3E-R6) have been put to use.

3.4.1 Test gases

All used test gases are shortly defined and characterized through their chemical composition, appearance and pollutant guidelines. The World Health Organization [63] as well as the European Parliament [64] have guidelines for pollutant acceptance levels for indoor-air quality and these references are used if not specified otherwise.

Ammonia (NH_3) is a very toxic gas at higher ppm concentrations. Nevertheless, it is one of the most produced inorganic chemicals with a wide use in the production of pharmaceuticals, explosives,

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cleaning products and as a precursor for fertilizers, with the latter alone being responsible for 80 % of the total NH_3 production [65]. Moreover, NH_3 can be related to the formation of secondary particulate matter by reacting with acidic species, like NO_x or sulfur dioxide (SO_2), to form ammonium-containing aerosols, which constitute the major fraction of $\text{PM}_{2.5}$ aerosols in the atmosphere [66].

Nitrogen dioxide (NO_2) can cause respiratory symptoms and has an acceptance level of 100 ppb annual average and 20 ppb for one hour exposure. It is mostly produced through internal combustion engine sources accountable for around 40.5% of NO_x emissions in Europe, followed by energy production (22.5%) [67].

Volatile organic compounds (VOCs) have unfortunately no universal definition. They are defined via the boiling points [68] over vapor pressures [69] of the molecules, or their participation in atmospheric photochemical reactions [70]. Although some of them are hazardous to humans even at very low concentrations, they are widely put to use in industry and everyday products as solvents. In this work, benzene and formaldehyde are used as model VOCs.

Benzene (C_6H_6) is a genotoxic aromatic compound, especially associated with leukemia, and has therefore very low acceptance levels. At the time of writing, France has with 0.6 ppb the lowest acceptance level [71]. According to the latest published WHO recommendations, however, there is no safe level for benzene. It is mostly produced as a byproduct of traffic and is, additionally, often used as a component of solvents in cleaning agents or paint [72].

Formaldehyde (CH_2O) has an acceptance level of 80 ppb and is genotoxic. In low concentrations, CH_2O usually does not pass beyond the respiratory system which limits direct cause to portal-of-entry effects like nasal cancer and sensory irritation. It emerges from combustion processes and is often used in its aqueous solution as disinfectant or conservative in everyday products as well as in the production of plastics [73].

All gases come with a purity level of 5.0 except nitrogen, which is generated from a liquid source and has a purity of 6.0 in gaseous

form. Table 3 gives an overview of the gases and their specifications for measurements performed in Linköping and Saarbrücken, respectively.

Table 3: Used test gases and their system properties.

Test gas	Linköping	Saarbrücken
	Bottle concentration (ppm)	Bottle concentration (ppm)
0-air ²	/	100 %
Nitrogen	100 % ³	100 %
Oxygen	100 %	/
Ammonia	2, 500	/
Benzene	0.5	0.1 ⁴ , 100
Formaldehyde	4	57
Nitrogen dioxide	1	10 ⁵

² 0-air is generated using a GT Plus ultra-zero air generator (VICI AG International, Schenkon, Switzerland) and is not retrieved from a gas bottle.

³ Nitrogen is generated from a liquid source and is not retrieved from a gas bottle.

⁴ 0.1 ppm source concentration from permeation tube at 80 °C.

⁵ Nitrogen dioxide used in Saarbrücken had air as bottle carrier gas.

4 Results and Discussion

This chapter presents and discusses the experimental results of the work. The first section describes integrity studies performed on the graphene samples before and after functionalization. Then the gas measurements of the different sensors with different gases and environmental influences are discussed. The last section deals with special data treatment to further improve the sensing properties.

4.1 Layer characterization

Before using a graphene chip for the production of a sensor device, its topography and structural integrity is analyzed. This step is repeated after the surface decoration.

4.1.1 Topography

To make sure that graphene formed a continuous layer and was free from contamination, the topography was measured using AFM. A typical topography of the grown pristine graphene layer is shown in Figure 4.1 (a). The steps from the SiC step bunching that occurs during the high temperature growth have a height of typically 0.5-1.5 nm and form terraces. The low height difference can be seen in the inset of Figure 4.1 (a), which shows the horizontal height profile for a 2 mm line scan. The surface roughness R_q within such a terrace is with 0.25 nm very small. The corresponding phase image (Figure 4.1 (b)) shows a very continuous value with the only exceptions being the step edges and a bi- or multilayer graphene patch in the lower left corner. This is an additional indicator for a high quality monolayer graphene lattice. Figure 4.1 (c) shows the C terminated backside surface of such a chip. It is still very flat, but shows a completely different crystalline structure pattern with presumably several layers of graphene grown on it.

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Figure 4.1: AFM images of (a) pristine graphene on Si-terminated 4H-SiC with height profile as inset, (b) its corresponding phase image and (c) backside (C-face) of SiC chip.

Furthermore, the samples were analyzed again after surface decoration. Figure 4.2 (a) shows the AFM image in of the Fe_3O_4 (0.1) NL DEG (see section 3.1.3) sample. The surface does not differ much from the pristine sample, as a very thin (~ 0.5 -1 nm) continuous layer is deposited onto the graphene surface. The dominating features are still the step edges formed by the SiC chip.

Figure 4.2: (a) AFM image of Fe_3O_4 NL (a) and NP (b) DEG sample.

After the decoration with Fe_3O_4 NPs, the graphene surface looks completely different (Figure 4.2 (b), here 0.5 min deposition time). The NPs are now dominating the surface roughness and the step-like plateaus with their small differences in height can hardly be resolved at the Z-scale needed to show all features of the NPs. The particle coverages and average particle diameters of the NP DEG samples investigated in this work are summarized in Table 4. The particle size, was calculated after evaluating 100 single particles and agglomerates per sample. For the Fe_3O_4 samples with different deposition times, the particle size should stay approximately constant, as no other deposition parameters have been modified. This is true to a large extent for single particles, but with a longer deposition time, more agglomerates are formed. An exemplary histogram of the particle size distribution is discussed in [Paper 2]. The particle size can have an impact on the sensor's sensitivity and selectivity and thus is another parameter that can be optimized for sensors performance tuning [6]. This was, however, not investigated in this work. With an increase in deposition time, the coverage should increase. As the sample deposited for 2 min exhibits a larger coverage than the one with 4 min deposition time (compare Table 4), it is believed, that they have been wrongly labelled during

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Table 4: Resulting coverages and particle sizes after the decoration with NPs.

Sputter material	Deposition time (min)	Avg. particle size (nm)	Coverage (%)
Fe ₃ O ₄	0.50	80 ±10	15 ±5
Fe ₃ O ₄	1.00	80 ±10	25 ±5
Fe ₃ O ₄	2.00	80 ±10	55 ±5
Fe ₃ O ₄	4.00	80 ±10	45 ±5
TiO ₂	0.25	90 ±10	15 ±5

the decoration step as otherwise the correlation between deposition time and coverage follows the expected trend. Regarding AFM images, all graphene samples are very clean, except for the deposited functionalization material.

4.1.2 Structural integrity

Raman measurements were performed to verify that the integrity of the graphene layer is still ensured even after the decoration with NPs or NLs. The comparison between PEG, Fe₃O₄ NP DEG and Fe₃O₄ (0.1) NL DEG is shown in Figure 4.3. For a better comparison, all spectra were normalized to the G peak. This is possible because the y-axis is in arbitrary units. The lower line belongs to the PEG reference which shows the G and 2D peaks, typical for sp² hybridized carbon, around 1610 cm⁻¹ and 2737 cm⁻¹, respectively [74]. The rather small full width at half maximum (FWHM) value of 35 cm⁻¹ at the 2D peak is indicative of uniform monolayer graphene within the irradiated spot [75]. The features above 1280 cm⁻¹ and extending into the G peak are related to the interfacial buffer layer between the graphene and the SiC substrate [74]. Although they overlap with the position of the D peak at 1350 cm⁻¹, they are not related to defects. If damage is induced into the graphene lattice, the

D peak would rise. It can be clearly seen that the spectra after decoration are almost the same as the reference, indicating that no damage was introduced. The position of the 2D peak is the same for all samples, but the G peak (1605 cm^{-1} for PEG) varies slightly with $\pm 10\text{ cm}^{-1}$. This is most likely be due to different levels of strain in the graphene lattices [76] or possibly a result of different doping in the graphene due to charge transfer between graphene and decoration material. Moreover, the 2D peak broadens for the NL DEG sample which could be related the inclusion of bi- or multilayer graphene in the measured spot. Also the lower G/2D peak ratio is another indication for this.

If the ambient pressure is decreased during the PLD deposition, damage starts to be induced into the graphene lattice. Figure 4.4 shows such a case where Fe_3O_4 NL was deposited using 0.05 mbar , introducing slight damage to the graphene lattice. This is due to an increase in disorder and impurities, which can be seen as an increase in the D peak around 1350 cm^{-1} . Similarly, damage is also induced if too many nanoparticles are deposited on top of the graphene lattice. Here, TiO_2 was deposited until it reached a covered almost the whole surface. The height of the D peak strongly increased and even surpasses the G peak.

Figure 4.3: Raman spectra of PEG, Fe_3O_4 (0.1) NL DEG and Fe_3O_4 NP DEG. Adapted from [Paper 1].

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Figure 4.4: Raman spectra of PEG, and Fe₃O₄ NP DEG and Fe₃O₄ (0.05) NL DEG.

4.1.3 Chemical composition

The integrity of the graphene lattice after surface decoration was already verified using Raman spectroscopy. Additionally, XPS measurements were performed to support the assumption of integrity and to gain information about the chemical composition of the sensor surface. This measurement was only performed with one graphene sample before and after the decoration with Fe₃O₄ NPs. Figure 4.5 shows the Fe2p and O1s core level spectra for PEG and Fe₃O₄ NP DEG. The Fe2p peak and the O1s peak should be at binding energies of about 711 and 532 eV [77]. The quantification of oxygen based on the XPS core level spectrum shows a five times higher oxygen concentration for Fe₃O₄ NP DEG compared to PEG. This strong difference, with an additional peak appearing at 530 eV, is in good agreement with the presence of Fe-O in the Fe₃O₄ NPs. Moreover, two peaks at 710.9 and 724.4 eV strongly suggest the presence of iron species, which cannot be seen before the decoration. These measurements support the assumption of a soft and clean NP deposition on top of the graphene lattice.

Figure 4.5: (a) O1s and (b) Fe2p XPS core level spectra for PEG (top) and Fe₃O₄ NP DEG (low) [Paper 2].

4.1.4 Theoretical considerations

DFT calculations have been performed to investigate the different adsorption energies between C₆H₆ and CH₂O, and PEG and Fe₃O₄ NP DEG, respectively, to theoretically verify that the NP decoration would increase the gas sensitivity. Figure 4.6 shows the energetically favored adsorption configurations of the gas molecules on PEG and DEG. The adsorption energy for C₆H₆ on DEG is $E_{\text{ads}} = 1.795$ eV, whereas the adsorption energy on PEG is with $E_{\text{ads}} = 0.284$ eV significantly lower. In the absence of the Fe₃O₄ NPs, the C₆H₆ molecule adsorbs parallel to the surface in the flat geometry. In this case, the center of C₆H₆ ring lays on top of a carbon atom

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belonging to the graphene. With Fe_3O_4 NPs being present, the formation of a strong chemical bond between the C_6H_6 ring and one of the Fe atoms, leading to a tilted C_6H_6 adsorption, is facilitated.

The CH_2O molecule behaves similarly with adsorption energies of 0.149 eV and 1.870 eV for the adsorption on PEG and DEG, respectively. In conclusion, weak physisorption of C_6H_6 and CH_2O on PEG can be altered to strong chemisorption with the presence of Fe_3O_4 NPs. To conclude, Fe_3O_4 DEG graphene should exhibit an enhanced response towards the exposure of C_6H_6 and CH_2O , with a slightly higher estimated interaction with CH_2O .

Figure 4.6: Optimized adsorption configurations of C_6H_6 on PEG (a) and DEG (b), and CH_2O on PEG (c) and DEG (d) [Paper 2].

4.2 Gas measurements

To evaluate the performance of the prepared EG-based gas sensors and their applicability in AQM, measurements with several test gases under varying operating conditions, such as sensor temperature and relative humidity of the ambient, have been performed. The sensor's resistance is used as signal and should change when the test gas is introduced. An exemplary response is shown in Figure 4.7, where a Fe_3O_4 NP DEG sensor was exposed to 30 min pulses of CH_2O at concentrations from 5 to 0.1 ppm.

Figure 4.7: Response of Fe_3O_4 NP DEG for CH_2O exposures at 150 °C at 0 %RH. Adapted from [Paper 2].

The relative response is then calculated as the relative change in resistance due to the gas exposure in relation to its baseline.

$$r = \frac{R - R_0}{R_0} \cdot 100 \% \quad (4.1)$$

R is either the saturated resistance signal or the last value of resistance before the gas exposure is switched back to background gas and R_0 corresponds to the baseline resistance before the gas exposure. In this example, the relative response would be 0.45 % for 1 ppm of formaldehyde.

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If not especially mentioned, all measurements have been performed with a 3 V measurement voltage over the contacts at 150 °C in dry air with a gas flow of 100 ml/min.

The only way to get a value for a time constant if the saturated response plateau is not reached is through extrapolation. Here, an exponential fit is applied to the gas response.

$$y = A_1 e^{-x/\tau} + y_0 \quad (4.2)$$

A_1 , τ and y_0 are the fitting parameters, whereof τ is the time constant defined as when 63 % of the change has happened (also referred to as τ_{63}). In this example, τ is about 300 s for 1 ppm exposure.

The signal to noise ratio (SNR) in decibel (dB) is a good value to compare sensor properties and is calculated as

$$SNR_{dB} = 20 \log_{10} \left(\frac{A_{signal}}{A_{noise}} \right) \quad (4.3)$$

where A_{signal} is the maximum absolute response at a given concentration and A_{noise} is three times the standard deviation of the baseline noise (also referred to as 3σ). For the absolute response of 1 ppm shown above (28 Ω), the standard deviation is 0.32 Ω and the SNR is 29 dB.

4.2.1 Influence of temperature

The sensor temperature plays an important role for the sensitivity of gas sensors. To ensure adsorption and reaction of gases at the sensor surface and thus a sensor signal, a specific activation energy has to be overcome [78]. This leads to different relaxation times caused by different rate constants for different gases [79]. As already mentioned, the current sensor setup limits the operating temperature to about 300 °C and no measurements were performed above 200 °C as a precaution. To be able to work at higher temperatures, sensors are usually annealed at an even higher temperature, which was not done here.

Figure 4.8: Response of Fe₃O₄ NP DEG for CH₂O and C₆H₆ exposures at different temperatures at 0 %RH.

Figure 4.8 shows the response of Fe₃O₄ NP DEG towards 1 ppm of CH₂O (blue) and C₆H₆ (red) for 30 min at temperatures ranging from 100 °C up to 170 °C in steps of 10 °C. The measurement clearly shows that the baseline resistance increases with increasing temperature. Moreover, a higher operating temperatures leads to higher responses. The response towards 1 ppm of CH₂O increases from 0.28 % at 100 °C to 0.67 % at 170 °C and from 0.16 % to 0.33 % for C₆H₆. Measurements above 150 °C also exhibit a small drift as the sensors have not been used at those temperatures before. To prevent the formation of a film of water on the sensor surface and achieve a reasonably high response at a fairly stable baseline, all further measurements using Fe₃O₄ NP DEG have been performed with an operating temperature of 150 °C.

A more systematic study of influence of temperature, humidity and UV irradiation influence was performed with the NL DEG samples. The response to 30 min exposure towards 25 and 100 ppm of NH₃ was tested at 125, 100, 75 and 50 °C at 50 %RH. In between exposures, the sensor chamber was purged with background gas for 90 min. Figure 4.9 shows the result exemplarily for the V₂O₅ (0.05) NL DEG sensor and the responses for all investigated NL samples

4 Results and Discussion

to 25 ppm NH_3 are summarized in Table 5. Values marked in bold are the highest observed absolute responses for each sample.

In contrast to the measurement discussed before (Figure 4.8), an increase in temperature means a decrease in response for all samples but ZrO_2 (0.1), which has its highest response at 125 °C. CuO (0.05) exhibits an almost constant response for all temperatures but a lower response at 50 °C. A higher response is, however, not always desired if it comes with slower time constants. This can be clearly seen in Figure 4.9, where only exposures at 125 °C lead to a steady-state sensor response during the 30 min gas exposure. τ is extrapolated for all four operating temperatures and it increases from approximately 150 s at 125 °C up to 550 s at 50 °C. Moreover, at lower temperatures the sensor is not always able to relax back to its baseline after 90 min at lower temperatures. The response of the CuO (0.1) sample show that both temperature and gas concentration contribute to the carrier concentration, and thus, the resistance of the sensor. The first exposure at 125 °C towards 25 ppm of NH_3 results in an increase in resistance and a positive response, whereas 100 ppm already leads to a negative response of -0.6 % (not shown here). The reason for this change in response direction is likely that with increasing gas adsorption enough electrons are donated to the

Figure 4.9: Response of V_2O_5 (0.05) NL DEG for NH_3 exposures at different temperatures at 50 %RH.

graphene for the Fermi level to move from below the Dirac point (p-type conductivity) to above the Dirac point (n-type conductivity). When changing the temperature to lower degrees, the response is always negative. This would also partly explain why the absolute response increases with lower temperatures as temperature and NH_3 concentration work against each other in terms of carrier generation. The other CuO sample, on the other hand, exhibits a positive response for all temperatures, similar to both V_2O_5 sensors. Fe_3O_4 and ZrO_2 show a negative response for all temperatures.

A compromise between level of response, response shape and relaxation has to be established. As a result of this, all other measurements conducted with NL DEG samples are operated at 75 °C except for ZrO_2 (0.1) at 125 °C.

Table 5: Relative responses of NL DEG sensors towards 25 ppm NH_3 at different temperatures at 50 %RH.

	Relative response (%)			
	125 °C	100 °C	75 °C	50 °C
CuO (0.05)	4.6	4.6	4.8	3.5
CuO (0.1)	0.9	-0.8	-2.9	-8.3
Fe_3O_4 (0.05)	-7.6	-10.8	-14.1	-18.9
Fe_3O_4 (0.1)	-5.9	-6.5	-8.1	-13.5
V_2O_5 (0.05)	4.2	5.8	6.6	9.2
V_2O_5 (0.1)	1.8	3.9	7.7	12.4
ZrO_2 (0.1)	-21.2	-14.3	-8.3	-8.0

4.2.2 Influence of humidity

Perhaps even more critical than temperature for the sensor response of some material/gas combinations, is the influence of relative humidity in the ambient. Many metal oxides have been found to exhibit a cross-sensitivity towards RH and for most materials, a higher level of RH means a lower sensitivity towards other gases, as they must compete with water for available adsorption sites. To explore the optimal sensitivity, most measurements shown are performed in a dry environment. To investigate the effect of RH, measurements with different samples, gases and levels of humidity have been performed.

Figure 4.10 shows the response of Fe_3O_4 NP DEG vs 1.6 and 0.8 ppm of CH_2O and 100 and 200 ppb of C_6H_6 for 30 min at 150 °C for 50, 25 and 0 %RH. No response is observed for any humidity above zero for both gases. This means that the complete sensor system for AQM would need to run in a dry environment. This is a drawback, but technologically possible.

Similar measurements were performed using NL DEG samples at 30 min exposure of 200 ppb C_6H_6 and CH_2O in dry and humid (50 %RH) conditions using three operating temperatures (150, 100 and 50 °C). The measurements performed in dry conditions are discussed in more detail in section 4.2.4. The results of the

Figure 4.10: Relative response of Fe_3O_4 NP DEG for CH_2O and C_6H_6 exposures at 150 °C at different RH.

Figure 4.11: Relative responses of NL DEG samples for C₆H₆ and CH₂O exposures at 150 °C at 50 %RH.

measurements with 50 %RH at 150 °C are summarized in Figure 4.11. None of the sensors reacted to the test gases at 100 or 50 °C and the sensors decorated with V₂O₅ did also not react at 150 °C. Similar to what was shown above, Fe₃O₄ (0.05) loses its sensitivity towards C₆H₆ and CH₂O under the influence of humidity. Fe₃O₄ (0.1), ZrO₂ (0.1) and both CuO DEG sensors show a small response at 150 °C for both gases. The response is much smaller compared to dry conditions, is not very stable and strongly influenced by drift induced with the introduction of humidity. The highest response towards C₆H₆ can be observed for ZrO₂ (0.1) with 0.12 %. All the NL samples show a lower response for CH₂O compared to C₆H₆, except for CuO (0.1) which has its highest response towards CH₂O (0.08 %).

The responses of the different NL DEG samples towards 25 ppm of NH₃ for 30 min at RH levels of 0, 20, 40 and 60 % is shown in Figure 4.12. The operating temperature was kept at 75 °C for all sensors except ZrO₂ (0.1) at 125 °C. All samples exhibit a decrease in sensitivity when changing from a dry environment to a humid one except V₂O₅ (0.05), which increases progressively from 8.8 % at 0 %RH to 13.8 % at 60 %RH. The responses of Fe₃O₄ (0.1) and CuO (0.05) decrease for each humidity step from initially -8.4 and

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Figure 4.12: Relative responses of NL DEG samples for NH_3 exposures at 75 °C (except ZrO_2 (0.1) at 125 °C) at different RH.

19.6 % in dry conditions down to -4.3 and 7.3 % at 60 %RH, respectively. Fe_3O_4 (0.05) and CuO (0.1), on the other hand, show a drop in resistance for the first humidity level (20 %RH), then stay almost the same for 40 %RH and increase for 60 %RH. It is interesting that an increase in humidity increases the response again for some samples, even exceeding the response at zero humidity (ZrO_2 (0.1)). This increase could be due to the reaction with OH groups or of products of reactions from OH groups and NH_3 instead. This phenomenon was shown to occur for metal oxide gas sensors when operating them at relatively low temperatures in a humid environment [80], [81].

4.2.3 Influence of UV irradiation

Figure 4.13 shows the response of a TiO_2 NP DEG sensor towards varying oxygen percentages without (black) and with UV irradiation (purple). The UV LED has a wavelength of 265 nm and an optical output power of 0.8 mW. The operating temperature was 100 °C and oxygen was varied from a baseline of 20 % to values between 16 and 1 %. It can be clearly seen that the measurement without UV irradiation shows changes in resistance when varying the oxygen concentration, but they are not distinct and cannot be

Figure 4.13: Relative response of TiO₂ NP DEG towards a change of oxygen from a background of 20 % to between 16 and 1 % without (black) and with UV irradiation (purple, 265 nm) at 100 °C at 0 %RH. Adapted from [Paper 1].

related to the specific concentrations. Introducing the UV irradiation, the baseline resistance drops by about 270 Ω. Moreover, the changes in oxygen concentration can now be distinctively observed as the resistance shows the typical shape of a gas sensor response. Unfortunately, the exposure time is with 10 min not enough to arrive at a saturated response level. The desorption process is enhanced under the irradiation as well, decreasing the time needed for the sensor to get back to its baseline after the gas exposure, making it faster and more effective. The low response without UV is likely due to an oxygen saturated surface in the background of 20 % O₂. UV irradiation promotes oxygen desorption, leading to an increased dynamic range for oxygen detection.

The influence of different UV wavelengths on the sensor response towards an exposure of 25 ppm NH₃ for 30 min is summarized for the NL DEG samples in Table 6. Values marked in bold are the highest observed absolute responses for each sample. The relative humidity was kept at 50 % and all samples were operated at 75 °C except ZrO₂ (0.1) at 125 °C. A clear trend for V₂O₅ can be observed as the relative sensor response is highest (14.3 and 13.3 %) at 355 nm UV irradiation and decreases over 265 nm down to no irradiation for both samples. For ZrO₂, on the other hand, only a

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small decrease is observed for UV irradiation (both wavelengths) compared to -21.3 % with no irradiation. Fe_3O_4 also exhibits a negative response and without UV irradiation, the response is lowest for both samples. Fe_3O_4 (0.05) shows a higher response for all three conditions compared to Fe_3O_4 (0.1), but has its highest absolute response with -19.4 % at 265 nm UV irradiation, while Fe_3O_4 (0.1) has its highest response (-15.2 %) at 355 nm UV irradiation. CuO (0.05) exhibits a small but positive response (1.9 %) at 355 nm UV irradiation but changes its direction of response at 265 nm UV irradiation, while giving the highest response of -4.8 % without irradiation. This indicates that the UV irradiation pushes the Fermi level through the Dirac point, hence switching the conduction behavior. CuO (0.1) reacts similar to V_2O_5 with the highest response (-14.3 %) at 355 nm UV irradiation and a decrease without irradiation.

Moreover, UV irradiation has also an effect on the time constant for some samples. For example, τ decreases for V_2O_5 from approximately 550 s without irradiation down to 400 s at 265 nm UV irradiation at 75 °C operating temperature. CuO behaves similarly with a drop about 200 s from 600 down to 400 s with 265 nm UV irradiation. An irradiation with 355 nm does decrease τ as well, but not as much as 265 nm UV irradiation. This could be due to irradiation with a shorter wavelength has a higher energy. For Fe_3O_4 , on the other hand, τ stays approximately constant at 350 s with and without UV irradiation.

The whole sensing mechanism for DEG is not fully understood and introducing one more variable like UV irradiation introduces additional complexity. It is known that if the band gap is below the wavelength energy (4.48 eV for 265 nm and 3.49 eV for 355 nm), there will be charge excitation changing the charge density also in the graphene. This could increase or counteract the effect of the gas response depending on the material/gas combination and should be more pronounced for the thicker layers, where the net charge excitation is higher. This also explains why ZrO_2 , with a band gap > 5 eV, shows no significant difference under UV irradiation.

Table 6: Relative responses of NL DEG sensors towards 25 ppm NH_3 at 50 %RH with different UV wavelengths at 75 °C except ZrO_2 (0.1) at 125 °C.

	Relative response (%)		
	No UV	265 nm	355 nm
CuO (0.05)	-4.8	-0.002	1.9
CuO (0.1)	-2.9	-12.2	-14.3
Fe_3O_4 (0.05)	-14.1	-19.4	-18.7
Fe_3O_4 (0.1)	-8.1	-11.8	-15.2
V_2O_5 (0.05)	7.7	/ ⁶	14.3
V_2O_5 (0.1)	6.6	11.2	13.3
ZrO_2 (0.1)	-21.3	-19.4	-19.3

4.2.4 Ammonia

The two best performing NL DEG sensors from measurements described above were used to test their capabilities of detecting ppb concentrations of NH_3 in a humid environment (see Figure 4.14). This is done to evaluate their capabilities for the application in breath analysis towards NH_3 as target gas. Hibbard and Killard state that there is a need of simple, non-invasive detection methods that can detect ammonia with a limit of detection of at least 50 ppb [82].

Similar to what was observed above, Fe_3O_4 (0.05) shows the highest response towards NH_3 and exhibits with -4.8 % towards 100 ppb more than twice the response of V_2O_5 (0.05). Moreover, the SNR for Fe_3O_4 (0.05) is with 47 dB better than the one for V_2O_5 (0.05) with 30 dB at 100 ppb. Although the response is not perfectly distinct for all tested concentrations, the lower detection limit should be much

⁶ V_2O_5 (0.05) broke down and could not be used for further measurements.

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Figure 4.14: Relative response of V₂O₅ (0.05) and Fe₃O₄ (0.05) NL DEG samples for NH₃ exposures at 75 °C at 40 %RH.

less than the tested 100 ppb considering the high SNR value. Assuming the worst case scenario of a linear relation between response in Ω and concentration in ppb, the lower detection limit can be extrapolated as 0.5 ppb assuming that the response has to be larger than 3σ . This, and the fact that it operates well under humid conditions at a relatively low temperature, would make this NL DEG a promising platform for breath analysis. Note that the human breath usually has a relative humidity of 91-96 % [82], but measurements could only be performed up to 60 %RH. Moreover, the dynamic range of response towards NH₃ is with at least three orders of magnitude quite broad. One of the main drawbacks though are still the slow ad- and desorption times. This issue is addressed in section 4.3.

4.2.5 Nitrogen dioxide

Fe₃O₄ NP DEG samples were also tested at low concentrations of NO₂ at 150 °C in a dry environment. The gas was applied for 15 min followed by a background exposure of 60 min. More measurements using NO₂ are discussed in section 4.3, where the response towards NO₂ is exemplarily used to test the introduction of the first-order time-derivative signal. Here, the sensor was only tested for 100,

Figure 4.15: Relative response of Fe_3O_4 NP DEG for NO_2 exposures at 150 °C at 0 %RH.

200, 300 and 400 ppb and the response over concentration is fairly linear in that region (see Figure 4.15). The response towards NO_2 is negative – for example -2 % at 100 ppb – which makes it clearly distinguishable from all the positive responses observed so far for the NP DEG samples for exposures of NH_3 , C_6H_6 and CH_2O . The time constant τ is approximately 500 s for 100 ppb exposure. The SNR (87 dB) at 100 ppb hints to a much lower detection limit than the tested concentrations. Assuming again a linear correlation and a detectable response larger than 3σ , the lower detection limit can be extrapolated to be approximately 1.5 ppb. This value demonstrates that the hourly average of 20 ppb NO_2 exposure for AQM could easily be detected and could even outperform state of the art commercial sensors, such as $\text{NO}_2\text{-A1}$ from Alphasense (Essex, United Kingdom) with a resolution of 20 ppb.

4.2.6 Benzene and Formaldehyde

One of the main findings of this work is the ability to detect the hazardous VOC, C_6H_6 and CH_2O quantitatively down to a single ppb and also over a large dynamic range of three orders of magnitude up to at least 5 ppm using Fe_3O_4 NP DEG sensors. The measurement shown in Figure 4.16 was performed at 150 °C at 0 %RH.

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The relative response is with 0.02 % and 0.04 % for 1 ppb of C_6H_6 and CH_2O not very large, but with a SNR of 1.6 dB for 5 ppb of C_6H_6 still easily detectable. The discussed measurement was performed at Saarland University, but using the same sensor at Linköping University can even improve the SNR to 35 dB for 5 ppb C_6H_6 .⁷ The WHO recommended safety limit for CH_2O (81 ppb over 30 min of exposure) is easily reached with a relative response above 0.1 %. The time constant τ lies around 300 s for both gases. The shown measurement was repeated twice in the same environment and once more approximately one year later with the same sensor. The measured responses show some small deviations between the measurements but without a clear trend of decreasing response over time. This is good as it shows the long-term stability of the sensor. What decreases though is the SNR. More noise can be seen for a sensor if operated over a longer time compared to a ‘fresh’ sample.

As already mentioned in section 4.2.2, NL DEG samples were tested towards 200 ppb of C_6H_6 and CH_2O as well. The operating temperature was set to 150, 100 and 50 °C with 30 min of gas

Figure 4.16: Relative response of Fe_3O_4 NP DEG for CH_2O and C_6H_6 exposures at 150 °C at 0 %RH. Adapted from [Paper 2].

⁷ Measurements performed at Saarland University exhibit a much higher background noise compared to measurements performed at Linköping University.

exposure and 60 min of relaxation phase in between exposures. The responses for 150 °C are summarized in Figure 4.17. At 150 °C, the response towards C_6H_6 was higher compared to CH_2O for all samples. CuO (0.1) exhibited with 1.9 % and 1.8 % for C_6H_6 and CH_2O , respectively, the absolute highest response for all samples. Table 7 summarizes the responses for 50 and 100 °C. Values marked in bold are the highest observed absolute responses for each sample. It can be seen that at lower temperatures the response towards CH_2O is slightly higher compared to C_6H_6 for Fe_3O_4 and V_2O_5 . ZrO_2 was only able to detect the gases at 150 °C and also Fe_3O_4 (0.05) and V_2O_5 (0.05) showed no response at 50 °C. The highest response in total was observed from CuO (0.1) at 50 °C with 3 % and 2.25 % for C_6H_6 and CH_2O , respectively. Time constants vary for the different materials and are between 100–200 s and 100–400 s for C_6H_6 and CH_2O , respectively. The fastest response for both gases was achieved with CuO and V_2O_5 (~100 s) and the slowest with ZrO_2 (200 and 400 s).

Comparing these results under dry conditions with the ones of NP DEG, it seems that the NL samples show a higher response towards C_6H_6 and CH_2O . Even more promising though is the response of CuO NL DEG under humid conditions, where still a response, even if rather small, can be observed. This is promising in

Figure 4.17: Relative responses of NL DEG samples for 200 ppb C_6H_6 and CH_2O exposures at 150 °C at 0 %RH.

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Table 7: Relative responses of NL DEG samples for 200 ppb C₆H₆ and CH₂O exposures at 50 and 100 °C at 0 %RH.

	Relative response (%)			
	C ₆ H ₆		CH ₂ O	
	50 °C	100 °C	50 °C	100 °C
CuO (0.05)	1.7	1.3	1.5	1.1
CuO (0.1)	3.0	1.9	2.3	1.6
Fe ₃ O ₄ (0.05)	0	0.07	0	0.08
Fe ₃ O ₄ (0.1)	0.8	0.4	0.8	0.5
V ₂ O ₅ (0.05)	0	0.1	0	0.13
ZrO ₂ (0.1)	0	0	0	0

so far as it would work for AQM without the problem of interfering humidity. More investigations with lower concentrations are needed to verify the applicability for AQM.

4.3 First-order time-derivate signal

As already mentioned before, a sensor with good sensitivity is not sufficient and properties like stability, selectivity and speed of response need to be addressed as well. One method to achieve faster time constants is the use of the sensor signal's first-order time-derivative [12]. In this section, the sensor response is evaluated based on the first-order time-derivative to introduce an alternative sensor signal. The response is calculated as

$$r_{dt} = R_{dt} - R_{0,dt} \quad (4.4)$$

R_{dt} is the highest absolute derivative signal during a gas pulse and $R_{0,dt}$ is the baseline value before gas exposure. For most sensors,

4.3 First-order time-derivate signal

further smoothening is necessary to eliminate the rapid fluctuations in the resistance value due to background noise. In this work, an adjacent average filter with 10 points smoothening was used if not specified otherwise.

Figure 4.18 shows the resistance over time of Fe_3O_4 NP DEG (upper black line) when exposed to different NO_2 concentrations for 15 min. This is the same raw data used to calculate the response in Figure 4.15. It can be clearly seen that 15 min of exposure is not enough for the sensor to reach a saturated response. During the recovery time of 60 min, it was also not possible for the sensor to fully relax to its initial baseline. This is a common problem for rather slow reacting sensors. If the signal does not reach a saturated response level during the exposure, it is not straightforward to calculate the real maximum response and, moreover, also the common time constants like τ_{90} cannot be calculated easily but need to be extrapolated. Therefore, a direct comparison with sensor performances reported in literature and product specification sheets is not possible. To overcome these issues without adding more exposure or relaxation time, the first-order time-derivative of the sensor resistance is introduced as an alternative sensor signal (see lower red line in Figure 4.18). Note that here the smoothening was performed with a 100 point window as the baseline signal was very

Figure 4.18: Resistance over time of Fe_3O_4 NP DEG (black, upper) with its corresponding time-derivative (red, lower) for NO_2 exposures at 150 °C at 0 %RH.

noisy. This will be discussed in more detail in section 4.3.3. The peaks of the first-order time-derivative signal arise much faster and are also concentration-dependent, which is in good agreement with Wu et al., stating that r_{dt} is directly proportional to the applied gas concentration [12]. Moreover, the desorption peak is concentration-dependent as well. The desorption response is normally not utilized as a standard indicator as it occurs after the adsorption, but it might be useful as a feature in multivariate statistics for selectivity enhancement [83]. Because the peak is reached much faster, it is also more robust against not sufficiently long exposure or relaxation times.

In the following sections, the influence of exposure and relaxations times, as well as of environmental factors such as temperature, humidity and UV irradiation are discussed. At the end, the time constants for all the investigated samples are compared to their corresponding alternative first-order time-derivative time constants.

4.3.1 Influence of exposure and relaxation time

If the exposure time is not long enough for the sensor to reach a saturated response, the maximum response increases with increasing exposure time, potentially leading to a misquantification. As the first-order time-derivative of the resistance signal is the slope of the change, it should be independent of the exposure time (if the exposure time is long enough for r_{dt} to reach its peak). Exactly this phenomenon can be seen in Figure 4.19 (a). The sensor response towards 50 ppb NO₂ increases from -0.2 % after 5 min to -0.9 % after 20 min. On the other hand, r_{dt} is reached much faster and remains at approximately -0.1 Ω/s, regardless of the exposure time. Note that a slight increase can be observed after the third (15 min) exposure time. The constant time-derivative response could be due to r_{dt} being determined by the initial adsorption/desorption phase during which the change in resistance is the highest. After this,

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Figure 4.19: Resistance over time of Fe₃O₄ NP DEG (black, upper) with its corresponding time-derivative (red, lower) for NO₂ exposures at 150 °C at 0 %RH with different (a) exposure and (b) relaxation times.

further adsorption/desorption proceeds at a slower speed.

Figure 4.19 (b) shows the sensor behavior with decreasing relaxation times. Here, the sensor was repeatedly exposed to 50 and 200 ppb NO₂ for 15 min, but altering the relaxation time from initially 60 down to 15 min. If the sensor is not able to fully relax to its initial baseline between gas exposures, a drift is induced which could lead to a possible misquantification of the measured gas concentration. Not only does the response magnitude decrease with decreasing relaxation time, also the ratio of response for 200 ppb over 50 ppb gradually decreases from 2.8 to 2.0 for relaxation times of 60 and 15 minutes, respectively. This is a clear indication of NO₂ molecules still occupying possible adsorption sites on the sensor surface.

The baseline of the first-order time-derivative signal relaxes much faster, thus exhibiting a constant ratio of responses at 200 ppb over 50 ppb (3.0 ± 0.1). This results in a problem-free quantification of both concentration at all tested relaxation times.

4.3.2 Environmental influences

It is known that not only the sensor response but also the speed of response heavily depends on the sensor temperature [79]. Considering this, also the first-order time-derivative signal should change with a change in temperature. Figure 4.20 shows the derivative response of Figure 4.9. The response of V_2O_5 (0.05) NL DEG is plotted over sensor temperature towards exposures of 25 ppm NH_3 exposures. As expected, the time-derivative response exhibits the same trend towards increasing temperature as what was observed for the standard response. The time needed for the derivative signal to reach its maximum although is not significantly dependent on the temperature and stays at around 15 s. This is unexpected, but could be due the relatively small tested temperature range, thus only small changes might occur. This was also evaluated for measurements of Fe_3O_4 NP DEG and all NL DEG samples for C_6H_6 and CH_2O exposures (compare section 4.2.6). The time-derivative response for different temperatures follows the standard response. τ_{dt} is not increasing with decreasing temperature, but stays approximately constant at 15 s.

Figure 4.20: Derivative response of V_2O_5 (0.05) NL DEG for 25 ppm NH_3 exposures at different temperatures at 50 %RH (see Figure 4.9).

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The responses towards exposures of 25 ppm NH_3 with varying RH investigated in section 4.2.2 (compare Figure 4.12) were analyzed towards changes in the first-order time-derivative response. For simplicity, only one sensor for each decoration material is shown. The changes in response for different RH levels is similar to what was observed before for the standard response. More interesting is the time needed to reach r_{dt} . As shown in Figure 4.21, the time to peak increases if humidity is introduced. The strongest influence could be observed for CuO (0.1), where τ_{dt} increased from 12 s at 0 %RH up to at 32 s at 60 %RH. This could be due to water molecules occupying possible reaction sites, or a competition between H_2O and NH_3 over available sites, and/ or reactions between the two molecules to form ammonium and hydroxyl groups on the sensor surface, thus limiting the reaction time.

Also the UV measurements from section 4.2.3 (compare Table 6) were analyzed towards changes in the first-order time-derivative response. It was found that the time-derivative response follows the same pattern as the standard response discussed before. However, the time to peak (τ_{dt}) does not change distinctively with or without UV irradiation and stays at approximately 15 ± 5 s for an exposure towards 25 ppm NH_3 . This is unexpected, as with a higher surface energy through the UV irradiation, also the surface reactions with the gas molecules should be increased, resulting in shorter time to peak in the time-derivative signal. The time constants are already very short and therefore, an additional small decrease is simply not observed.

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Figure 4.21: τ_{dt} of first-order time-derivative response of NL DEG samples for 25 ppm NH_3 exposures at 75 °C (except ZrO_2 (0.1) at 125 °C) at different RH.

4.3.3 Time constants

Especially for indoor air quality monitoring, the sampling rate should be as fast as possible and within a range of a few minutes to allow real-time monitoring [9]. As already mentioned above, the peaks of the derivative signal reach their highest points already after a short period of time. A comparison between the standard response times and their corresponding first-order time-derivative response times for the different material/gas combinations tested is presented in Table 8. For better comparability, all time-derivative calculations were evaluated with a 10 point smoothening. τ is shown as a range for all NL samples and τ_{dt} is shown as the average of all NL samples. The time needed to reach r_{dt} depends on the combination of sensor material and test gas, but should be applicable to all resistive type gas sensors. τ_{dt} of the example figure for Fe_3O_4 NP DEG towards NO_2 exposure lies around 10 s (Figure 4.18) which is 25 times faster compared to the extrapolated time constant of the standard response. Other measurements suggest a decrease of time constants from approximately 300 s down to 50 s for measurements

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with the same sensor towards C_6H_6 and CH_2O [Paper 2]⁸. For a TiO_2 NP DEG sample, the time constants with oxygen measurements could be decreased from 1500 s down to 25 s [Paper 1]⁹. This is an improvement with a factor of 60 times faster response compared to the standard resistance signal. For the NL samples an average τ_{dt} of 10 s was found for exposures towards 200 ppb C_6H_6 and CH_2O . τ_{dt} for 25 ppm NH_3 , however, lies around 15 ± 5 s. For most samples, the time-derivative response for 100 ppm exposures was about 5 seconds faster compared to 25 ppm. This could be because more gas molecules are available directly from the start of the gas exposure, thus more active surface sites can react at the same time. Moreover, the UV irradiation did not seem to have an effect on τ_{dt} for any of the studied material combinations or gases.

The first-order time-derivative signal can get very noisy if the resistance signal does not exhibit a very smooth baseline. Therefore, an adjacent average smoothing filter was used. However, τ_{dt} highly depends on the applied smoothing filter. Figure 4.22 shows a zoomed in version of the third peak (exposure towards 200 ppb NO_2) of Figure 4.18. Without any smoothing, τ_{dt} is only 5 s, whereas it increases to 10 s for 10 point smoothing and 100 s for 100 point smoothing. Especially the latter one does highly modify the original response and forms a ‘false’ peak. Therefore, one has to be very careful when choosing the applied smoothing filter. 100 point smoothing was used here only to better demonstrate the features in Figure 4.18 and Figure 4.19.

⁸ In [Paper 2], τ_{dt} is specified with 50 s and smoothing was performed with 500 points. This is necessary, as the baseline signal exhibits strong noise.

⁹ In [Paper 1], τ_{dt} is specified with 60 s. This is due to the smoothing was performed with 100 points.

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Table 8: Comparison of the regular (τ) and derivative (τ_{dt}) time constants for different EG decorated materials and test gases.

	Test gas (ppm)	T (°C)	Exp. time (min)	UV (nm)	τ (s)	τ_{dt} (s)
Fe ₃ O ₄ NP	C ₆ H ₆ 1	150	30	/	300	50 ¹⁰
Fe ₃ O ₄ NP	CH ₂ O 1	150	30	/	300	50 ¹⁰
TiO ₂ NP	O ₂ 10 %	200	90	265	1500	25 ¹¹
Fe ₃ O ₄ NP	NO ₂ 0.2	150	15	/	250	10
NL DEG	NH ₃ 25	75	30	/	350–550	15 ± 5
NL DEG	NH ₃ 25	75	30	265	325–500	15 ± 5
NL DEG	NH ₃ 25	75	30	355	325–550	15 ± 5
NL DEG	C ₆ H ₆ 0.2	150	30	/	100–200	10
NL DEG	CH ₂ O 0.2	150	30	/	100–400	10

It should be noted that in the practical applications of gas sensors, the change in the gas concentration in the studied environment usually does not occur by leaps and bounds, but rather slow-changing processes. Therefore, the applied method might not be useful for processes where the time constant of the gas concentration change will be close to the time constant of the sensor. One

¹⁰ See footnote ⁸ on page 67.

¹¹ See footnote ⁹ on page 67.

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method to overcome this issue in real applications would be the use of a sampling pump instead of a continuous gas flow over the sensor. It can also be used as an additional sensor signal to create more transient data which could be used for multivariate statistic analysis to enhance sensitivity.

Figure 4.22: Third peak (exposure towards 200 ppb NO₂) of Figure 4.18 with different adjacent average smoothing filters.

5 Conclusions and outlook

In summary, the work presented in this thesis focused on how to utilize epitaxially grown graphene on SiC as an ultra-sensitive gas sensor. Three main approaches have been tested and evaluated to increase the sensitivity, selectivity, speed of response and stability of the graphene based gas sensors.

First, the decoration with different metal oxide nanoparticles and nanolayers was investigated. With the iron oxide NP DEG sensor, it was easily possible to detect and quantitatively measure concentrations down to a single ppb of benzene and formaldehyde, making it very promising for air quality monitoring. Several NL DEG samples have been evaluated towards their sensitivity to the two mentioned VOCs and ammonia under varying environmental influences. Again, iron oxide was shown to be a very promising decoration material as that sensor was able to detect trace amounts of ammonia at rather low temperatures with humidity. This could be a very interesting combination for breath analysis applications with focus on ammonia sensing. The integrity of the graphene lattice was maintained after functionalization, which was verified for each sample using characterization methods like AFM, Raman and XPS.

The second approach, using UV irradiation during the measurement, is well known and was also here shown to have a huge impact for some material/gas combinations. For example, the titanium oxide NP DEG sensor was only distinctively sensitive towards changes of oxygen if illuminated with UV light. However, we could also show that UV irradiation is not good for all gas sensors as it can also decrease the sensitivity or simply not affect the measurement at all.

As a last step, the first-order time-derivative was investigated as an alternative sensor signal instead of the sensor's resistance. We could demonstrate that not only a more stable baseline can be

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achieved, but also that the time constants can be drastically reduced as the peak of slope reaches its maximum much faster compared to the resistance value. This peak is concentration dependent and almost independent of exposure and relaxation times. With this method, the time constants can be drastically decreased, which opens an opportunity for rather slow gas sensors in areas where a fast gas sensor readout is compulsory. Moreover, reduced time constants can save lab testing time, thus saving time, resources and money during research activities.

All three investigated methods show very promising results to improve sensing performance, opening new fields of possible sensor applications. More time will be invested to further improve sensitivity, selectivity, speed of response and stability of the graphene-based gas sensors. This can be done, for example, through the exploration of different sensing materials for decoration, but also by using newly developed two-dimensional catalytic metals based on the same SiC bulk. Moreover, with the creation of more transient data, selectivity could be enhanced using multivariate statistic analysis tools.

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Abbreviations

AFM	Atomic Force Microscopy
AQM	Air Quality Monitoring
BSSE	Basis Set Superposition Error
BZ	Brillouin Zone
CNT	Carbonanotube
CCD	Charge-Coupled Device
CVD	Chemical Vapor Deposition
DEG	Decorated Epitaxial Graphene
DFT	Density Functional Theory
DOS	Density Of States
EG	Epitaxial Graphene
FET	Field Effect Transistor
FWHM	Full Width at Half Maximum
GMA	Gas Mixing Apparatus
LANL2DZ	Los Alamos National Laboratory 2 Double-Zeta
LED	Light Emitting Diode
MFC	Mass Flow Controller
MOS	Metal Oxide Semiconductor
NL	Nanolayer
NP	Nanoparticle
PEG	Pristine Epitaxial Graphene
PFA	Perfluoroalkoxy Alkane
PLD	Pulsed Laser Deposition
PVD	Physical Vapor Deposition
QHE	Quantum Hall Effect
RH	Relative Humidity
SNR	Signal to Noise Ratio
UV	Ultraviolet
VOC	Volatile Organic Compound
WHO	World Health Organization
XPS	X-ray Photoelectron Spectroscopy

Papers

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