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Scientific discipline: Automation, Electronics, Electrical Engineering and Space Technologies

DOCTORAL DISSERTATION

Title of doctoral dissertation: System of gas detection by two-dimensional materials

Title of doctoral dissertation (in Polish): System detekcji gazów z wykorzystaniem materiałów dwuwymiarowych

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DESCRIPTION OF DOCTORAL DISSERTATION

The Author of the doctoral dissertation: Katarzyna Drozdowska

Title of doctoral dissertation: System of gas detection by two-dimensional materials

Title of doctoral dissertation in Polish: System detekcji gazów z wykorzystaniem materiałów dwuwymiarowych

Language of doctoral dissertation: English

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Keywords of doctoral dissertation in Polish: czujnik gazów, rezystancyjne czujniki gazów, detekcja gazów wspomagana światłem, materiały dwuwymiarowe, grafen, półprzewodniki 2D, nanomateriały, promieniowanie UV, szum $1/f$, detekcja wykorzystująca fluktuacje rezystancji.

Keywords of doctoral dissertation in English: gas sensor, resistive gas sensors, light-assisted gas detection, two-dimensional materials, graphene, 2D semiconductors, nanomaterials, UV irradiation, $1/f$ noise, fluctuation-enhanced sensing.

Summary of doctoral dissertation in Polish: Niniejsza rozprawa przedstawia badania nad detekcją gazów wspomaganą promieniowaniem widzialnym lub UV wykorzystującą niskowymiarowe struktury (grafen i dwuwymiarowe chalcogenki metali). W ramach pracy doktorskiej zbadano prototypowe grafenowe czujniki rezystancyjne, których właściwości gazoczułe zależą od konfiguracji urządzenia oraz zastosowanego podłoża. Potwierdzono, że czujniki w konfiguracji diody Schottky'ego z grafenem osadzonym bezpośrednio na krzemie posiadają wysoką czułość i stabilność przy niższych napięciach polaryzacji w porównaniu do grafenowych tranzystorów. W ten sposób pokazano, że istnieje możliwość produkcji czujników grafenowych o niskiej konsumpcji energii. Dodatkowo, w pracy przedstawiono technikę drukowania warstw gazoczułych z roztworu dwuwymiarowych płatków jako alternatywę dla bardziej skomplikowanych metod wytwarzania czujników. Na podstawie badań nad disiarczkiem molibdenu oraz trisiarczkiem cyrkonu wykazano, że mechanizmy detekcji molekularnej mogą być uniwersalne dla różnych materiałów półprzewodnikowych o podobnej strukturze. Porównanie właściwości gazoczułych wybranych materiałów stanowi krok w kierunku optymalizacji systemów detekcji gazów, jak również zrozumienia jej mechanizmów.

Summary of doctoral dissertation in English: This thesis demonstrates light-assisted gas sensing by low-dimensional structures (graphene and two-dimensional metal chalcogenides). Studies on the prototype graphene-based resistive sensors show that the configuration of the device and the used substrate affect sensing properties. The sensors with Schottky diode configuration with graphene deposited directly on silicon exhibited high sensitivity and stability at lower voltage bias compared to graphene transistors. This confirms the possibility of adjusting sensor fabrication toward low-power consumption devices. Furthermore, the thesis demonstrates the solution-based printing of gas-sensitive layers from two-dimensional flakes as an alternative to more complex deposition techniques. The subsequent studies on molybdenum disulfide and zirconium trisulfide showed that light-enhanced molecular detection is potentially driven by similar mechanisms for materials of similar structure. The comparison between the sensing performance of the selected materials is a step toward optimizing detection systems as well as understanding gas sensing mechanisms.



I would like to warmly thank all those who helped me realize my doctoral research and supported me in preparing this doctoral thesis.

I am very grateful to my Supervisor – Prof. dr hab. inż. Janusz Smulko for constant mentoring, fruitful discussions, and ongoing support in all kinds of scientific challenges I have encountered during four years of doctoral studies. I am incredibly thankful for the constant encouragement to develop and expand my scientific career.

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Lastly, I am truly grateful for all the support from my closest ones – my family, who was always intrigued by my doctoral work and supported my PhD career even though the topics always sounded extremely complicated to them, and also my fiancée, my greatest companion in scientific and non-scientific challenges.

Pragnę złożyć serdeczne podziękowania dla wszystkich tych, którzy pomogli w realizacji moich badań doktorskich oraz wspierali mnie w przygotowaniu niniejszej pracy.

Jestem niezmiernie wdzięczna mojemu Promotorowi – Prof. Prof. dr hab. inż. Januszowi Smulko za mentoring, owocne dyskusje i ciągle wsparcie we wszystkich naukowych wyzwaniach, które napotkałam w trakcie trwania czteroletniego kształcenia doktoranckiego. Bardzo dziękuję za ciągle zachęcanie do tego, abym rozwijała swój warsztat badawczy.

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Rozprawę dedykuję Rodzicom i Kubie

ABSTRACT

The attractive properties of low-dimensional materials and structures pave the way toward producing highly sensitive and selective sensing devices for efficient detection of traces of analytes. Effective sensing of low concentrations of gases is applicable in indoor and outdoor environmental monitoring, food freshness assessment, explosives detection, and medical diagnosing. The high surface-to-volume ratio with increased surface activity of two-dimensional structures offers enhanced detection at a molecular level. To improve the sensing performance, light activation of sensing surfaces can induce the optoelectronic effect (increased photocurrent and, thus, charge transfer during molecular adsorption) and photocatalytic effect (when ultraviolet irradiation carries energy sufficient to accelerate surface processes). Selectivity of the gas sensors based on low-scale materials is another relevant figure of merit that can be improved by either modification of the material on the fabrication level or implementing a specific methodology of measurements and data analysis. Understanding mechanisms of gas detection by different low-dimensional materials enhanced by irradiation and comparing their performance is crucial for optimizing the fabrication of sensitive layers and the production of efficient gas sensors.

This thesis discusses light-assisted (visible light, UV irradiation) chemiresistive gas sensing by low-dimensional structures, focusing on graphene and metal chalcogenides as two-dimensional representatives. The prototype graphene-based sensors exhibited different sensing properties dependent on the configuration of the device and the used substrate. Field-effect transistors with silicon/silicon dioxide substrate and graphene channel exhibited at least a few times higher resistive responses to organic gases than transistors with graphene acting as a gate with gallium nitride substrate. The same magnitude of resistive responses was obtained when graphene was deposited directly on silicon, forming a Schottky junction. In this case, the voltage bias required to observe high responsivity was reduced at least ten times compared to graphene transistors. This indicates the possibility of adjusting sensor fabrication toward low-power consumption devices. The subsequent studies on semiconducting two-dimensional molybdenum disulfide and zirconium trisulfide showed that light-enhanced molecular detection is potentially driven by similar mechanisms in the family of low-dimensional metal sulfides. Furthermore, the simple procedure of solution-based printing of gas-sensitive layers from two-dimensional flakes was demonstrated to be an alternative fabrication process to more complex deposition techniques.

Overall, the thesis demonstrates the possibilities of employing various two-dimensional structures as gas-sensitive layers in electrical devices of different configurations. Comparing the sensing performance of the investigated materials constitutes a step toward optimizing detection systems and understanding the microscopic mechanisms driving processes responsible for macroscopic observations.

STRESZCZENIE

Niskowymiarowe materiały i struktury posiadają niezwykle atrakcyjne właściwości dla produkcji czujników oraz wydajnej detekcji śladowych ilości substancji analitycznych. Efektywna detekcja niskich stężeń gazów może znaleźć zastosowanie w monitorowaniu środowiskowym, ocenie świeżości produktów spożywczych, detekcji materiałów wybuchowych czy diagnostyce medycznej. Duży stosunek powierzchni do objętości oraz zwiększona aktywność powierzchniowa struktur dwuwymiarowych oferuje lepszą detekcję na poziomie cząsteczkowym. W celu zwiększenia czułości, powierzchnia materiału może zostać oświetlona żeby uzyskać efekt optoelektryczny (zwiększenie fotoprądu i transferu ładunku podczas adsorpcji molekularnej) oraz efekt fotokatalityczny (kiedy promieniowanie ultrafioletowe posiada energię wystarczającą do aktywacji procesów powierzchniowych). Z kolei selektywność, która jest kolejną ważną cechą wydajnego czujnika może zostać poprawiona albo poprzez modyfikacje materiałowe na etapie wytwarzania albo poprzez wykorzystanie odpowiedniej metodologii w pomiarach i analizie danych. Zrozumienie mechanizmów stojących za detekcją gazów przez różne materiały niskowymiarowe oraz porównanie ich działania jest kluczowe do optymalizacji procesu wytwarzania warstw gazoczułych.

W niniejszej rozprawie przedstawiono detekcję gazów wspomaganą promieniowaniem widzialnym lub UV wykorzystującą niskowymiarowe struktury, w szczególności grafen oraz chalkogenki metali, które występują w postaci dwuwymiarowej. Prototypowe czujniki grafenowe wykazały właściwości gazoczułe zależne od zastosowanej konfiguracji urządzenia oraz podłoża. Tranzystory polowe z kanałem grafenowym i podłożem krzem/ditlenek krzemu osiągnęły co najmniej kilkukrotnie większą odpowiedź rezystancyjną na gazy organiczne niż tranzystory z grafenową bramką i podłożem z azotku galu. Podobne zmiany rezystancyjne osiągnięto, gdy grafen został osadzony bezpośrednio na krzemie tworząc z podłożem złącze Schottky'ego. W tym przypadku napięcie polaryzujące czujnik, przy którym zaobserwowano wysoką czułość, było co najmniej dziesięciokrotnie mniejsze w porównaniu do konfiguracji tranzystora. To wskazuje na możliwość dostosowania procesu wytwarzania czujników tak, aby produkować urządzenia o niskiej konsumpcji energii. Badania nad dwuwymiarowym disiarczkiem molibdenu oraz trisiarczkiem cyrkonu pokazały, że mechanizmy detekcji molekularnej mogą być uniwersalne dla różnych materiałów półprzewodnikowych o podobnej strukturze. Dodatkowo, technika drukowania warstw gazoczułych z roztworu dwuwymiarowych płatków może stanowić alternatywę dla bardziej skomplikowanych metod.

W ogólności, rozprawa przedstawia możliwości wykorzystania różnych struktur dwuwymiarowych jako warstw gazoczułych w urządzeniach elektrycznych o różnych konfiguracjach. Porównanie właściwości gazoczułych kilku badanych materiałów stanowi krok w kierunku optymalizacji systemów detekcji, jak również zrozumienia mechanizmów w skali mikroskopowej, które wpływają na procesy obserwowane w skali makro.

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LIST OF IMPORTANT SYMBOLS AND ABBREVIATIONS

1D	–	one-dimensional
2D	–	two-dimensional
AuNPs	–	gold nanoparticles
CNT	–	carbon nanotube
CVD	–	chemical vapor deposition
DC	–	direct-current
DL	–	detection limit
E_F	–	Fermi level energy (eV)
E_G	–	band gap energy (eV)
f	–	frequency (Hz)
f_c	–	corner frequency (Hz)
FES	–	fluctuation-enhanced sensing
FET	–	field-effect transistor
GFET	–	field-effect transistor with graphene channel
G-R	–	generation-recombination event
IDES	–	interdigitated electrodes
I_s	–	DC current flowing through the sensor (A)
I_{DS}	–	drain-source current flowing through the channel in a field-effect transistor (A)
k	–	voltage gain
k_B	–	Boltzmann constant equal to $8.62 \cdot 10^{-5}$ eV/K
LED	–	light emitting diode
LSPR	–	localized surface plasmon resonance
ppb	–	parts per billion (a measure of analyte concentration)
ppm	–	parts per million (a measure of analyte concentration)
R^2	–	a statistical figure of merit showing how well the model fits the experimental data

R_0	–	baseline sensor resistance in air or inert atmosphere (Ω)
R_s	–	sensor resistance (Ω)
R_{Sdiff}	–	differential sensor resistance (Ω)
S	–	sensor response (resistive, conductive, or current)
S.A.	–	synthetic air
SBH	–	Schottky barrier height (eV)
$S_i(f)$	–	power spectral density of current fluctuations dependent on frequency (A^2/Hz)
$S_V(f)$	–	power spectral density of voltage fluctuations dependent on frequency (V^2/Hz)
$S_R(f)$	–	power spectral density of resistance fluctuations dependent on frequency (Ω^2/Hz)
$S_N(f)$	–	power spectral density of fluctuations from trapping of N carriers (Ω^2/Hz)
THF	–	tetrahydrofuran
TMDC	–	transition metal dichalcogenide
TMTC	–	transition metal trichalcogenide
V_s	–	DC voltage across the sensor (V)
V_{DS}	–	drain-source voltage in a field-effect transistor (V)
V_G	–	gate voltage in a field-effect transistor (V)
VOC	–	volatile organic compound
α_H	–	Hooge constant (dimensionless)
μ	–	mobility ($m^2V^{-1}s^{-1}$)
η	–	ideality factor of a Schottky junction (dimensionless)
σ	–	conductivity (S/m)
σ_N	–	variance of fluctuations caused by trapping of N carriers
τ	–	lifetime or relaxation time of a trapping state (s)
τ_{rec}	–	sensor recovery time (s)
τ_{res}	–	sensor response time (s)

1. INTRODUCTION AND OBJECTIVES OF THE THESIS

With rapid technological development, new solutions requiring novel materials and methodologies are constantly being introduced in science sectors to facilitate human activities in various fields. Among these, different kinds of sensing devices are necessary to secure the safety of people and the environment, providing the possibility of instant *in situ* monitoring of changes in physical and chemical parameters in the system. In the field of gas sensing devices, sensitivity, selectivity, fast operation, stability in time, and low cost are only a few requirements set for novel sensors that are still in the scope of today's research. The importance of gas detection and sensors reaching ultra-low detection limits down to single molecule levels is dictated by environmental, safety, and health monitoring needs [1]. Traces of toxic gases and pollutants are produced daily, either during large-scale industrial processes or people's daily activities, such as driving, air conditioning, and heating systems [2]. Detection of specific volatile species may also play a significant role in food freshness assessment, medical diagnosing, and exhaled breath sample analysis when volatile species remain biomarkers of diseases such as diabetes, halitosis, respiratory system disorders, or cancers [3–5]. In this regard, the urgency of producing highly effective and reliable sensing devices with low-concentration detection requires adjusting methodologies and novel materials.

In conjunction with charge carrier transport, surface science plays a crucial role in gas detection by structures and materials from the micro-, nano-, and atomic scales. Low-dimensional structures offer attractive properties, including high surface activity and effective charge carrier transport, which are crucial in accelerating surface processes and leading to more effective detection. Various nanomaterials and nanostructures have been investigated as sensors for small-molecule gases such as NO₂, NO, SO₂, CO₂, CO, NH₃, H₂S, H₂, O₂, O₃, H₂O, and different volatile organic compounds (VOCs) such as ethanol, acetone, formaldehyde, methane, methanol, tetrahydrofuran, acetonitrile, and others [2,6–9]. Metal oxide (MOx) nanostructures [2,10–15], graphene and its derivatives – graphene oxide (GO) and reduced graphene oxide (rGO) [16–19], carbon nanotubes [20], two-dimensional (2D) transition metal di- or trichalcogenides (TMDCs or TMTCs) [21–23], polymer nanostructures [24], and their hybrids [25–29] can be listed as potential candidates for gas detection.

This thesis focuses on employing low-scale structures (focusing on two-dimensional materials) as gas-sensitive components in detection systems and studying possible ways to improve sensors performance. The high surface-to-volume ratio of nanostructures may lead to enhanced sensing; however, gas molecules usually require additional energy to overcome chemical barriers and adsorb effectively at the surface. Elevated temperature is one of the methods for providing the energy necessary for efficient gas detection, and this approach has been used for conventional gas sensors based on metal oxides. Thermal energy delivered during the heating process stabilizes the sensors response and accelerates the surface processes,

improving the detection limit and performance at low gas concentrations. However, the working temperature for nanocrystalline MOx sensors often reaches 200–500 °C [30,31]. Therefore, it limits the detection of flammable and explosive gases, leads to high energy consumption, or even degrades the sensing material [32,33]. The aforementioned shortcomings of heated sensors ushered in the exploration of other possibilities for enhancing the surface activity of gas-sensitive materials and structures, including light enhancement.

Irradiation in the ultraviolet (UV) spectral range has been proven to be the alternative for high-temperature sensing, offering a promising tool for room-temperature gas detection [32,34]. Room-temperature sensing remains attractive from a practical point of view, specifically for portable, wearable sensing devices. The UV Light Emitting Diode (LED) power supply, usually of several microwatts or less, allows a much lower energy consumption than traditional heaters employed in gas detection setups. Experimental studies showing the advantages of UV-induced gas sensing were presented for nanocrystalline metal oxides, carbon nanotubes, graphene, and other 2D materials [22,35–37]. UV irradiation enhances surface activity by increasing the charge carrier density, inducing photocurrent, and providing more active sites. Furthermore, adjusting the optical properties of UV LEDs proved crucial for detection process optimization and improvement [38]. Therefore, light enhancement, a less invasive method of detection acceleration than annealing, may lead to low-power sensing devices of high stability and less degradability. UV light sources characterized by different optical parameters can affect the surface processes differently, especially if other environmental parameters, such as temperature or humidity, constitute variables in the system. Moreover, UV-induced detection mechanisms may vary for semiconductors with specific band gaps and carbon nanomaterials of metal-like electron conductivity. The dimensions of the sensing area could also play an essential role in the detection process, as smaller surfaces can be susceptible to specific gaseous species [39].

As mentioned before, nanoscale materials and atomically thin layers (2D semiconductors or carbon-based structures) are, by nature, beneficial for high-performance and low-power electronics. Their intact structures at the nanoscale and optoelectronic properties provide a solid base for highly sensitive devices. Simultaneously, the selectivity of gas sensors based on individual materials still poses a challenge for practical applications. Thus, various routes of selectivity improvement need to be considered. Combining resistive measurements with low-frequency noise studies is one of the methods for selectivity enhancement by providing distinct noise spectra for surface reactions at the sensing material-gas interface. Along with chemiresistive measurements, distinguishable low-frequency noise signals can be collected for specific gases. This way, both the DC resistance and its fluctuations carry the information about the molecular processes. The abovementioned considerations motivate me to study low-dimensional materials-based sensing devices for molecular detection enhanced by irradiation with a focus on sensing mechanisms. An optimized system for high-performance gas sensing can be provided, potentially being used as a low-power consumption sensor for real-life applications.

The research presented in this thesis aims to propose a system of gas detection using two-dimensional materials as active layers and to investigate, evaluate, and compare the gas-sensing performance of selected low-scale structures. The research includes studying and proposing possible mechanisms of gas detection connected with the physicochemical reactions occurring at the sensing surface and inducing low-frequency noise during light-assisted gas sensing.

The main objectives of the thesis include:

- a study of sensing properties of different low-scale materials fabricated by either vacuum deposition techniques or printing methods;
- investigation of the structural and electrical properties of the proposed sensing platforms, a study of the light modulation (UV or visible) effect on gas sensor properties, and analysis of electrical and low-frequency noise responses of the proposed sensors under selected ambient gases;
- assessment of possibilities of using gas sensors based on two-dimensional materials for real-environment gas sensing and explaining mechanisms of light-assisted gas detection.

To achieve the research aim, three main hypotheses were formulated in the dissertation:

- I. **Low-frequency noise utilized for gas detection by back-gated graphene can be scaled up to larger surfaces, facilitating simpler gas sensor production.**
- II. **The sensitivity and stability of the gas sensors based on two-dimensional materials can be improved by substrate selection.**
- III. **Low-cost ink-printed molybdenum disulfide (MoS_2) flakes can detect selected gases at ppb level.**

The dissertation is divided into ten main sections, the first being the introduction to the thesis. The second chapter focuses on chemiresistive gas sensing by 2D materials in devices of selected configurations and the theoretical background for light-assisted gas sensing. The third chapter presents the method of fluctuation-enhanced sensing in graphene and 2D semiconductors. The fourth section is devoted to research methodology, which summarizes fabrication methods of gas sensors and structural, electrical, and noise characterization of the structures investigated within the research. The fifth chapter guides through the most significant results obtained as part of the doctoral thesis. It discusses selected two-dimensional materials for gas detection systems proposed within the dissertation. The sixth section of the thesis is devoted to conclusions and prospects of the topic undertaken for doctoral research. A bibliography, list of figures, tables, and papers published as a part of the dissertation are provided in the last chapters.

2. CHEMIRESISTIVE GAS SENSING BY 2D MATERIALS

2.1 2D materials for gas sensing applications

A broad group of low-dimensional structures can be potentially used for gas sensing. Figure 2.1 shows that metal oxides, carbon nanotubes, conductive polymers, and 2D structures represent semiconducting materials for gas sensors. The wide class of 2D materials includes graphene as the representative of carbon nanomaterials, as well as a broad range of 2D semiconductors with a high diversity in structural and optoelectronic properties. Metal chalcogenides (e.g., WSe₂ monolayers as depicted in Figure 2.1 as an example), MXenes (metal carbides and nitrides), phosphorene, silicene, tellurene, germanene, and resembling structures possess highly active surfaces for gas sensing. However, not all are stable in real-environment conditions [40,41]. Among this vast class of materials, three types of 2D structures were selected for experimental studies for the doctoral research: carbon nanomaterials (graphene and carbon nanotubes), transition-metal dichalcogenides (molybdenum disulfide, MoS₂), and transition-metal trichalcogenides (zirconium trisulfide, ZrS₃).

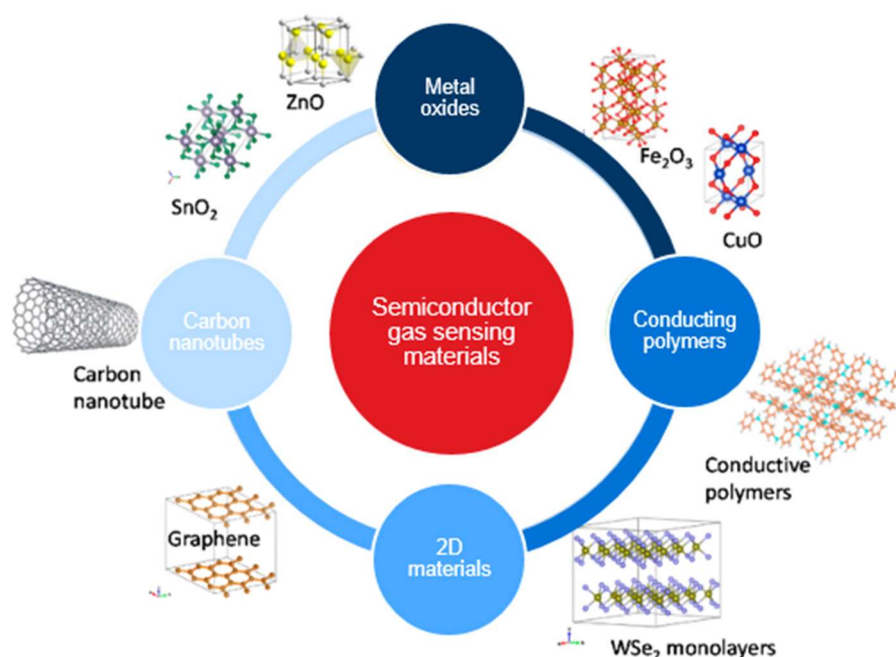


Figure 2.1 Examples of low-dimensional materials used in gas sensing devices. The class of 2D materials includes graphene, transition metal di- or trichalcogenides (TMDCs or TMTCs), and their combinations as an example [42].

Pristine graphene is formed by a honeycomb structure consisting of only carbon atoms (Figure 2.2a – left panel). This 2D material possesses excellent carrier transport properties with electron mobility much greater than values for Si or GaAs and a high surface-to-volume ratio with a specific surface area of ~2600 m²/g, making it extremely sensitive to molecular events [18].

Graphene is considered a semiconductor with zero band gap, characterized by linear dispersion relation as an ideal monolayer (Figure 2.2a – right panel). At the same time, its conductivity reaches values typical for conventional metals. Moreover, it displays an ambipolar electric field effect and can act as a conductor for electrons and holes depending on the voltage bias. Charge carriers can be tuned continuously between electrons and holes in concentrations as high as 10^{13} cm^{-2} , with mobilities of up to $15\,000 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ at room temperature [43]. Due to its high carrier mobility and low intrinsic noise, graphene surfaces can react to and detect single molecules [7]. Interestingly, the rolled-up graphene possesses significantly different properties than the original 2D surface. Thus, devices based on carbon nanotubes being a 1D structural derivative of graphene might have different operating parameters. Relevantly, the conductivity type for carbon nanomaterials may be related to the ambient atmosphere, doping, defects, or geometry of single- or multi-walled nanotubes and direct the sensing response [32,44].

Transition metal dichalcogenides (TMDCs) belong to 2D materials that also could be used as effective sensing probes in gas detection systems. In general, TMDCs are materials characterized by the chemical formula MX_2 , where M refers to a transition metal (Mo, W, Hf, Ti, Zr, V, Nb, Ta, Re, *etc.*) and X represents a chalcogen atom (S, Se or Te) [45]. Among these, TMDCs that exhibit semiconducting properties include MoS_2 , WS_2 , MoSe_2 , WSe_2 and many more. Molybdenum disulfide (MoS_2) is the primary representative of this group. The bulky MoS_2 consists of 2D S-Mo-S layers attracted to each other by weak van der Waals forces. Such an analogous structure to graphite that can be exfoliated to atomically thin graphene makes MoS_2 a material that can be easily exfoliated to its 2D form as well, either chemically or mechanically (Figure 2.2b – left panel). Usually, 2D MoS_2 is an *n*-type semiconductor in ambient conditions; however, its conductivity can be shifted toward *p*-type depending on the synthesis process or when forming a junction with other materials [46,47]. Interestingly, the electronic band gap of MoS_2 changes with several layers (between 1.2 eV in bulk and 1.9 eV for a monolayer – Figure 2.2b – right panel), creating a possibility of tuning its optoelectronic properties on a fabrication level [48].

The relatively new class of transition-metal trichalcogenides (TMTCs) is characterized by the MX_3 formula composed of transition metal (M) and chalcogen atoms (X). Similarly to graphene and TMDCs, bulky trichalcogenides can be exfoliated to 2D form due to weak van der Waals interlayer interactions (Figure 2.2c – left panel). However, 2D layers of TMTCs exhibit in-plane solid anisotropy, resulting in quasi-one-dimensional (quasi-1D) electronic properties [23,49]. Theoretical investigations of the optical properties of TMTCs reveal that their bulky counterparts exhibit band gaps E_g between 0.21–2.13 eV, suggesting the possibility of effective absorption in the visible and infrared spectral range [50]. For instance, TiS_3 with ~ 1 eV band gap constitutes an alternative to silicon in miniaturized electronics (E_g of Si is ~ 1.17 eV) [51,52]. Among other less-studied TMTCs, zirconium trisulfide (ZrS_3) is an *n*-type semiconductor in the nanoscale. It possesses a wide direct band gap of 2.13 eV and an indirect band gap of 1.83 eV as a monolayer, offering the potential for effective visible light absorption (Figure 2.2c – right panel) [53].

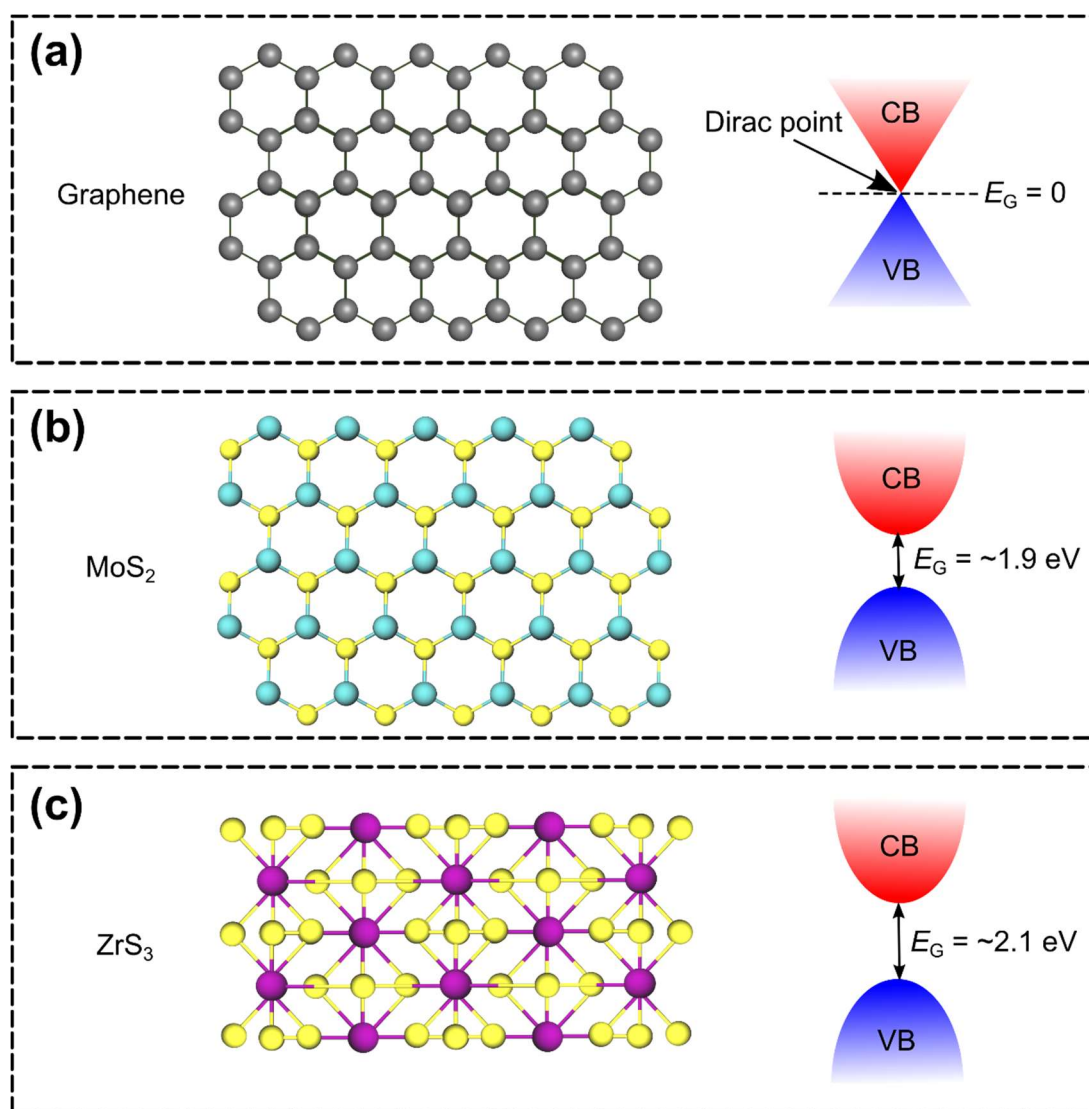


Figure 2.2 Top-view atomic structure and electronic band structure of 2D pristine **(a)** graphene, **(b)** molybdenum disulfide (MoS₂), and **(c)** zirconium trisulfide (ZrS₃). CB, VB, and E_G denote the conduction band, valence band, and band gap energy, respectively. E_G values marked on the scheme refer to direct optical band gaps. Grey, yellow, teal, and purple atoms represent carbon, sulfur, molybdenum, and zirconium.

In general, the detection mechanisms of low-scale structures depend on the properties of the sensing material and the target gas. In the case of the active material, its dimensions, structure, conducting properties, and configuration of the whole device may cause distinct responses during detection processes. In the case of analytic species, their physicochemical properties, such as structural configuration, polarity, and affinity to the active material, play a critical part. Additionally, specific defects in the low-scale structures influence the surface processes of gas detection. A 2D plane without a considerable number of dangling bonds is less energetically favorable for gas molecules to adsorb than edges of the same structure [54]. Moreover, controlling the density of specific defects in the 2D structure by target assembly or

alignment, doping, or decoration with nanoparticles can enhance the surface activity and sensitivity toward selected gases [55–57]. Thus, the complexity of detection systems based on low-scale structures imposes in-depth investigations on processes driving the gas sensing. Theoretical computations proved that small inorganic molecules such as NO₂, NH₃, or H₂S exhibit distinct adsorption energies, leading to differences in adsorption mechanisms on graphene or metal oxide nanostructures [32–34]. Other first-principles studies compared mechanisms of interaction between organic molecules (acetone, chloroform, toluene, ethanol, methanol, acetonitrile, hexane, tetrahydrofuran, and others) and graphene, MoS₂, or conventional semiconductors (Si, Ge) [35–40]. From both theoretical and experimental studies, we learn that charge transfer and charge rearrangement between target molecules and the sensing surface directly impact the electrical properties of the 2D material. The change in electrical properties can be easily observed by controlling the sensor resistance or changes in current-voltage characteristics if the sensing device operates in the Schottky diode or field-effect transistor (FET) configurations. In chemiresistive gas sensors, the surface processes of adsorption and desorption directly affect the electrical properties of the active layer, and the charge transfer properties are strictly connected with the arrangement of nanostructures and material mobility. Environmental conditions such as temperature, humidity, light irradiation, and optical properties of the light sources are other variables that alter sensor responses.

Chemiresistive gas sensors rely on a simple principle of operation utilizing the change in electrical properties of the sensing material induced by surface reactions. The adsorption processes at the interface may be purely physical when the molecules bond to the surface through weak van der Waals interactions with low adsorption energies. On the other hand, when chemical reactions start between gas molecules and the sensitive material, chemisorption with high adsorption energies occurs. Intermolecular interactions have a broad adsorption energy spectrum depending on their binding strength guided by various forces. Among volatile organic compounds (VOCs), some species adsorb *via* weak van der Waals forces. However, other stronger interactions exist, including dipole-dipole, hydrogen bonding, charge transfer, π - π stacking, acid-base, ion-ion, or donor-acceptor (Lewis pairs) formation [58].

The charge transfer and specific charge rearrangement at the interface change the carrier concentration and, hence, conductivity. The charge transfer direction guides the changes in the material resistance, depending on whether the target molecules have oxidizing or reducing properties. For instance, O₂, NO₂, NO, and SO₂ are oxidizing gases, whereas NH₃, H₂, and most VOCs are reducing agents. Depending on the conductivity profile of the sensing material, molecular adsorption can shift its resistance in a particular direction. As an example, the change in the type of graphene conductivity may be schematically depicted in Figure 2.3 with the dispersion relation of pristine and *p*-doped graphene along with the lowest unoccupied molecular orbital (LUMO) of an exemplary oxidizing molecule (NO₂). The NO₂ energy level is significantly lower than the Fermi level in graphene; hence, the transport of electrons from higher to lower

energy levels is highly favorable [59]. Change of electron concentration in graphene leads to increased conductivity in *p*-doped material but would decrease it for *n*-doped graphene. Similar changes can be introduced by molecular adsorption on other 2D materials.

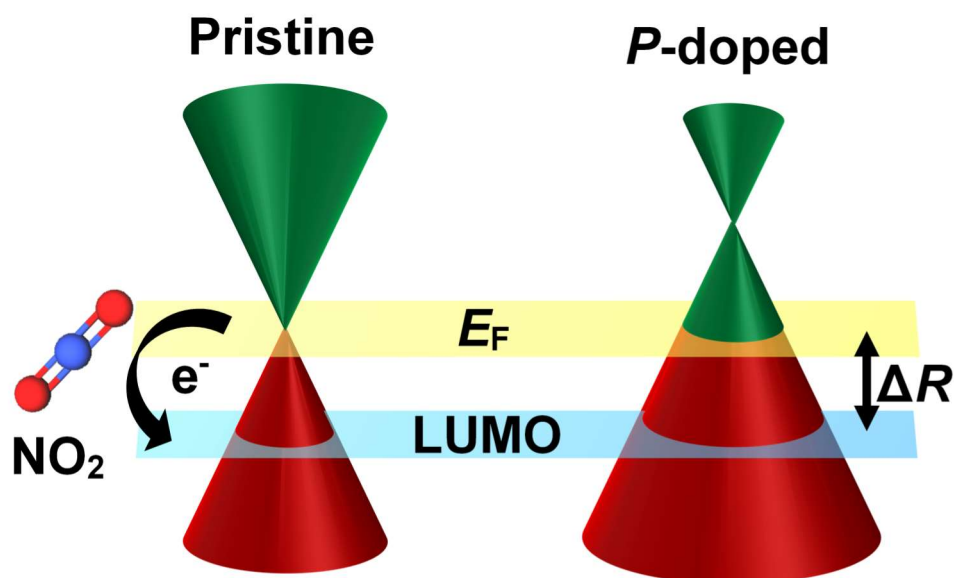


Figure 2.3 Schematic representation of linear dispersion relation for pristine and *p*-doped graphene. The lower energy level of NO_2 leads to electron transfer from graphene Fermi level (E_F) to LUMO of NO_2 , causing a change in material resistance R .

As mentioned in the Introduction, reliable, effective gas sensors must fulfill specific requirements. These include the 4S requirements: sensitivity, selectivity, stability, and speed of operation. Other significant factors are the simplicity of manufacturing, the possibility of miniaturization, low power consumption, and low cost. Specific figures of merit have been introduced to evaluate the sensors performance and compare their potential. Table 2.1 presents the most critical parameters useful for sensor performance evaluation with their symbols and short descriptions.

The configuration of the sensing device can significantly enhance gas sensing performance by tuning the electrical properties of the sensor. A resistor is the most straightforward configuration for a gas sensor to monitor changes in the resistance of the sensing layer. 2D material is then deposited between two electrodes (usually metal), enabling contact with the gas-sensitive layer. The substrate does not have to be conductive, so glass or flexible polymers can be used. On the other hand, 2D structures can be employed as active materials in more complex configurations, such as field-effect transistors or Schottky diodes. In these cases, the type of substrate and junction that 2D material forms with it play a critical part in directing the electrical properties of the whole device.

Table 2.1 Key parameters for chemiresistive gas sensors.

Parameter	Symbol/formula	Description
Response (resistive)	$S = (R_S - R_0)/R_0^*$	The relative change in the sensor resistance due to the introduction of target gas in reference to baseline resistance (usually in air or inert ambience)
Response time	τ_{res}	The time when the sensor reaches 90% of its overall saturated response to the target gas
Recovery time	τ_{rec}	The time when the sensor recovers in 90% back to its baseline
Detection limit	DL	A theoretical minimum gas concentration that the sensor can detect, determined by the signal-to-noise ratio (S/N) for a particular material (usually S/N = 3)

* R_S and R_0 denote sensor resistance in the target gas and reference atmosphere.

2.2 FET configuration sensing devices

What distinguishes a field-effect transistor (FET) from a resistor is that the FET-configuration device has three electrodes (source, drain, gate) and enables additional gate voltage modulation. The channel is primarily polarized with the voltage applied between the source and drain. Additionally, the voltage between the gate and source significantly affects the electric field around the channel. Usually, the 2D material deposited between two contacts serves as a channel in a FET gas sensor, and the gate voltage is applied between the substrate (usually silicon/silicon oxide, Si/SiO₂) and one of the metal contacts (source). However, there are reports of graphene being used as one of the electrodes (source or gate) in more complex sensing devices [60,61]. Among 2D materials, graphene has the most distinct properties when used in FET devices and is biased with gate voltage due to its conducting profile. Compared to conventional *n*- or *p*-type semiconducting materials, the FET device with a pristine graphene channel is characterized by its unique ambipolar behavior resulting in transfer characteristics (drain-source current I_{DS} vs. gate voltage V_G), as depicted schematically in Figure 2.4. Ideal monolayered graphene exhibits the point of minimum current or maximum resistance at $V_G = 0$ V with a hole regime for negative V_G and an electron regime for positive V_G . At this point, the Fermi level lies between the conduction and valence bands. In other words, the extremum point on the transfer characteristic corresponds to the Dirac point (charge neutrality point). Due to its high conductivity, the graphene FET device is always in the normally ON state. The concentration of holes and electrons is almost equal at the Dirac point, and the more ideal the layer, the sharper extremum should be observed. Modulation of V_G influences the Fermi level position. Positive gate voltages shift E_F to the conduction band, whereas negative V_G shifts E_F to the hole region. Such modulation results in different graphene-FET (GFET) operating principles exposed to various gases. Additionally, unless graphene operates in an inert atmosphere, the material is already of *p*-type conductivity in atmospheric air due to the adsorption of oxygen species, so its charge

neutrality point moves toward the right side of the graph. In this case, the hole regime dominates at 0 V, so higher positive gate voltages are required to observe both branches of the graphene conductivity profile. Such uniqueness of graphene-FET devices holds great promise for highly sensitive gas sensors. For instance, N. Harada *et al.* demonstrated that graphene-based transistors could exhibit more than one order of magnitude greater sensitivity than graphene resistors or commercial gas sensors [60].

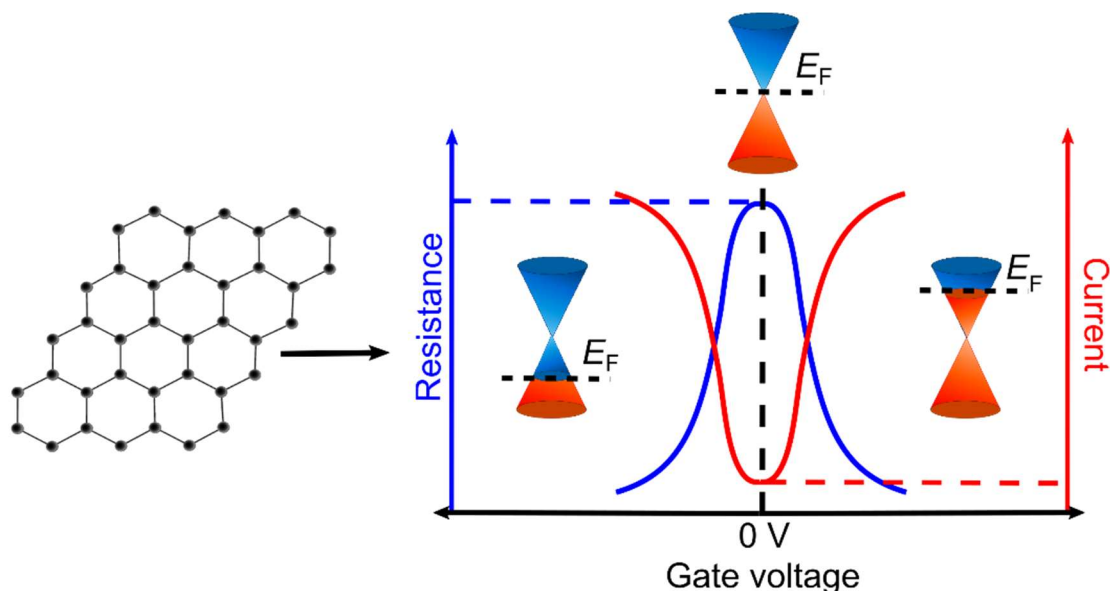


Figure 2.4 Schematic of the transfer characteristic of graphene-based FET with Dirac point at $V_G = 0$ V and changes in Fermi level position for hole and electron regime. A negative V_G range indicates p -type conductivity and a positive V_G range corresponds to the n -type conductivity of graphene.

To provide a more detailed explanation of surface processes, T. Hayasaka *et al.* divided the changes in graphene conductivity profile (corresponding to I_D vs. V_G profile) into four types, proposing the physical phenomena behind the interactions of GFET with gas molecules, as depicted in Figure 2.5 [62]. Figure 2.5a illustrates a lateral shift of the conductivity profile corresponding to the charge transfer between a gas molecule and graphene. Figures 2.5b and 2.5c depict the change in the slope of the hole branch or electron branch due to the Coulomb interactions between molecules and holes or electrons. Lastly, the height of the charge neutrality point is altered due to the modulated residual carrier concentration in graphene (Figure 2.5d). Thus, the surface processes during the interaction of gas with 2D material can be complex, and various gases can distinctly produce characteristic changes in DC profiles.

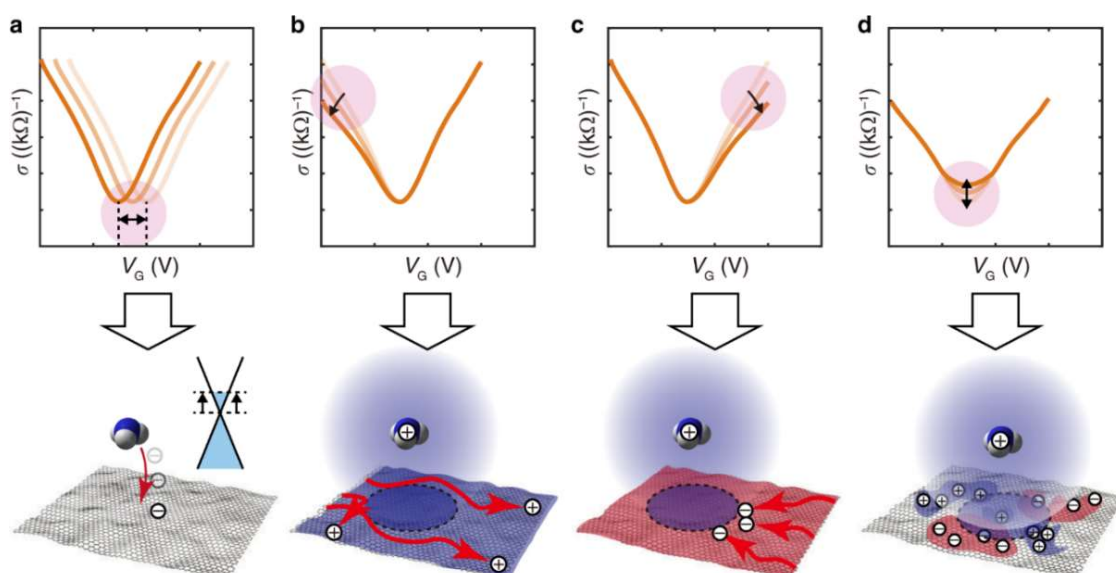


Figure 2.5 Schematic illustrations of the conductivity σ vs. applied gate voltage V_G and the corresponding physical phenomena for a GFET: **(a)** the lateral shift of charge neutrality point due to the charge transfer between a gas molecule and graphene, **(b)** the change in hole branch due to Coulomb interactions of the gas molecule with holes, **(c)** the change in electron branch due to Coulomb interactions of the gas molecule with electrons, **(d)** the vertical change in charge neutrality point position due to the modulated residual carrier concentration by gas molecule. Reprinted with permission from [62]. Copyright 2020

T. Hayasaka *et al.*

In contrast to graphene, other 2D semiconductors do not exhibit the constant ON state as transistors. Depending on their structure, the type of their conductivity, and potential light activation, they can exhibit an ON/OFF ratio of a few orders of magnitude and high transconductance. For *n*-type MoS₂, its active region (saturation region) is the electron regime at positive gate voltages. In this case, modulation with gate voltage can shift between different modes of operation for the MoS₂ sensor – low currents region, slope of the transfer curve, or saturation (high current) regime. Interestingly, H. Tabata *et al.* suggested that shifts in the transfer curve and changes in its slope decide whether the detection mechanism falls within the charge-transfer or carrier-mobility models [63]. The authors described changes induced by NO₂ molecules under visible light irradiation in two ways (Figure 2.6). The vertical shift of the current-voltage (*I*-*V*) characteristic indicates a shift in threshold voltage and charge transfer between gas molecules and MoS₂. The change in transconductance equal to the change in the slope of the *I*-*V* curve suggests the impact on carriers mobility caused by the scattering of carriers on adsorbed NO₂ molecules. In this regard, the authors suggest that the transitional region of the *I*-*V* characteristic for MoS₂ FET can be highly informative about mechanisms of light-assisted gas sensing.

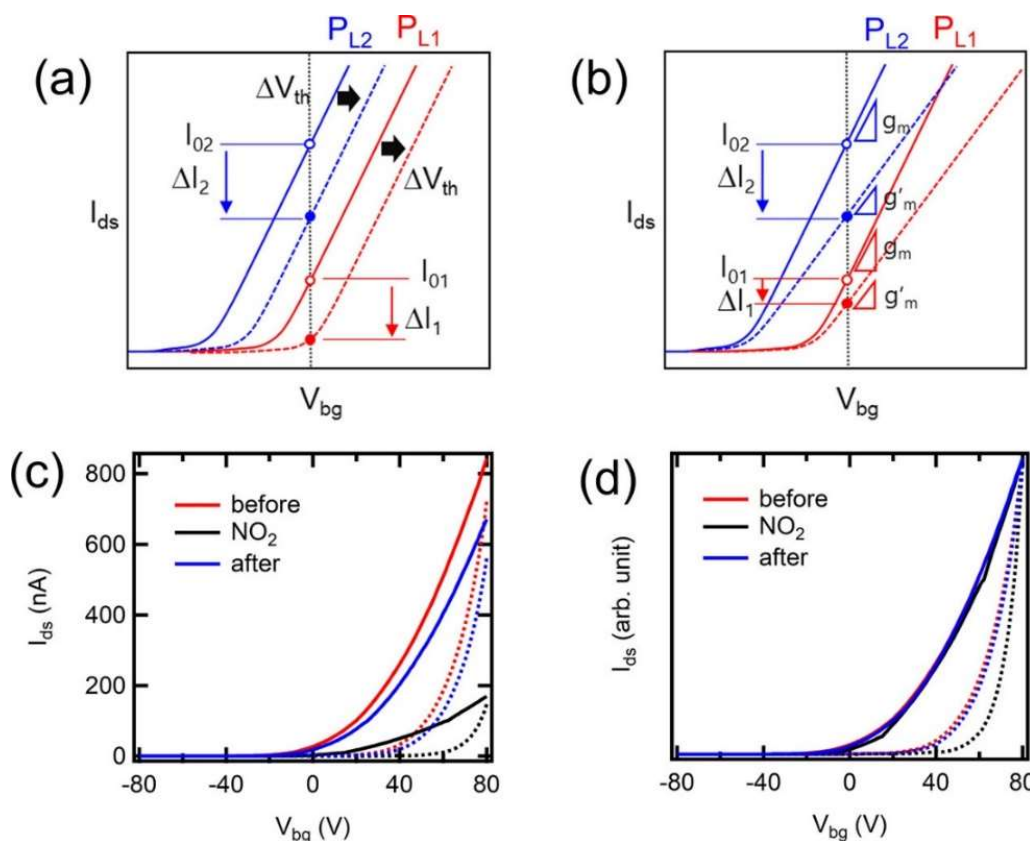


Figure 2.6 Theoretical graphs describing the changes in the transfer curve during NO₂ exposure under different irradiances: **(a)** charge-transfer and **(b)** carrier-mobility modulation model. P_{L1} and P_{L2} denote different irradiances (P_{L1} < P_{L2}). The solid and dashed lines represent the characteristics before and after NO₂ detection. I₀₁₍₂₎ and ΔI₁₍₂₎ are the initial current and change in current under an irradiance of P_{L1(2)}. V_{th} and g_m represent threshold voltage and transconductance. **(c)** Experimental characteristics measured before, during, and after exposure to 100 ppb NO₂, and **(d)** the same transfer curves normalized for easier comparison. The solid and dotted curves are forward and reverse sweeps, respectively. Reprinted with permission from [63]. Copyright 2021 American Chemical Society.

2.3 Schottky diode configuration sensing devices

Since FETs based on 2D materials were observed to produce higher sensing responses (at particular V_G bias) than regular resistive sensors, other types of junctions utilizing 2D materials as the main part started to attract greater attention, including the Schottky diode. The contact between two materials often leads to Schottky junction formation due to differences in their work functions and concentration of surface states. For instance, junctions can be formed between two metals, two semiconductors of the same or opposite type of conductivity (*e.g.*, *p-n* junction), or between a metal and semiconductor. The last one can be a Schottky junction with rectifying behavior when the interface barrier (Schottky barrier) is larger than $k_B T$, where k_B is the Boltzmann constant equal to $8.62 \cdot 10^{-5}$ eV/K and T is the absolute temperature expressed in Kelvin [64]. Otherwise, the formed contact is ohmic (non-rectifying). The difference in work functions of both

materials determines the Schottky barrier height (SBH). Work function is the minimum energy required to transfer the electron from the solid to the point in the vacuum (outside the solid surface). For *n*-type semiconductors, the Schottky junction is formed when it has a lower work function than the metal. Then, after contacting both materials, the electrons are transferred from the semiconductor to the metal, forming the depletion region. On the contrary, to produce a depletion region leading to the Schottky contact between a *p*-type semiconductor and a metal, the work function of the semiconductor must be higher than that of the metal.

Due to the high conductivity of graphene, the properties of the graphene-semiconductor interface are close to the metal-semiconductor contact; thus, graphene can form the Schottky junction with selected semiconducting materials. One of the most straightforward configurations for graphene-based Schottky diodes is when the 2D material is deposited directly onto a doped Si substrate. Here, the difference between a Schottky junction and a GFET is the lack of SiO₂ insulating layer between Si and graphene. This detail changes the properties of the whole junction, influencing the gas-sensing properties of the device. Figure 2.7 illustrates the difference between the FET and Schottky diode configurations based on graphene. The high sensitivity of graphene-Si Schottky diodes relates to the exponential changes in their *I*-*V* characteristics that, in correlation with the conductivity of graphene, can be altered by the changes in the surrounding atmosphere. The *I*-*V* characteristic of the Schottky diode can be divided into forward and reverse regions. Usually, in the forward bias, the diode series resistance (originating mainly from graphene) dominates the overall resistance of the diode-configuration sensor. This region of the *I*-*V* characteristic can be highly affected by the surrounding gases since it reflects the changes in the conductivity of graphene, being a sensitive detection platform. The same region moderately depends on the SBH, especially for high positive voltage bias. However, an exponential current change can be observed due to changes in the SBH in the reverse region of the *I*-*V* curve [65]. For exemplary junctions based on reduced graphene oxide, it was reported that even minor changes in SBH (1.4–2.4%) resulted in significant changes in the current (more than 100% of change depending on the voltage bias) [66]. At the same time, only a few reports demonstrate light-assisted gas sensing with Schottky diodes based on graphene [65,66]. Thus, the principle of operation and mechanisms behind the gas sensing performance of such sensors still require supplementation.

Regarding 2D materials other than graphene, scientific reports focus primarily on semiconducting TMDCs forming a Schottky junction with metals such as Au, Pd, Pt, or Ti. As mentioned before, the properties of the junction and the SBH depend on the work functions of the contacting materials. In the case of TMDCs, the Schottky contact appears between the active layer (e.g., MoS₂, MoSe₂, WS₂, WSe₂, etc.) and the metallic electrode, although the whole device operates as a chemiresistor or FET [67]. The changes in SBH are then accompanied by the charge transfer due to the adsorption of target gases and can supplement the explanation of gas detection mechanisms for such systems.

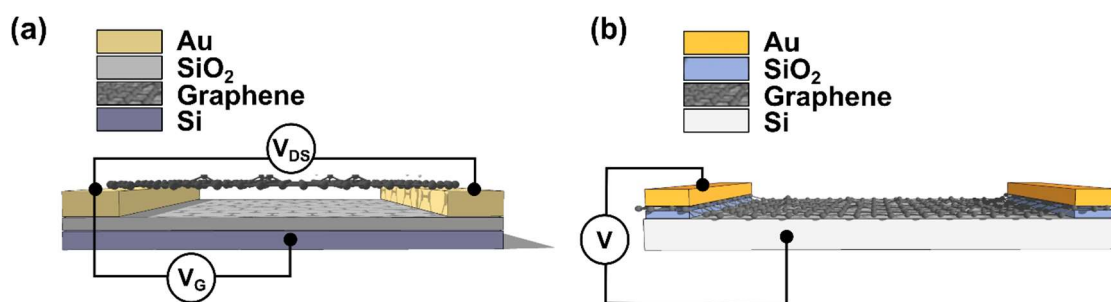


Figure 2.7 Schematic illustrations of graphene-based device based on (a) a field-effect transistor and (b) a Schottky diode configuration. The principal difference between the two devices is the oxide layer (SiO₂) under the whole graphene channel in FET and only between the Au electrode and Si substrate in the Schottky diode. V_{DS} , V_G , and V denote the drain-source voltage, back-gate voltage, and voltage polarizing the diode.

2.4 Light-assisted gas sensing

The influence of light on matter and interactions occurring during irradiation of the objects of interest have been extensively studied for decades. The main interactions between light and irradiated matter, including transmission, absorption, emission, reflection, and scattering, create the basics for different spectroscopic methods of studying bulky and low-scale structures. Incident light carries photon energy, which may excite the material, and this effect can be attractive in the gas detection field. In the case of gas sensing, the surface processes of molecular adsorption and desorption can be accelerated by additional energy carried by light. However, the final effect is strongly correlated with the energy of the light and electronic properties of the material. All the same, the facilitation and acceleration of molecular detection are crucial for high-performance gas sensors.

UV irradiation was reported to facilitate room operation of chemiresistive gas sensors based on 2D materials and their hybrids with metal nanoparticles or metal oxides [58]. Unfortunately, the straightforward proposals of mechanisms of light-enhanced gas detection for different materials are incomplete and constantly under development. As an additional variable in the system, irradiation complicates the physics behind the gas detection process since other surface reactions and excitation of the irradiated sensing layer occur. By using irradiation from the UV spectral range (wavelengths between 100–400 nm), photons that interact with the active layer carry enough energy to generate free charge carriers according to the equation:

$$h\nu_{(UV)} \rightarrow e_{(h\nu)}^- + h_{(h\nu)}^+. \quad (2.1)$$

The photo-induced carriers can transfer the charge between the sensing material and the target gas. Furthermore, environmental conditions must be considered for more practical use of gas-sensitive materials. These include the surrounding atmospheric air (oxygen content, temperature,

pressure) and the presence of humidity in the environment. When the sensing material is exposed to a humid, oxygen-rich ambiance, oxygen and water molecules readily adsorb on its surface, creating negatively charged ions according to the formulas:



For temperatures higher than room temperature (RT), the oxygen species formed at the surface of the sensing material are O^- in the temperature range of 100–300 °C and O^{2-} above 300 °C [42]. For temperatures below 100 °C, the dominant ions are reported to be O_2^- according to (2.2). The processes mentioned above lead to the extraction of electrons and a change in the material conductivity. For *n*-type semiconductors, for which the electrons are the majority carriers, the reduction in their number results in the growth of resistance. Moreover, negative ions occupy the adsorption sites at the material surface, limiting the number of binding spots for target gas molecules. The longer the exposition to air and humidity, the lower the probability of target gas adsorption and efficient detection of low concentrations. In the case of carbon nanotubes, studies on sensor performance revealed a less stable response with slower recovery when the sensor was exposed to air than under an inert atmosphere (nitrogen or argon) [33]. However, UV light treatment is a promising tool for overcoming this problem, providing efficient desorption and, thus, faster sensor recovery in atmospheric air. Several research groups reported the phenomenon of surface cleaning using UV irradiation, observed for graphene, carbon nanotubes, and MOx, such as ZnO or SnO₂ [68–71]. The pre-adsorbed oxygen and water desorption leaves the material surface partially cleaned and prepared for the target gas adsorption. Such operation seems exceptionally significant if the sensors are employed in natural environments rather than laboratory conditions. The desorption process of oxygen ions and water vapor may then be presented as follows:



Although some general principles of carriers excitation or surface activity to O₂ and H₂O exist, light-assisted gas sensing mechanisms strongly depend on the specific sensing material. Thus, the optoelectronic properties and how a particular structure responds to the irradiation steer the process of molecular adsorption enhanced by light.

2.4.1 Light-assisted gas sensing with graphene

The unique structural, optical, electrical, and mechanical properties of graphene make it theoretically an ideal candidate for light-assisted gas sensing [44,72]. Irradiation of graphene surface with UV light may act as a catalyst of surface processes, leading to gas sensors with a more significant response and faster recovery. UV light of specific wavelengths supports overcoming energy barriers for target molecules, triggering the adsorption-desorption processes. The UV irradiation that enhances graphene sensitivity to target gases can be employed in several ways. It can be used continuously during the whole detection process (response and recovery of the sensor). Another option is to apply UV light only before gas sensing to activate the surface of graphene and clean it from unwanted oxygenic species. The last option is to employ UV light only in the recovery phase to enhance the desorption of the target gas and facilitate the return to the baseline resistance. Since UV irradiation is expected to improve graphene-based sensors responses, understanding light-driven detection mechanisms in graphene systems is necessary to produce reliable sensing devices.

The spectroscopic studies in the ultraviolet and visible range (UV-vis) confirmed that the transmittance of graphene decreases for wavelengths lower than 400 nm, which means the material should strongly absorb UV light [70]. M.Z Iqbal *et al.* reported UV-light-driven doping modulation of the graphene-based device, revealing the characteristic feature of graphene irradiated at oxygen-rich and inert ambiances [73]. As mentioned before, the pristine, unprocessed graphene is characterized by its ambipolar behavior, meaning its Fermi level can be moved by applying an electric field, allowing both hole and electron conductivity. The charge neutrality point (Dirac point) associated with the Fermi level remains for gate bias of 0 V for an ideal structure in the FET configuration. However, it shifts for doped and defective graphene. If graphene is exposed to air, the maximum point moves towards positive gate voltages, indicating higher *p*-type doping. Electrical measurements complemented with X-ray photoelectron spectroscopy (XPS) studies confirmed that an inert atmosphere of nitrogen and UV irradiation (220 nm) shifts the Dirac point back to its original position, acting as *n*-type doping of graphene. Moreover, the shift in dark conditions was much less evident, meaning UV light enhances the doping process in oxygen and nitrogen by significantly increasing carrier density. Similar reversible charge density modulation was obtained for the graphene-based device in argon ambient under deep UV irradiation [74].

Moreover, the electrical properties of light-assisted FET devices based on graphene may be significantly influenced by the presence of oxygen, ambient humidity level, or temperature, as reported by T. Hayasaka *et al.* [75]. Due to the ambipolar behavior of graphene and its susceptibility to atmospheric air, the target molecules are expected to produce distinct shifts of sensor resistance at a specific V_G range. Thermal annealing can increase the total FET resistance, whereas the UV light treatment can serve as a modulating factor, changing the

position of the Dirac point twofold. Firstly, the change in the current is observed since photo-induced charge carriers influence the channel conductivity. Secondly, the threshold voltage shift occurs, so the Dirac point moves to the sides. Those two effects, namely photoconductive and photogating (photovoltaic) effects, were described for low-dimensional photodetectors based on graphene, MoS₂, InSe, WSe₂, In₂Se₃, MoTe₂, ReS₂, or BP [76]. The same approach could be incorporated for the 2D materials-based sensors [63,77]. As mentioned before, UV light generates electron-hole pairs that may participate in surface processes and gas detection by 2D materials. A significant number of charge carriers induced in the gas-sensitive layer by the UV light affects channel conductance. Therefore, the generated photocurrent affects the sensor resistance, so the transfer characteristic shifts vertically. The sideways shift of FET threshold voltage results from the photogating effect. Thus, the transfer curve moves left or right under UV light depending on the reducing or oxidizing properties of the ambient gas.

UV-assisted graphene-based devices were primarily used as chemiresistive sensors of inorganic gases, exhibiting detection limits reaching beyond the ppm level, especially for nitrogen species. Among small-molecule, inorganic species, nitrogen oxides (NO₂ and NO) are the prominent representatives that usually induce high sensing responses in the graphene systems. NO₂ is a toxic gas produced by burning fossil fuels, car exhaust, and industrial processes that can harm the human respiratory system and pollute the environment even at low concentrations [78]. Chemically, NO₂ is a strongly oxidizing molecule with high reactivity due to one free electron in its structure. NO is a metastable compound, usually reacting with oxygen from atmospheric air to form NO₂; however, on its own, it can reduce other chemical compounds, creating free radicals that are dangerous for human organisms. Chen *et al.* applied continuous UV irradiation for the detection using pristine graphene [69]. Their results showed a sub-ppb detection limit for nitric oxide (NO) at room temperature. Low DL was also achieved for NO₂, NH₃, N₂O, O₂, SO₂, CO₂, and H₂O. Unfortunately, the lowest DL values were obtained when graphene operated under an inert atmosphere (nitrogen or argon), which does not support using such a sensor in a real environment. Nevertheless, the study showed that graphene, without surface modifications or chemical doping, can be an extremely sensitive material toward small molecules when light-induced surface cleaning occurs. Such an improvement was also confirmed in another work by X. Yan *et al.*, who used UV light (265 nm) for NO₂ sensing, reaching a few times greater response for irradiated graphene sensors [79]. The authors observed high sensor repeatability and durability during 60 days of exploitation as well as selectivity towards NO₂. The authors suggested that the sensing mechanism consists of two main processes. First, the UV-assisted desorption of atmospheric molecules creates free adsorption centers for target gas molecules. Second, the energy of UV light used in the experiment is sufficient to excite electron-hole pairs in graphene (following formula (2.1)). Photo-induced carriers participate in charge transfer and contribute to further changes in graphene resistance. When the sensor is exposed to an electron acceptor

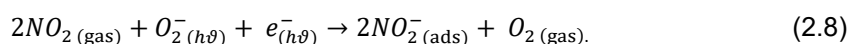
such as NO₂, gas molecules extract electrons from the material, leaving extra holes in the graphene structure according to the relation below:



Simultaneously, photo-induced electrons react with atmospheric oxygen, creating additional photo-induced oxygen ions adsorbed on the surface:



Consequently, there are two types of adsorbed oxygen molecules on the surface: primarily adsorbed ones O_{2(ads)}⁻ and molecules adsorbed *via* UV-generated electrons O_{2(hν)}⁻. Photo-induced oxygen ions are weakly bonded to the surface and may contribute to gas adsorption, accelerating the process:



The reactions described above contribute to more enhanced *p*-type doping of graphene. Additionally, the effect of simultaneous UV irradiation and annealing of graphene-based NO₂ sensors was investigated by C. Yang et al., demonstrating the contribution of high temperature to sensor recovery time [59]. Annealing up to 300 °C improved sensor response four times but somewhat extended the recovery time. The authors suggest that optimizing the UV irradiation time can overcome incomplete recovery by enhancing the desorption of molecules. However, rapid thermal annealing can still be used as a pre-treatment for removing any residues before gas sensing.

NO₂ is often chosen as a target analyte for studying the gas-sensing properties of the system due to its high adsorption energies towards different materials. Nevertheless, studies on other inorganic gases (e.g., NH₃, SO₂) or volatile organic compounds (VOCs) detection using UV-assisted graphene or its derivatives remain an interesting yet incomplete subject. Regarding VOCs, C. Yang *et al.* reported the UV light effect on resistive graphene sensors for acetone detection [70]. Concentrations of acetone vapor exceeding 1.8 ppm in human breath can potentially inform about patients' diabetes; therefore, acetone detection is of great value for practical purposes. The group reported that the graphene resistance increases significantly with continuous UV irradiation (370 nm) due to the desorption of oxygen species, resulting in immediate surface cleaning. Consequently, hole concentration decreases in graphene, leading to increased sensor resistivity. Thus, graphene behavior is shifted towards *n*-type conductivity. During UV irradiation, the desorption of atmospheric molecules leaves more active sites for acetone molecule adsorption, which acts as a weak electron acceptor. Overall, a concentration

as low as 300 ppb of acetone was detected by UV-irradiated graphene, suggesting that DL is at least at the ppb level.

In other work, J. Park *et al.* proved that UV irradiation improves GFET sensing performance towards water vapor, ethanol, and dimethyl methylphosphonate (DMMP), resulting in sensitivity enhancement factors up to 4.2, 54, and 2, respectively [80]. In the case of water and ethanol, the resistance change direction was even reversed under irradiation. The authors demonstrated that UV light acted as a doping factor alongside gate voltage biasing and modulated sensor responses. Moreover, as seen in transient curves in Figure 2.8, visible (405 nm) and near-infrared irradiation (850 nm) produced a few times lower responses to DMMP due to lower energy delivered to the sensing surface, which does not promote efficient gas detection.

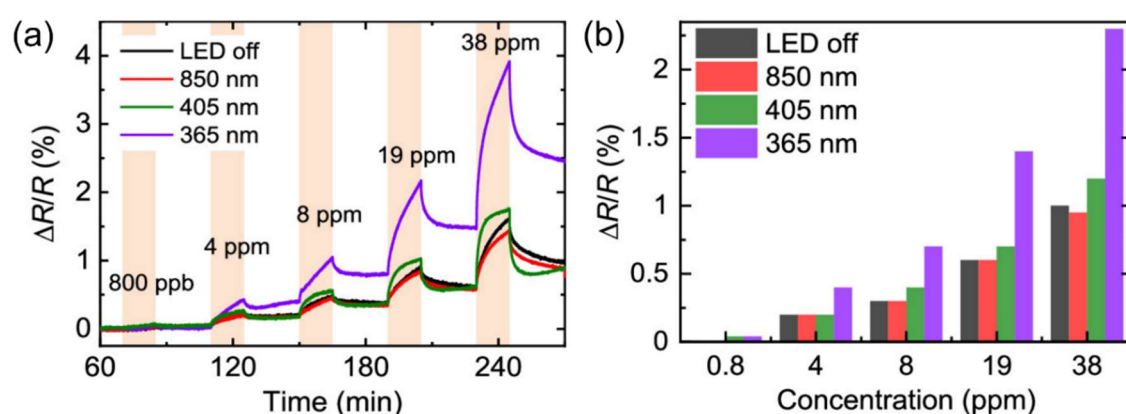


Figure 2.8 (a) Sensor response for DMMP vapor at five concentrations under LED irradiation with three different wavelengths (365, 405, and 850 nm) and (b) peak-to-peak responses corresponding to the data in (a) revealing the highest impact of the shortest UV wavelength (365 nm). Reprinted with permission from [80]. Copyright 2021 American Chemical Society.

Even though UV-activated graphene holds promise for ultra-sensitive gas sensors, few reports on UV-assisted gas detection by unmodified graphene have been published recently. Table 2.2 summarizes those published in 2019 and later, showing that NO_2 and NH_3 are the target gases most common for prototype testing of electrical sensors based on pristine graphene. The lack of new reports on VOCs such as acetone suggests that the optimization of organic species sensing by graphene is still an open issue. Interestingly, there are many more reports on gas sensing by graphene-based hybrid devices (with metallic nanoparticles, metal oxides, or other 2D materials) or by chemically modified graphene (surface functionalization or doping) [16,81]. Unfortunately, such sensors require more complex fabrication procedures than applying external irradiation. Instead of chemical functionalization of the graphene surface, light-assisted gas sensing can modulate the sensor responses at a low cost, but it still requires more in-depth investigation.

Table 2.2 Summary of reports on UV-assisted gas sensing by unmodified graphene at RT published from 2019.

Gas	Irradiation	Response*	DL	Comments	Year/Ref.
NO ₂	UV 370 nm**	25% (1 ppm)	-	Graphene annealed at 300 °C before testing	2019/[59]
NO ₂	UV 265 nm	26% (100 ppm)	42.18 ppb	Graphene as a channel in FET	2019/[79]
NO ₂	UV 390 nm**	~9% (1 ppm)	~50 ppb	Suspended graphene arrays	2021/[82]
NH ₃	UV 370 nm**	7% (5 ppm)	-	Graphene annealed at 300 °C before testing	2019/[59]
NH ₃	UV 265 nm	1.5% (100 ppm)	-	Graphene as a channel in FET	2019/[79]
NH ₃	UV 390 nm**	~5% (200 ppm)	~34 ppm	Suspended graphene arrays	2021/[82]
Ethanol	UV 365 nm	2.7% (2800 ppm)	-	Graphene annealed at 400 °C for 1 h before testing	2021/[80]
DMMP	UV 365 nm	4% (38 ppm)	-	Graphene annealed at 400 °C for 1 h before testing	2021/[80]

*Response = the absolute value of the relative change in the sensor resistance in reference to air/inert atmosphere

**UV irradiation applied only for the recovery phase

2.4.2 Light-assisted gas sensing with other 2D materials

Due to zero band gap and metal-like electrical properties, the light activation of graphene differs from that of other 2D semiconductors. There is a wide range of 2D materials of semiconducting nature with a specific electronic band structure. It means that the optimal energy for excitation of these materials corresponds to their optical band gap, E_G . Additional electrons in the conduction band and holes in the valence band are generated during light excitation. Irradiation of energies higher than E_G may also induce free carriers, but the excess energy is usually dissipated through phonons (lattice vibration), making the excitation process less efficient. At the same time, lower energies may contribute to the excitation of the material if any discrete defect levels are present below the conduction band, which can be observed in defective or doped materials.

The single-layered MoS₂ exhibits a 1.8–1.9 eV direct bandgap, corresponding to the red light (660–690 nm). Thus, the material can be activated by visible light of energy sufficient to generate electron-hole pairs and induce photocurrent (optoelectronic effect) [63]. Another option is to apply UV light that induces photocarriers and activates the material surface by partly desorbing oxygen species and humidity and creating oxygen photo-ions that can be easily replaced by target gas molecules (photocatalytic effect) [38]. A report on MoS₂-based sensors showed a superior sensing response to NO₂ under UV irradiation at RT than under temperatures

up to 100 °C. This observation confirmed that photoexcitation is more efficient than thermal excitation, which suppresses the efficient adsorption of NO₂ [83]. In other work, M. Khan *et al.* reported on UV light (220 nm) absorption and induction of photocurrent by MoS₂ layers of different thicknesses (monolayer, bilayer, and multilayer of >10 layers) [84]. The authors observed that deep UV irradiation induced the highest photocurrent in the multilayered MoS₂ with the fastest recovery. Additionally, the effect of UV light activation was suppressed in the oxygenic atmosphere for mono- and bilayer, but not in the case of the thickest sample. Similarly to graphene, the surrounding atmosphere highly influences light-enhanced MoS₂ FETs.

Table 2.3 Summary of reports on UV-assisted gas sensing by MoS₂ at RT published from 2019.

Gas	Irradiation	Response*	DL	Comments	Year/Ref.
NO ₂	Red 660 nm	50% (25 ppb)	0.1 ppb	Nitrogen as a reference atmosphere	2019/[85]
NO ₂	UV 280 nm**	25.3% (10 ppm)	-	UV light provided faster recovery than blue or white light	2019/[86]
NO ₂	Solar simulator	20% (50 ppb)	0.15 ppb	Response calculated based on current changes	2021/[63]
NO ₂	UV 254 nm**	~70% (100 ppb)	10 ppb	Response calculated based on current changes	2023/[87]
NO	UV 254 nm	72.45% (100 ppm)	-	Response under UV light higher than at temperatures up to 100 °C	2019/[88]
NO	UV 365 nm	60.25% (100 ppm)	-	Response under UV light higher than at temperatures up to 100 °C	2019/[88]
NO	UV 365 nm	200% (60 ppb)	-	Cone-shaped MoS ₂ bilayer	2019/[89]
NO	White light	75% (60 ppb)	-	Cone-shaped MoS ₂ bilayer	2019/[89]
NH ₃	UV 280 nm**	~2% (10 ppm)	-	UV light provided faster recovery than blue or white light	2019/[86]
NH ₃	UV 254 nm**	~1% (2 ppm)	0.5 ppm	Response calculated based on current changes	2023/[87]

*Response = the absolute value of the relative change in the sensor resistance in reference to air/inert atmosphere

**UV irradiation applied only for the recovery phase

Additionally, theoretical studies by first-principles density functional theory (DFT) presented by B. Cho *et al.* demonstrate that charge transfer between gas molecules and MoS₂ drives the gas detection process, similarly to graphene. In terms of inorganic gas sensing, the negative adsorption energies calculated for both NO₂ and NH₃ indicate exothermic reactions with electron-accepting properties of NO₂ and electron-donating properties of NH₃. Table 2.3

summarizes selected reports on light-assisted gas sensing by MoS₂ published in 2019 and later. Notably, mostly inorganic species are reported to be successfully detected by light-assisted MoS₂.

As mentioned before, TMTCs form another group of interest among 2D semiconductors for light-assisted gas sensing. For instance, the single-layered ZrS₃ with a direct bandgap of ~2.1 eV can be excited by wavelengths from the visible light range. Although ZrS₃ was studied as a photodetector, scientific literature lacks reports on light-enhanced gas detection by this material or mechanisms of light-enhanced molecular adsorption by the class of TMTCs in general, which creates a wide room for further exploration of the topic.

3. FLUCTUATION-ENHANCED GAS SENSING (FES)

In general, DC resistance measurements are the most common way of investigating resistive gas sensors. These include time-domain studies of either voltage across the sensor or current flowing through the active layer and then converting these values to sensor DC resistance. Although graphene and other 2D materials-based sensors exhibit high sensitivity to molecular interactions, they often lack selectivity in their pristine form. Gas adsorption on graphene surface may lead to similar electrical responses for various species, especially when low gas concentrations and subtle responses are present. Chemically modified graphene was repeatedly proved to respond selectively towards NO₂; however, it required additional processing and elaborated chemical procedures [81,90,91]. Other ways of increasing sensor selectivity include doping or nanoparticle decoration, resulting in more complicated fabrication procedures than plain material growth [92,93]. Thus, utilizing measurement techniques that enable discrimination between responses to different gases seems a much simpler way of obtaining sensor selectivity, simultaneously limiting redundant processing during fabrication.

The observation of physical phenomena is always accompanied by the noise generated in the systems. There are different types of observed noise, including thermal, shot, burst, generation-recombination, or $1/f$ noise, each with distinct origins and mechanisms of generation. The development in the field of electronics and semiconductors attracted attention to studying mechanisms of noise generation, which is a limiting factor for some applications of electronic devices such as signal transmission and analysis [94]. Nevertheless, later, the noise started to be perceived not only as a fault of the device but also as an additional information tool to assess the quality of electronic devices, to study corrosion processes, or to increase the sensitivity and selectivity of the sensing devices. Regarding gas sensors, $1/f$ noise in the low-frequency range was later proved to provide helpful information in various systems, including those based on nanomaterials and structures with constraint dimensions.

The power spectral density of noise of a specific sample depends on the current I , bias voltage V , or DC resistance R , usually in the second power, according to the relation:

$$\frac{S_I(f)}{I^2} = \frac{S_V(f)}{V^2} = \frac{S_R(f)}{R^2}, \quad (3.1)$$

where $S_I(f)$, $S_V(f)$, and $S_R(f)$ represent the power spectral density of current, voltage and resistance fluctuations, respectively. Such a dependence, proved in 1976 by Voss and Clarke, indicates that $1/f$ noise will be observed as resistance fluctuations even without polarizing the sample. This also means that polarization is required only to convert the resistance fluctuations already manifested in the sample for the fluctuations of current or voltage that are possible to be measured directly.

In general, electrical current I is proportional to the number of charge carriers N and mobility μ ($I \propto qN\mu$, where q is the elemental charge), so the fluctuations of the electrical current are connected with the fluctuations of the number of charge carriers and mobility according to the relation [95]:

$$\delta I \propto q(\delta N)\mu + qN(\delta\mu). \quad (3.2)$$

Similarly, voltage or resistance fluctuations will depend on fluctuations in concentrations of charge carriers and their mobility. Accordingly, models proposed to explain the origin of $1/f$ noise can be carrier-number-fluctuations models or mobility-fluctuations models [39]. Up to now, a few independent models for flicker noise generation mechanisms have been proposed. These include the surface-fluctuations model proposed by McWhorter, the volume-fluctuations model proposed by Hooge or Voss and Clark's temperature-fluctuations model [96]. Unfortunately, each model is limited by specific conditions and cannot be applied to all types of materials and devices; thus, the universal model for $1/f$ noise has not been established yet. It is now accepted that the dominance of either charge carrier number fluctuations or mobility fluctuations in the system is related to the specific material and its electronic and structural properties. Thus, different noise generation mechanisms are expected for metals of high conductivity and semiconductors of specific band gaps.

One of the most popular models is the one proposed by McWhorter, which assumes a semiconductor with homogeneously distributed traps in the oxide layer. Charge carriers capture or emission process in such a structure triggers conductivity fluctuations. Each trap in the surface process is characterized by a particular time constant τ (lifetime, relaxation time) corresponding to a specific frequency f_c . The superposition of such generation-recombination (G-R) events over a wide distribution of relaxation times contributes to the inverse relation between resistance fluctuations and frequency, which we observe as $1/f$ noise. In general, fluctuations in the number of carriers can be induced by trapping/de-trapping processes, G-R events, or molecular adsorption/desorption. Additionally, if any G-R event dominates, it can be observed as a distinct Lorentzian in the $1/f$ spectrum, as depicted in Figure 3.1. The probability of charge capture by traps and the number of traps determines the noise intensity. The power spectral density, $S_N(f)$, of resistance fluctuations caused by trapping of N carriers by a trapping state of lifetime τ can be described with the formula [94]:

$$S_N(f) = \sigma_N^2 \frac{4\tau}{1 + (2\pi f\tau)^2}, \quad (3.3)$$

where σ_N^2 is the variance of the number of trapped carriers, which is constant below characteristic frequency $f_c = 1/(2\pi\tau)$ and decreases proportionally to $1/f^2$ above f_c (depicted as the red dashed

curve in Figure 3.1). The variance σ_N^2 depends on the number of charge carriers and the average number of occupied and empty traps. If the noise is caused by a few types of traps of distinct lifetimes, the overall noise spectrum is a sum of n Lorentzians:

$$S_N(f) = \sigma_N^2 \sum_{i=1}^n \frac{4\tau_i}{1 + (2\pi f \tau_i)^2}. \quad (3.4)$$

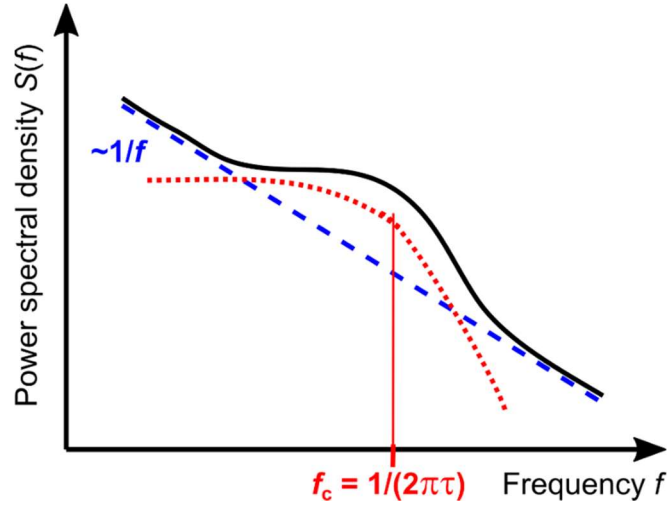


Figure 3.1 The exemplary illustration of power spectral density $S(f)$ of fluctuations as a function of frequency f (both in logarithmic scales). The dashed blue line corresponds to $1/f$ noise, and the dotted red curve denotes the dominating Lorentzian with the maximum point for a frequency f_c . The overall noise is illustrated with the black curve.

The $1/f$ noise observed for conventional semiconductors such as Si, Ge, or GaAs agrees with McWhorter's model, suggesting that $1/f$ noise is generated primarily by fluctuations in the number of charge carriers in these materials (trapping and de-trapping processes) [97]. Unfortunately, the model assumes that the fluctuations are generated only in the surface layer. To consider the fluctuations in the volume of semiconductors (or metals), another model was proposed by Hooge. In this case, the power spectral density of current, voltage, or resistance fluctuations normalized to respective DC parameters is inversely proportional to the number of free carriers N and frequency f :

$$\frac{S_I(f)}{I^2} = \frac{S_V(f)}{V^2} = \frac{S_R(f)}{R^2} = \frac{\alpha_H}{Nf}. \quad (3.5)$$

The proportionality factor α_H is the Hooge constant; however, it does not have a constant value and depends on the structural order of the material. Additionally, the lower the material quality, the higher the noise level. The more significant number of defects means a higher probability of

trap states existence and, thus, more probable fluctuations. On the other hand, noise generated in the volume can be attributed to mobility fluctuations triggered by the scattering of carriers on the phonons (lattice vibrations). Unfortunately, no straightforward proposal for a mobility-fluctuation model has been introduced; however, investigating samples under specific conditions (changing temperature, electric or magnetic field) enables determining the dominant type of fluctuations.

In chemiresistive gas sensors, a few sources of low-frequency noise can be distinguished, including the surface and the volume of the sensing material and the interface between the sensing material and the substrate or electrodes [98]. Fluctuation-enhanced sensing (FES) method utilizes information about low-frequency noise generated during detection processes in the sensing devices, providing additional tools for more selective and sensitive gas detection. In 1991, A. Dziedzic *et al.* presented the idea of utilizing noise information (power spectral density of voltage fluctuations) in chemiresistive sensing [99]. In 2000, L.B. Kish *et al.* reported that noise spectra observed during adsorption/desorption processes and charge carriers trapping/de-trapping events might be used in chemical sensor applications [100]. The information extracted from the noise spectra revealed the differences between the analytes, which varied in their chemical nature or microstructure. Hereafter, the FES method appeared appealing and functional in gas detection systems such as electronic noses and tongues. S. Gomri *et al.* proposed modeling of adsorption-desorption processes in MOx gas sensors using Langmuir and Wolkenstein models for adsorption [101]. The main difference between assumptions in both models is that the Langmuir approach assumes that the binding energy between adsorbent and adsorbate is constant. On the other hand, the Wolkenstein model includes the electronic interaction between the adsorbed molecules and the sensing layer. According to this approach, during chemisorption with charge transfer, the binding energy differs with the degree of coverage of the semiconducting surface. Since both models consider only fluctuations in the number of charge carriers, they utilize the formula 3.3 to estimate the power spectral density in the semiconducting sample. The difference between the Langmuir and Wolkenstein approach is manifested in the trap lifetimes, as the latter considers the chemisorption-induced surface potential. The simulation of oxygen adsorption on an *n*-type semiconductor by both models showed that ambient gas produces the Lorentzian component with the same characteristic frequency (being the contribution of a single activation energy); however, the $S(f)$ level is higher for the Wolkenstein model. In another work, the same authors considered the contribution of mobility fluctuations to the Wolkenstein approach, demonstrating the shift of the characteristic frequency toward lower values than when considering only fluctuations of the carriers concentration [102]. The authors indicate that in real semiconducting sensors, the $1/f$ noise is presumably a superposition of multiple Lorentzians over a wide frequency range, as real samples possess multiple types of traps. Overall, theoretical simulations and initial experimental studies confirmed that FES can be a highly informative tool for analyzing gas detection and differentiating

adsorbed species. However, the miniaturization of the systems, scaling down the materials and proposing novel sensing devices utilizing low-dimensional materials as active layers determine a new focus on $1/f$ noise measurements and the FES method.

3.1 Low-frequency noise in graphene

The origin of $1/f$ noise in carbon nanomaterials, including graphene and its derivatives, is likely to be more complex since it does not follow McWhorter's model for conventional semiconductors. In 2013, A. A. Balandin explained the considerations about resistance fluctuations in graphene and how they possibly originate from the combination of mobility and charge carrier number fluctuations [39]. On the one hand, graphene is an atomically thin structure with electrons subjected to traps, surface impurities, or charged impurities from the substrate, resulting in fluctuations in the number of charge carriers. On the other hand, due to the metal-like conductivity of graphene, electrons can be scattered and contribute to mobility fluctuations. Both mechanisms can affect one another, resulting in a complex noise generation origin. Moreover, noise features can change with a number of graphene layers and differ for a single layer, bilayer, and multilayered structure [103]. Since graphene exhibits considerably low resistance, a relatively high current will flow through it at a particular voltage bias. This indicates that measuring noise (current fluctuations) in graphene samples is technologically simple, but the normalized noise (S_I/I^2) reaches low values. Additionally, the $1/f$ noise can strongly depend on gate bias when the FET configuration of the graphene-based device is used. Studying noise generated in small-area graphene revealed interesting noise spectra when the 2D structure was exposed to various organic vapors, showing a high spectrum shape dependence on the target gas type [8]. Along with the resistive response of the graphene-based sensor, the information collected from noise spectra allowed discrimination between gases. Flicker noise has been experimentally established for single-layered, bilayered, and multilayered graphene with an area reaching individual μm^2 , exhibiting various spectrum shapes for different organic gases, including ethanol, chloroform, methanol, acetonitrile, tetrahydrofuran, and toluene [104]. Noise features, namely characteristic frequency at which local maximum occurs (corner frequency f_c) and relative resistance change, served as a unique signature of each gas, enabling discrimination among organic species.

3.2 Low-frequency noise in 2D semiconducting materials

Interesting observations provided by noise spectroscopy studies for graphene encouraged scientists to explore the noise characteristics of devices based on other 2D materials, including MoS_2 . Additionally, when combined with DC electrical studies, the FES method offers a tool for selectivity improvement [105]. Thus, low-frequency noise in graphene devices was compared to MoS_2 -based devices designed for gas sensing [106,107]. The comparative study of noise in graphene and MoS_2 FETs showed that both materials exhibit highly different noise characteristics. Compared to graphene, the MoS_2 channel exhibits much higher resistance and

I - V characteristics typical for n -type semiconductors with an ON/OFF ratio of at least 10^5 [107]. Even in the saturation region of the characteristic, the current flowing through the MoS₂ (either mono- or multilayered channel) is lower than in graphene due to the superior mobility of the carbon structure. This results in a low level of current fluctuations in MoS₂, which are technologically challenging to measure, but at the same time, the normalized noise (S_I/P) reaches high values, which stands in complete opposition to the graphene case. At low gate voltages, $1/f$ noise in MoS₂ followed McWhorter's model, suggesting the dominance of fluctuations in carrier concentration. However, at high gate voltages, the effect of contact noise contributed to the fluctuations more significantly. Although MoS₂ layers exhibited sensitivity towards different vapors in electrical studies (current vs. time), they lacked characteristic features on the noise spectra, and only graphene exhibited characteristic plateau regions (Lorentzians) on the $1/f$ noise spectrum, enabling distinguishing of gases *via* noise measurements. The authors concluded that $1/f$ noise characteristics are better sensing parameters for graphene sensors than MoS₂-based devices, although they could be used as a hybrid device.

Some scientific reports demonstrate low-frequency noise studies for other van der Waals materials, e.g., quasi-2D FePS₃ or quasi-1D TaSe₃ [108,109]. The measurements presented in these reports are referred to as noise spectroscopy and support studying phase transitions in the selected temperature range (110–300 K for FePS₃) or electromigration process at higher temperatures (~400 K for TaSe₃). In general, noise spectroscopy enables observing exciting features for materials of constrained dimensions, often exhibiting phenomena such as charge density wave, electron correlation, spin-orbit coupling, or superconductivity due to quantum confinement.

The interesting, although limited, reports on using low-frequency noise to enhance the sensitivity and selectivity of gas sensors based on 2D materials show great potential for combining DC measurements with the FES method. Thus, next to light-assisted gas sensing, $1/f$ noise studies of selected gas detection systems based on 2D materials remain one of the main focuses of the thesis as a method of enhancing the gas-sensing performance of the proposed devices.

4. RESEARCH METHODOLOGY

4.1 *Methods of fabrication of low-dimensional materials for gas sensing*

Fabricating low-dimensional materials for gas sensing applications requires specific routes and techniques to obtain structures of particular properties. All the methods of manufacturing nanomaterials can be divided into two principal groups: top-down and bottom-up techniques. Top-down methods include mechanical, thermal, or chemical exfoliation from crystals, milling and grinding the bulky material, etching, laser ablation, or thermal evaporation. On the other hand, direct growth from precursors, epitaxy, sputtering, and chemical or physical vapor deposition constitute bottom-up techniques [110]. Each of these methods has advantages and disadvantages and affects the quality of the produced material. Especially for large-scale production and commercial applications, factors such as reproducibility, time-stability, mechanical, thermal, and chemical durability, and low cost are to be considered. For gas-sensing purposes, plain structures (e.g., high-quality pristine graphene) usually lack high sensitivity to surface processes and offer insufficient binding spots for target gas molecules. This suggests that producing monolayered graphene with a high density of defects or manufacturing layers composed of randomly oriented 2D flakes can be beneficial from the detection point of view. Additionally, fabricating 2D materials of lower quality can be a low-cost approach.

Selected 2D materials investigated in the doctoral research were fabricated using two approaches. Graphene monolayers and randomly oriented carbon nanotube networks were produced *via* the bottom-up approach by chemical vapor deposition utilizing high-vacuum conditions and subsequent transfer to the selected substrates. Graphene layers and carbon nanotube networks were fabricated by the group from the Institute of High-Pressure Physics (Warsaw, Poland). MoS₂ layers comprising randomly oriented nanoflakes and ZrS₃ nanostructures were obtained *via* top-down techniques. MoS₂ layers were prepared by the author of the thesis at Gdańsk University of Technology using ink printing from the dispersion of flakes in an ethanol-water solution. The ready dispersion of MoS₂ nanoflakes obtained using chemical exfoliation was purchased from Graphene Supermarket and used for ink printing. ZrS₃ layers were deposited after mechanical exfoliation from bulk crystals by the group from the University of California, Riverside (USA). The author of the thesis performed optical and structural characterization of graphene monolayers and MoS₂ nanoflakes at Gdańsk University of Technology. All gas sensing experiments, including DC resistance and low-frequency noise measurements of the materials mentioned above, were realized by the author of the thesis at Gdańsk University of Technology.

4.1.1 Chemical vapor deposition

In the case of producing pristine graphene or 2D semiconductors, epitaxy, mechanical exfoliation *via* adhesive tape, chemical exfoliation in specific solvents, and chemical vapor deposition (CVD) are the most common techniques to obtain atomically thin layers [43]. CVD is one of the vacuum deposition techniques to produce thin films. A typical CVD process occurs in a reaction chamber where the heated substrate (e.g., Si/SiO₂ wafer) is exposed to volatile precursors selected based on the desired final product. The precursors react or decompose on the substrate surface, forming a thin film. Any side products from the deposition process are removed from the chamber with the carrier gas flow.

CVD-grown graphene on copper (Cu) foil enables the fabrication of large-area monolayers that can be further transferred to the substrate of interest. Fabricating FETs on Si/SiO₂ substrates based on large-area graphene (GFETs) utilized within the doctoral research consists of several processes that can be schematically depicted in Figure 4.1. The growth and transfer of graphene to the Si/SiO₂ substrate impose the characteristic defective morphology of graphene, which will be described in detail in the following subsection. A similar procedure was employed to fabricate Graphene-Silicon (G-Si) Schottky diodes with the additional step of etching selected areas of SiO₂ prior to the transfer of graphene to provide direct contact between the *n*-type Si wafer and graphene (Schottky contact). The gold electrode deposited on top of the graphene ensured contact with the 2D material (anode). The bottom of the Si substrate etched with hydrofluoric acid (HF) and metalized with chromium (Cr) served as the direct contact to Si (cathode, grounded) for electrical measurements of the Schottky junction.

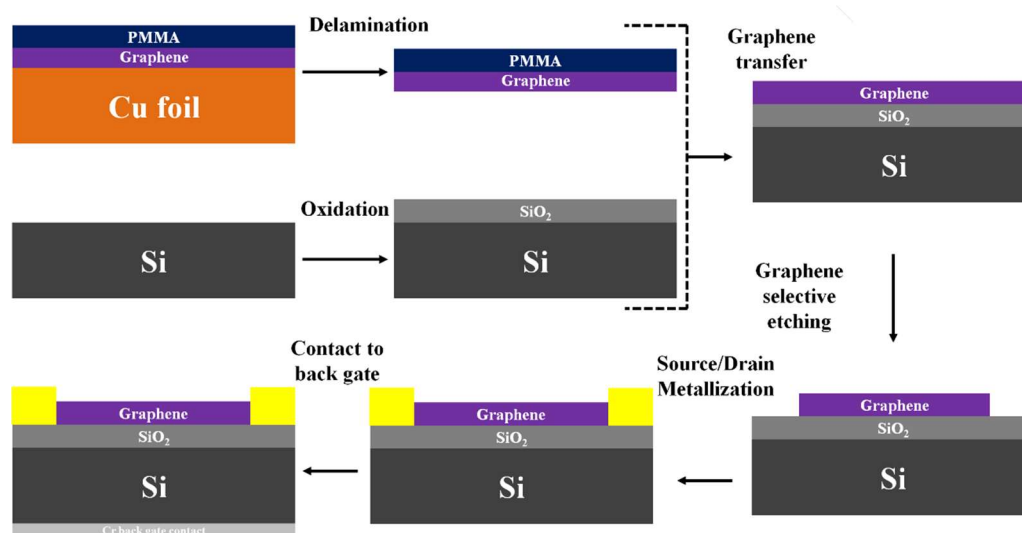


Figure 4.1 The schematic procedure of GFET fabrication, including delamination of Cu-grown graphene layer with poly(methyl methacrylate) (PMMA) handle, graphene transfer onto oxidized Si substrate, selective etching of graphene to produce a source-drain channel of specific dimensions, and metallization (sputtering) to produce source (gold), drain (gold), and back-gate electrode (chromium).

The CVD method can also be used to obtain single-walled carbon nanotubes (CNTs) [111]. The randomly oriented nanotubes forming a porous network are the final product that can be transferred to the selected substrates (Si/SiO₂ for electrical and noise measurements or glass substrates for optical characterization). To control the density of the carbon nanotube networks investigated for gas sensing purposes, the grown nanotubes were precipitated on nitrocellulose filters of particular transparencies prior to dry transfer to the final substrates. The density of the network, corresponding to the optical transparency of the layer, depended on the precipitation process time.

CVD synthesis can also be used to grow other 2D materials, including TMDCs or TMTCs, as the final product depends primarily on the precursors delivered to the sensing surface. For instance, sulfur sources and MoO₃ or WO₃ precursors are required to obtain layers of MoS₂ or WS₂ [112,113]. Similarly, chalcogens (S, Se, Te) and transition metals (Ti, Zr, Nb, Ta, *etc.*) in the form of powders, sheets, or pellets are used as precursors to obtain TMTCs [23]. Compared to graphene grown on Cu foil, MoS₂ or WS₂ obtained during CVD are often in the form of 2D triangular clusters of a few up to tens of μm in size, whereas TMTCs often take the form of nanowires, nanoribbons, or nanosheets. Hence, the devices based on such structures usually have miniaturized dimensions and require specific processing with etching and contact deposition. In the case of ZrS₃ nanostructures, the chemical vapor transport can be used to grow bulk crystals, which then can be mechanically exfoliated to obtain gas-sensitive layers of a few μm^2 in size. However, to simplify the fabrication procedure, low-cost methods of additive manufacturing, including solution processing with subsequent coating or printing, may be beneficial to fabricate gas-sensitive layers from 2D semiconductors, and this approach was utilized to produce MoS₂-based sensors.

4.1.2 Ink printing

Additive manufacturing with solution processing has a high potential to produce dispersions (and further – coatings) of low-dimensional materials at a high production yield and low production cost. Specifically, compared to vacuum deposition techniques (CVD, epitaxy, molecular assembly) or mechanical exfoliation, solution processing constitutes a cheaper and more reproducible alternative for the large-scale fabrication of devices based on 2D structures [114]. Ink printing is classified as one of the solution-based methods for manufacturing functional layers. Usually, liquid exfoliation is used to obtain 2D flakes of a specific material suspended in the solvent, and such dispersions are now commercially available for further use in ink printing applications. Essentially, a few components are needed in order to formulate an ink for printed devices, including functional materials (gas-sensitive materials for detection), solvents (water, alcohols, or others), binders (polymers, glass powder, resins or cellulose), and additives to stabilize the dispersion [115]. The addition of binders and other additives supports optimizing the basic properties of the ink, including viscosity and density, whereas the type of solvent affects the

surface tension of the ink (e.g., polar compounds exhibit higher surface tension than nonpolar ones) [116]. The amount of binders or additives can be reduced partially or entirely if the active material forms a stable dispersion in a selected solvent or a mixture of solvents and the ink exhibits the required physical properties. Various types of printing (inkjet, screen, gravure, or flexographic) set different requirements for the properties of the formulated ink and the ratios of its components. Among the ones mentioned above, inkjet printing requires inks of relatively low viscosity and the lowest amount of binders (if any) [114].

A few principal factors must be considered for successfully realizing printed gas sensors. These include the reduction of the coffee ring effect and the creation of the percolation network in the active layer of the printed device [117]. The coffee ring effect is directly connected with the concentration of the flakes in the dispersion, the solvent and additives, as well as the wetting properties of the substrate. It is usually formed when using solvents of low viscosity (e.g., ethanol). The percolation network is necessary for any electrical measurements of the printed layer, so it is crucial for resistive gas sensors. In this case, apart from the properties of the ink and the substrate, the printing repetitions are essential in going from isolated 2D clusters to a network with overlapping flakes.

Ink printing from nanoflake dispersion was used to fabricate MoS₂-based sensors investigated as a part of the doctoral research. The dispersion consisted of MoS₂ flakes of 100–400 nm lateral size and thickness of 1–8 monolayers and mixed ethanol-water solvent. The concentration of flakes provided by the producer was 18 mg/L (Graphene Supermarket). MoS₂ flakes were subjected to ultrasonication for 30 minutes to reduce aggregates and further deposited onto the ceramic (Al₂O₃) substrates from Tesla (type KBI2). Each sensing substrate includes a Pt 1000 temperature sensor, heater, and platinum interdigitated electrodes structure (IDES) of line/gap width of 15/15 µm, enabling measurements at elevated temperatures. Ink printing was realized using Nordson Precision Fluid Dispenser (type Ultimius Plus II). Droplets covering the IDES were formed using the needle tip of the inner diameter of 610 µm, and the printing was repeated ten times due to the low concentration of flakes in the dispersion. After deposition of each layer, the material was dried in airflow (~50–60 °C) to evaporate the residuals of the solvent. Multiple printing repetitions ensured that the randomly oriented nanoflakes overlapped and provided the percolation network between the terminals for electrical measurements. Table 4.1 summarizes the printing parameters, and Figure 4.2 illustrates the printing process.

Table 4.1 Printing parameters for MoS₂-based sensors.

Temperature of the substrate/dispersion	RT/RT
Drying temperature	~50–60 °C
Carrier gas pressure	~0.04 bar (0.6 psi)
Time of deposition (releasing a single droplet)	0.05 s

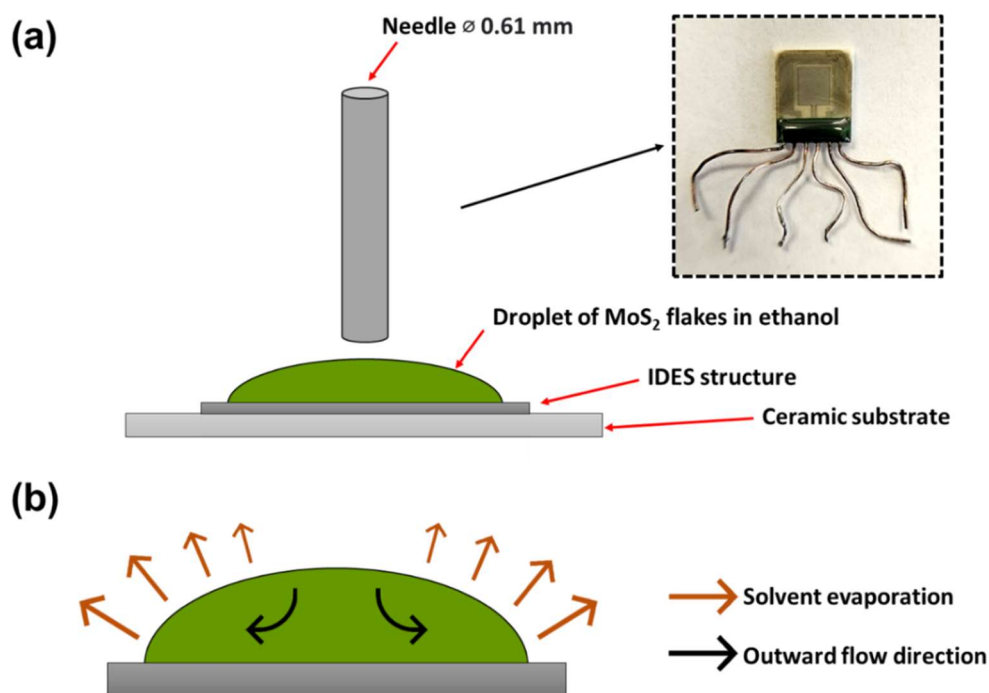


Figure 4.2 Schematic representation of the MoS₂ layers printing procedure: **(a)** MoS₂ dispersion deposited onto a ceramic substrate with interdigitated electrodes (IDES); **(b)** the fastest solvent evaporation and accelerated aggregation of MoS₂ at the edges of the droplet results in the coffee ring effect and non-uniform flakes distribution. The picture presents the sensor produced with ten layers of MoS₂ flakes on the ceramic substrate.

4.2 Material characterization methods of gas-sensitive layers

Electrical measurements are often insufficient to establish the sensing mechanisms ultimately, and other complementary studies, including materials characterization methods, are necessary. Since surface processes underlie gas detection mechanisms, spectroscopic studies such as optical microscopy imaging, Fourier transform infrared spectroscopy (FTIR), Raman spectroscopy, X-ray photoelectron spectroscopy (XPS), Brunauer-Emmett-Teller (BET) method, and others [47,118,119] supplement sensor electrical responses and give insight into surface interactions, especially when conducted *in situ* [120]. Material characterization methods complement the analysis of gas sensors performance by providing information on the structural characteristics of the sensing surface as well as optical properties relevant from the light-assisted detection point of view.

To characterize the surface of the sensing materials selected for the doctoral research, optical microscopy or scanning electron microscopy (SEM) was used. The Cu-grown graphene transferred to the Si/SiO₂ is expected to exhibit a high density of morphological defects. These include point and edge defects due to partial overlapping of the monolayers and cracks exposing

their edges, resulting from the growth and transfer processes. Figure 4.3 shows the structure of the GFET, where graphene of approximately 0.2 mm^2 size serves as a transistor channel. The confocal microscopy image confirms the defective morphology of graphene prepared for gas sensing. The magnified region demonstrates a high density of defects that can constitute binding sites for molecular adsorption.

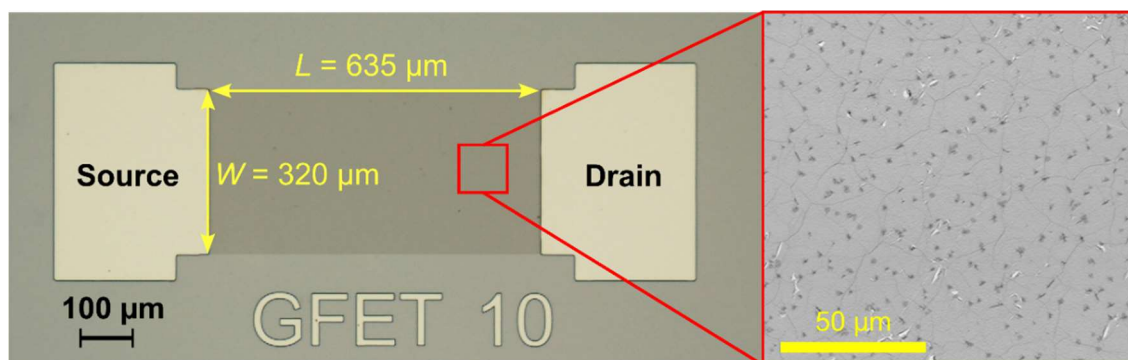


Figure 4.3 Confocal microscopy image of an investigated GFET. The area of the graphene channel is $\sim 0.2 \text{ mm}^2$. The magnified region shows a significant number of point and edge defects. Imaging was performed with Olympus, 3D LEXT OLS5100 [121].

For carbon nanotube networks, SEM imaging (Zeiss Auriga 60) confirmed that layers exhibiting different densities of randomly oriented nanostructures correlate with their optical transparency [122]. The structural properties of CNTs were additionally investigated *via* Raman spectroscopy using Renishaw inVia Raman microscope. The deconvolution of the Raman spectra showed that the diameter of the dominating nanotubes was 2.02, 1.76, 1.89, 1.82, and 1.98 nm for networks of 60, 70, 80, 90, and 95% transparency, respectively. The UV-vis spectroscopy (performed with LAMBDA 1050 spectrophotometer) of networks of different transparencies confirmed that high-density samples exhibit higher visible and UV light absorbance.

In the case of the ink-printed MoS_2 sensors, optical imaging (Figure 4.4a) indicated that the sensing layer consists of sub- μm structures forming a non-uniform layer with aggregates at the edges of the substrate (coffee ring effect reported for similarly deposited materials [123]). Moreover, UV-vis spectroscopy studies of the MoS_2 dispersion and the position of main absorption peaks on the spectrum (Figure 4.4b) revealed characteristic optical and structural properties of the material. A-B doublet at 602 and 660 nm is associated with the optical properties of the material; particularly, the A band at 660 nm corresponds to the energy of 1.9 eV ascribed to the direct optical bandgap in MoS_2 . The position of the A band can also indicate the thickness of the MoS_2 layers, suggesting that MoS_2 flakes in the dispersion are mainly bilayers and monolayers, according to the approach presented elsewhere [124]. Additionally, the C-D doublet characterizes the nanoflakes, and its position can be blue-shifted with their decreasing size.

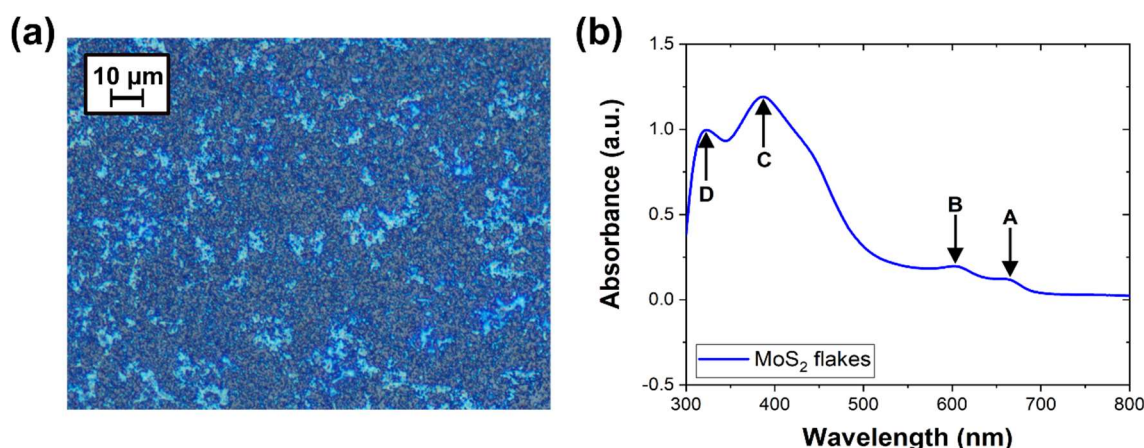


Figure 4.4 (a) Optical microscope image (500x magnification) of 10-layered MoS₂ structure consisting of nanoflakes, and (b) UV-vis absorbance spectrum for MoS₂ flakes dispersion used for gas-sensitive layers printing. Letters A and B (660 nm and 602 nm) represent optical band transitions independent from the lateral dimensions of the MoS₂ flakes. Letters C and D (387 nm and 323 nm) represent the excitonic bands ascribed to the nanosized sheets of MoS₂. Optical imaging was performed with a Delta Optical MET-1000-TRF microscope, and UV-vis spectra were collected using Evolution One Plus UV-vis two-beam spectrophotometer (Thermo Scientific).

4.3 Resistive response measurements

DC measurements are the most common for studying the performance of electrical gas sensors. These types of sensors utilize the fact that the changes in the surrounding atmosphere affect the electrical properties of the active component that can be easily measurable as an electrical signal, *i.e.*, change of current flowing through the sensing layer or voltage across the sensor induced by material resistance changes. Chemiresistive sensors operate as signal transducers for chemically-driven surface processes that affect the electronic properties of the active material, resulting in the change of layer conductivity in specific ambiances. The simplest way to measure chemiresistive sensor performance is to monitor electrical quantities – current, voltage, or resistance – in time. Usually, the resistive sensor response $S = (R_s - R_0)/R_0$ is defined as the relative change of the sensor resistance R_s at investigated gas in reference to the resistance R_0 in the inert atmosphere (N₂ or Ar), synthetic air, or laboratory air (as presented in Table 2.1). The transient curves (change in R_s vs. time) can be further used to derive several quantities of the sensor, such as the maximum resistive response S_{max} in a single cycle, response time τ_{res} , recovery time τ_{rec} , or the short-time drift character (Figure 4.5). If it can be observed that the drifting baseline follows a specific dependence in time (*e.g.*, exponential or linear), the fitted function can be used to subtract the drift from the experimental data. Additionally, collecting maximum resistive responses for selected concentrations of target gas enables detection limit estimation.

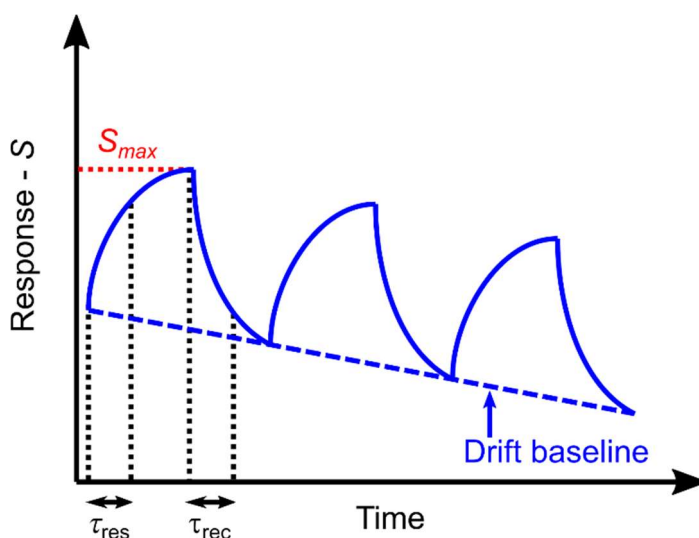


Figure 4.5 Illustration of an exemplary transient curve (consecutive cycles of response-recovery) obtained during three cycles of gas detection. The fundamental quantities derived from the curve are maximum response (S_{max}), response time (τ_{res}), recovery time (τ_{rec}) (definitions provided in Table 2.1), and drift baseline.

Generally, the sensor response to gases can be positive or negative, depending on whether the resistance increases or decreases during exposure to the target gas. The direction of resistance changes can vary for different gaseous species, mainly depending on the oxidizing or reducing properties of ambient gas as well as the type of conductivity of the gas-sensitive layer. For simplicity, semiconducting materials can be divided into n -type with electrons as majority charge carriers and p -type with holes as majority charge carriers. Moreover, gaseous species can be divided due to their oxidizing or reducing properties, defined by their ability to accept or donate electrons. Oxidizing agents such as NO_2 , NO , SO_2 , or O_3 are capable of withdrawing electrons from the sensing material during surface interactions. Thus, after the adsorption of these molecules, the capture of electrons causes the growth of resistance for materials of n -type conductivity and, on the contrary – the drop of resistance for p -type semiconductors. Exemplary reducing agents such as NH_3 , H_2 , or VOCs cause the opposite effect since they donate electrons. Therefore, resistive responses can provide information about the direction of charge transfer at the interface between molecules and the sensing material or the possibility of redox reactions occurring at the surface.

A simple resistor configuration of the sensing device is required to realize the abovementioned measurements. Two contact pads (usually metallic) with a deposited sensing layer in between allow transient curve monitoring. The substrates used for resistive sensors are often Si/SiO_2 . However, a resistive configuration of the sensing device enables the use of glass, paper, or polymeric substrates as well since they do not have to be conducting. This way, miniaturized, thin, and flexible sensors can also be obtained [125]. Other configurations of electrical gas sensing devices enable additional modulation that may enhance sensing

performance. One option is fabricating sensors as field-effect transistors, providing the gate electrode for additional tuning. The gas-sensitive layer is deposited between the two contacts (source and drain) and serves as a channel in a FET sensor. The third electrode – gate – is often applied between the substrate and one of the metal contacts. Gate voltage modulation enables measurements of current-voltage characteristics and possibly finding the optimum parameters for the highest sensor responses. For FET-configured sensing devices, transfer curves (I_{DS} vs. V_G) are usually collected to observe the impact of gate voltage modulation on sensor responses. In the case of Schottky diode-configured sensing devices, I - V characteristics can be collected to see at which voltage bias the sensing responses are the highest. Additionally, Schottky barrier properties can be derived from the I - V curves and associated with the changing ambience.

This thesis demonstrates and investigates three sensor configuration types: a resistor with ink-printed MoS_2 flakes or carbon nanotube network, FET with graphene as a channel or gate or FET with a ZrS_3 channel, and a diode with a graphene-Si Schottky junction. Due to differences in configurations of the measured devices, two setups were used for the sensors performance investigation and data collection. Each setup consists of three main parts:

1. gas control and distribution system,
2. the station with the investigated sample, light source (LED), gas inlet/outlet,
3. units for biasing and measuring the sample and data collection.

Figure 4.6 illustrates the experimental setup for realizing DC measurements and gas sensing experiments with prototype sensors proposed in the research. Different configurations of the investigated samples required two independent gas sensing chambers connected with controlling, measuring, and data acquisition units (part designated as 2 in the experimental setup presented in Figure 4.6). The resistive sensors with MoS_2 flakes utilized ceramic (Al_2O_3) substrates with six terminals (Ag wires of $\varnothing$ 0.25 mm) to connect the temperature sensor, heater, and interdigitated electrodes (IDES) with a deposited gas-sensitive layer. Metallic terminals enabled connecting the sensor to the necessary units *via* the Teflon board. The station with the investigated sample consisted of a glass gas chamber of 100 mL volume with a gas inlet and outlet for electrical measurements of resistors in selected gases (Figure 4.7). On the other hand, FETs, Schottky diodes, and carbon nanotubes-based resistors investigated in this research were prepared on the Si substrates with deposited metallic electrodes that did not facilitate bonding of the sample with the PCB board. The probe station with manipulators with titanium needles was used to connect the sample electrodes with the measuring and biasing units for their measurements. The exact positioning of the needles was realized under microscopic magnification. The probe station was put inside a metal shielding box that limited the external interferences from the laboratory airflow and external light sources. The photographs in Figure 4.8 demonstrate two investigated samples: graphene FET (GFET) and graphene-silicon (G-Si) Schottky diode put in the probe station for gas sensing experiments. All DC parameters

measurements were realized using a parameter analyzer, Keithley, type 4200A-SCS, with two source-measure units (Keithley, type 4201-SMU).

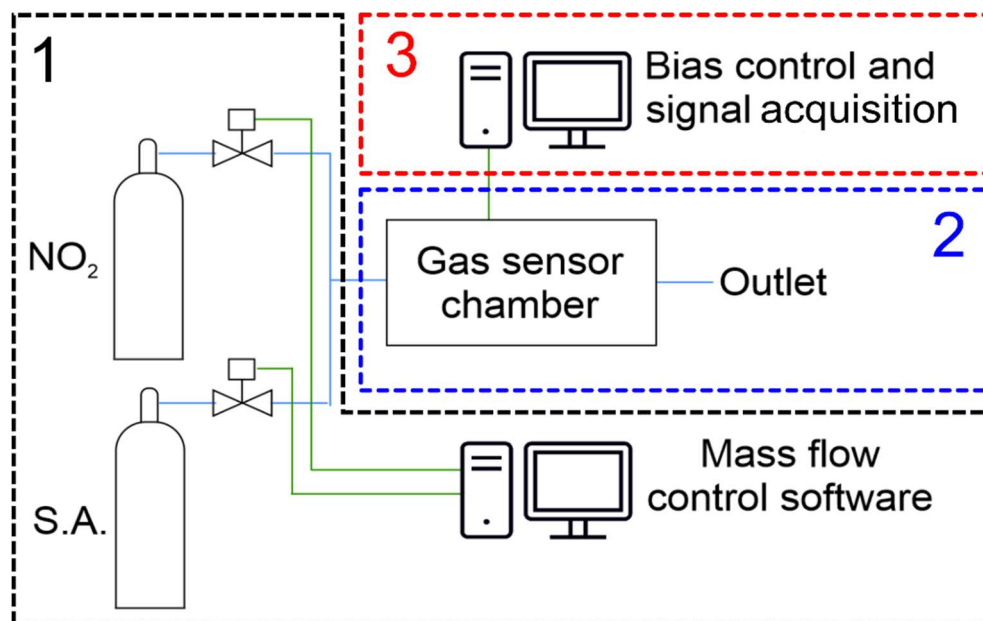


Figure 4.6 The experimental setup for measuring DC gas sensing responses of prototype sensors based on a resistor, FET or Schottky diode configuration divided into three main parts: 1 – gas distribution system with mass flow control software – two calibration bottles are depicted as an exemplary target gas (NO_2) and carrier gas (synthetic air – S.A.); 2 – gas sensor chamber with gas inlet/outlet; 3 – system for biasing and measuring sensors with signal acquisition unit.

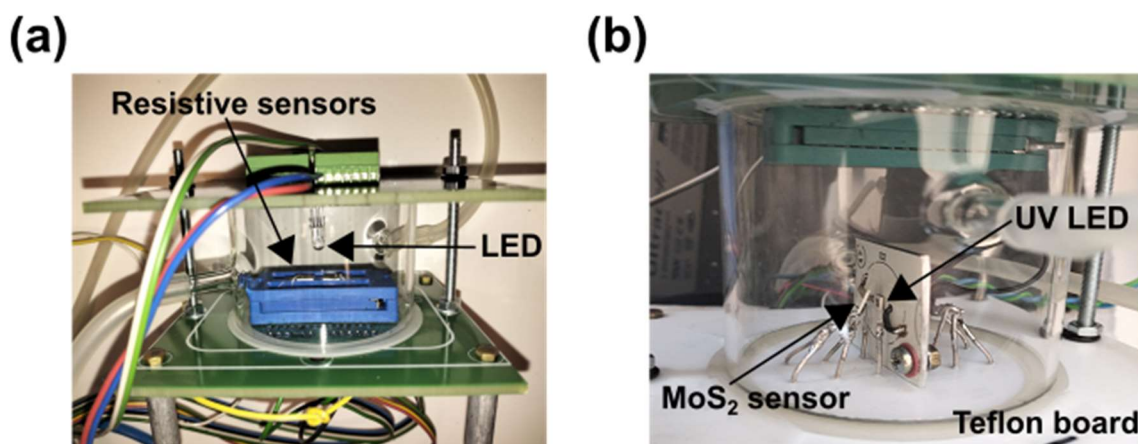


Figure 4.7 (a) Photograph presenting the gas sensor chamber for measuring resistive sensors under selected LED irradiation. For measurements of the MoS_2 sensor of high resistance ($\text{M}\Omega$ to $\text{G}\Omega$ range), Teflon board was used on one side of the chamber instead of PCB to reduce leakage currents as depicted in **(b)**. Selected UV LED was placed close to the sensing surface of MoS_2 (less than 0.5 cm of distance).

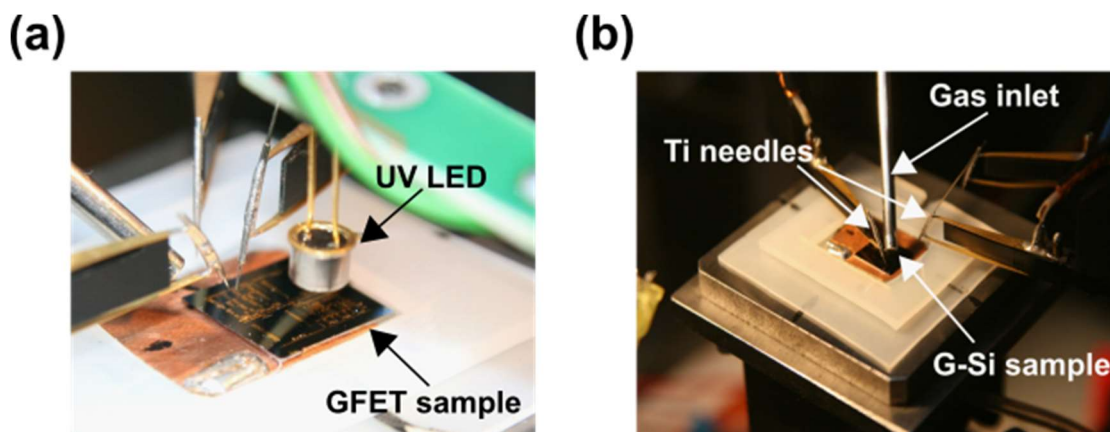


Figure 4.8 Photographs presenting the probe station with titanium (Ti) needles connecting the (a) GFET sensor and (b) G-Si Schottky sensor with the necessary measuring and biasing units. The metal pipe visible in both images delivers the target gas to the sensing surface. Selected LEDs can be placed close to the sensors (less than 0.5 cm of distance) *via* the individual manipulator.

4.4 Low-frequency resistance noise measurements

The DC resistance of different 2D materials used as active components in gas detection systems imposed on adjusting the setup for low-frequency noise measurements. As mentioned in Chapter 3, graphene-based devices exhibit intense voltage or current fluctuations, whereas the normalized current noise S_I/P is low due to the high current flowing through the graphene at a certain voltage bias (equal to low resistances of carbon nanomaterial). On the contrary, 2D semiconductors such as MoS_2 or ZrS_3 exhibit so high resistances (the range of $\text{M}\Omega$ or even $\text{G}\Omega$) that it is challenging to measure their noise, but the normalized power spectral density of current fluctuations is much higher than for graphene and carbon nanotubes. In the case of highly resistive samples, the $1/f$ noise measured at the device can be so low that it is partially or entirely suppressed by the background noise (primarily inherent noise of the measurement setup), so measuring such devices requires a specific setup. For simplicity, the gas sensors investigated within the research were divided into low/middle-resistance (resistances in the Ω and $\text{k}\Omega$ range) and high-resistance (resistances in the $\text{M}\Omega$ or even $\text{G}\Omega$ range).

The low-frequency noise measured in the sensing systems utilizing GFETs and carbon nanotube resistors employed a low-noise operational amplifier and a current source with biasing current depending on the specific device and active material. The maximum voltage gain k obtained in the circuit was up to 1000. The G-Si Schottky diode exhibited more than ten times higher resistances than GFET ($\sim 500 \text{ k}\Omega$ at 4 V bias), so an independent circuit was used to record voltage fluctuations $v(t)$ as depicted in Figure 4.9. The same illustration can generally demonstrate the circuit for low-frequency noise measurements of the low/middle-resistance devices (below $1 \text{ M}\Omega$). The elements marked in red can be changed and adjusted based on the selected device

under test (DUT) and a complementary resistor R with resistance close to the resistance of DUT ($R = 475 \text{ k}\Omega$ in the case of the G-Si sample).

Figure 4.10 illustrates the circuit applied for low-frequency noise measurements of high-resistance samples, including MoS_2 resistors and ZrS_3 transistors. Here, due to highly resistive samples, the voltage fluctuations are measured at the complementary sensor $R = 47 \text{ k}\Omega$, and they are then converted into current fluctuations at the sensor R_s . The voltage V_R measured across the resistor R is used to calculate the current flowing through the sensor R_s for normalization of the current noise. A low-noise voltage amplifier (Stanford, model SR560) and data acquisition board (National Instruments, type USB-4431) or a dynamic spectrum analyzer (Stanford Research Systems, model SR785) were used for low-frequency noise measurements of the samples based on graphene, carbon nanotubes, G-Si junction, MoS_2 , and ZrS_3 .

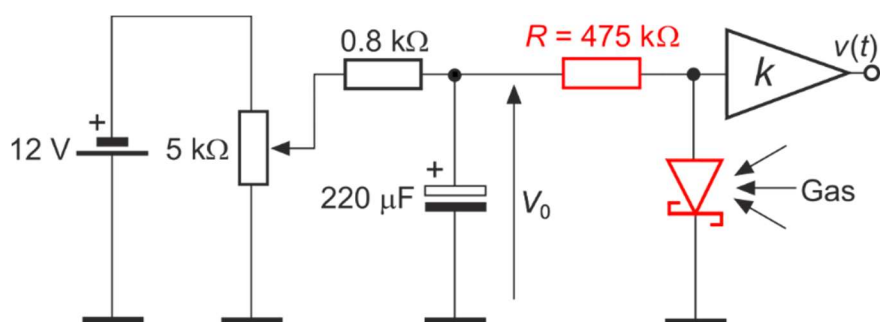


Figure 4.9 Schematic of the circuit for low-frequency noise measurements for the low/middle-resistance sensors (here for G-Si Schottky diodes). The resistance R was adjusted to be close to the diode resistance. The voltage gain k was equal to 1000. Biasing voltage V_0 was between 1.20 and 3.64 V for the G-Si sample.

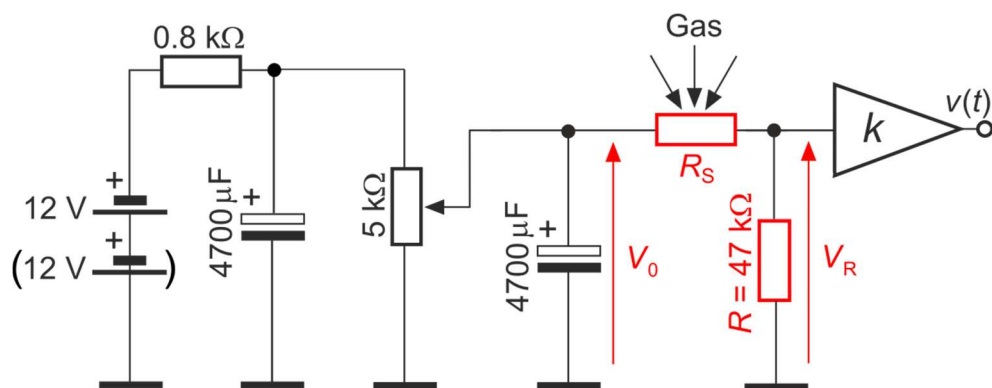


Figure 4.10 Schematic of the circuit for low-frequency noise measurements for the high-resistance sensors (based on MoS_2 and ZrS_3). The voltage across the resistor R (V_R) was monitored to obtain the current I flowing through the sensor R_s . The voltage gain k was adjusted for each device and was equal to 200 for the MoS_2 - and 2000 for the ZrS_3 -based sensor. Biasing voltage V_0 was set to 20 V for MoS_2 and 6 V for ZrS_3 devices, which depended on DC characteristics collected for both samples. One of the batteries is marked as optional (in brackets) since it was only required for MoS_2 samples to obtain an input voltage exceeding 12 V.

5. EXPERIMENTAL RESULTS AND DISCUSSIONS

This section is devoted to the most important experimental results collected within the doctoral research on the system of gas detection by selected 2D materials. The section is divided into a discussion on gas sensors based on carbon nanomaterials with a focus on graphene-based sensors and carbon nanotubes case as supplementary research and 2D semiconducting materials, including the representatives of TMDCs (MoS_2) and TMTCs (ZrS_3).

5.1 Gas sensors based on carbon materials

5.1.1 Graphene back-gated FET

Graphene, a leading representative of the 2D materials class, was considered a primary candidate to serve as an active component in the system of gas detection proposed within the doctoral research. Based on the literature review provided in Chapter 2, the most relevant issues that still require optimization and improvement in graphene-based gas sensors are selectivity, long-term stability and reproducibility of responses, room-temperature processing and operation, and simple manufacturing procedures of graphene layers. Thus, the methodology of fabrication and measurements performed on the graphene-based sensors was selected and developed in a way that attempted to tackle and fulfill these requirements. Moreover, the research was devoted to understanding and proposing a method of gas detection based on DC and noise response studies.

The graphene-based FETs (GFETs) were fabricated *via* the procedure illustrated in Figure 4.1 and characterized by a high density of surface defects, as depicted in Figure 4.3, based on laser confocal microscopy imaging. The exemplary GFET sensor had $\sim 0.2 \text{ mm}^2$ of the channel area (active sensing area). The advantage of using CVD-graphene grown on Cu foil with subsequent transfer to the selected substrates is the simplicity of producing large-area graphene of defective surface potentially beneficial for gas sensing. To improve the selectivity of pure graphene, the methodology of experiments and sensing analysis included the combination of DC resistance measurements and fluctuation-enhanced sensing. The responsivity of the GFET sensor to selected organic vapors was studied in the dark and under UV irradiation (wavelength of 275 nm, optical power density up to 1.59 mW/cm^2). DC response studies were conducted according to the scheme illustrated in Figure 4.6 and utilized the probe station depicted in Figure 4.8a. Details of GFET fabrication, measurement procedures, and gas sensing experiments are described in the article Drozdowska K. *et al.* (2022). *Organic Vapor Sensing Mechanisms by Large-Area Graphene Back-Gated Field-Effect Transistors under UV Irradiation*. *ACS Sensors*, 7, 3094-3101 and Supplementary Material provided with the article [121]. The most important results of DC characteristics and low-frequency noise measurements are succinctly discussed and concluded below.

Figure 5.1a presents the DC characteristics of the GFET sensor resistance R_s as a function of back-gate voltage V_G for nitrogen, acetonitrile (156 ppm), tetrahydrofuran (100 ppm), and chloroform (100 ppm). Nitrogen was a reference atmosphere and simultaneously a carrier gas to produce organic vapors. The R_s - V_G characteristics were collected at room temperature in the dark and after irradiation with UV light for 20 minutes. Monitoring the voltage drop across the sensor supported controlling the steady state for the GFET operating in the selected conditions. The characteristics collected in the reference atmosphere confirm that the graphene channel has *p*-type semiconducting properties, as the hole-conductivity region of the transfer curve is visible over the whole investigated voltage range. This also means that the charge neutrality point is shifted toward high positive gate voltages exceeding 60 V, which agrees with the graphene properties in the atmospheric air. Figure 5.1a shows that the GFET sensor exhibits a distinct response to each organic gas. Additionally, the relative changes of the sensor resistance increase with increasing positive voltage bias. The response was determined as the difference between the sensor resistance in the target gas and the reference gas divided by the resistance in the reference ambience (according to the description provided in Table 2.1). The acetonitrile vapor produces the least significant DC response (-0.15 of the response being a relative resistance change at $V_G = 60$ V in the dark), and UV light even decreases the sensitivity (response of -0.09). Presumably, the adsorption energy of acetonitrile on graphene in the investigated system is low, and UV irradiation causes its partial desorption instead of stronger interaction with the sensing surface. Chloroform induces the same direction of resistance changes as acetonitrile, with a similar response in the dark but more than four times greater under UV light (response of -0.13 in the dark and -0.37 under UV light). Interestingly, only tetrahydrofuran (THF) shifts the R_s - V_G curve toward negative voltages, revealing the Dirac point at ~ 50 V. The direction of changes induced by THF suggests that it acts as a strong *n*-type dopant for graphene, whereas chloroform and acetonitrile enhance *p*-type doping. Considering the chemical nature of the organic vapors investigated for gas detection by GFET, the differences in polarity and structural configuration of organic molecules are expected to induce differences in charge transfer at the molecule-graphene interface. Additionally, the presence of specific functional groups and the geometric configuration influence the adsorption energy. According to first-principles calculations, these can cause a significant charge rearrangement (accumulation or depletion) due to induced dipole interactions [126]. Considering the reduction of GFET resistance caused by acetonitrile and chloroform adsorption and the differences in their adsorption energies on graphene reported in other studies (234–286 meV for acetonitrile [127] and 357 meV for chloroform [128]), it can be concluded that chloroform creates a depletion layer at the sensing surface resulting in majority carriers (holes) accumulation in graphene. In contrast, acetonitrile demonstrates weaker and presumably dispersive interaction with the GFET channel.

Since the THF vapor caused the most significant change in the GFET transfer curve and demonstrated strong *n*-type doping of graphene, this case was investigated more thoroughly in

order to explain possible light-enhanced sensing mechanisms of the investigated system. Figure 5.1b presents the shift (a close-up of the region between -30 and 30 V) observed between the transfer curve in the dark (solid green) and under UV light (dashed green). The shifted curve (dashed black) overlies the dark-case curve with a vertical shift of 128.8Ω (ΔR_s) and a horizontal shift of 15.35 V (ΔV_G). Since UV light can have a twofold effect on the conducting properties of 2D systems (photoconductive and photogating effects described in Chapter 2.4.1), a similar phenomenon can be considered for UV-assisted gas sensing by GFET, and the transfer curve obtained under irradiation can be decomposed accordingly. With the simplifying assumption that photoconductive and photogating effects occur independently in graphene, they can be assigned to vertical and horizontal shifts in the R_s - V_G curve, respectively. ΔR_s corresponds to 4% of the relative change of channel resistance, and ΔV_G constitutes a 13%-change regarding the investigated voltage range (-60 to 60 V). This confirms that the photogating effect appearing as the horizontal shift in gate voltage induced by UV light dominates over the photoconductivity. The photogating during THF exposure can be ascribed to strong charge accumulation and creating potential acting as additional gate voltage for the graphene channel.

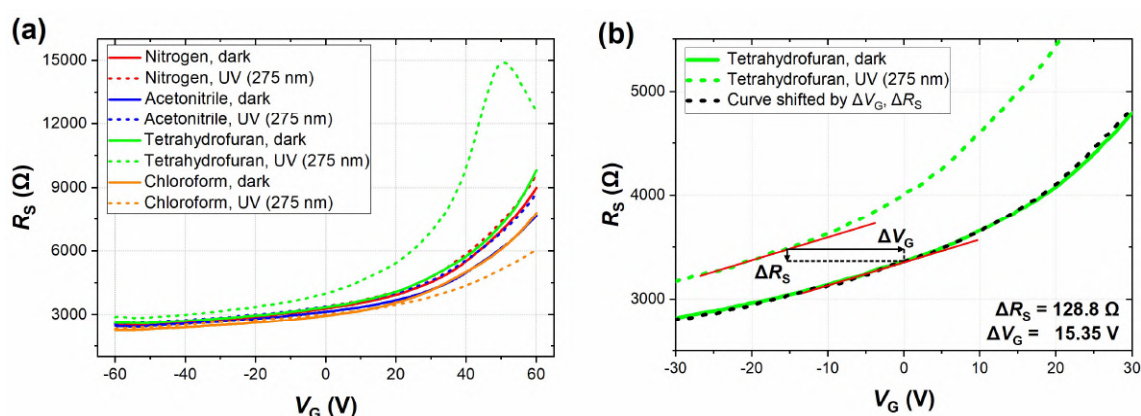


Figure 5.1 (a) DC resistance R_s of the GFET sensor between the drain and source as a function of gate voltage V_G for selected gases in the dark and under UV irradiation (275 nm), and (b) a close-up of characteristics for THF, showing that UV light shifts both sensor resistance and gate voltage. The black dashed curve overlapping the solid green one refers to the curve under UV (275 nm) after the shift by ΔR_s and ΔV_G marked by black arrows.

To complement DC response studies of the GFET, low-frequency noise measurements were conducted under the same gas and light conditions. Figure 5.2 presents the product of power spectral density of voltage fluctuations $S_V(f)$ (normalized to the squared voltage across the sensor V_s^2) and frequency f . The GFET exhibits characteristic Lorentzians emerging from the $1/f$ noise spectra in the dark and under UV irradiation. The most distinct maxima appear below 1 Hz for THF, between 1 and 2 Hz for acetonitrile, and at ~ 1 and ~ 30 Hz for chloroform in dark conditions. Under UV light, these characteristic frequencies change, leading to similarly shaped spectra for three organic gases. UV light is observed to shift the characteristic frequencies below 1 Hz, suggesting the presence of fluctuations originating from processes of longer lifetimes. Thus,

for the investigated frequency range (0.5–500 Hz), noise measured in the dark ensures higher selectivity of the GFET sensor, even though target gases were more distinguishable from DC characteristics under UV light. Comparing the obtained low-frequency noise results with the reports of A. Balandin *et al.* [39] and S. Rumyantsev *et al.* [8], it can be seen that the characteristic frequencies appear in similar ranges with minor shifts for the investigated organic vapors. It suggests that the active material in the sensor (graphene) is the crucial factor in obtaining Lorentzian characteristics for the adsorption of specific gases. Additionally, the abovementioned reports demonstrated high-quality graphene of $\sim 10 \mu\text{m}^2$ size, much more challenging to fabricate with reproducible features than large-area graphene grown on Cu foil with a high density of surface defects.

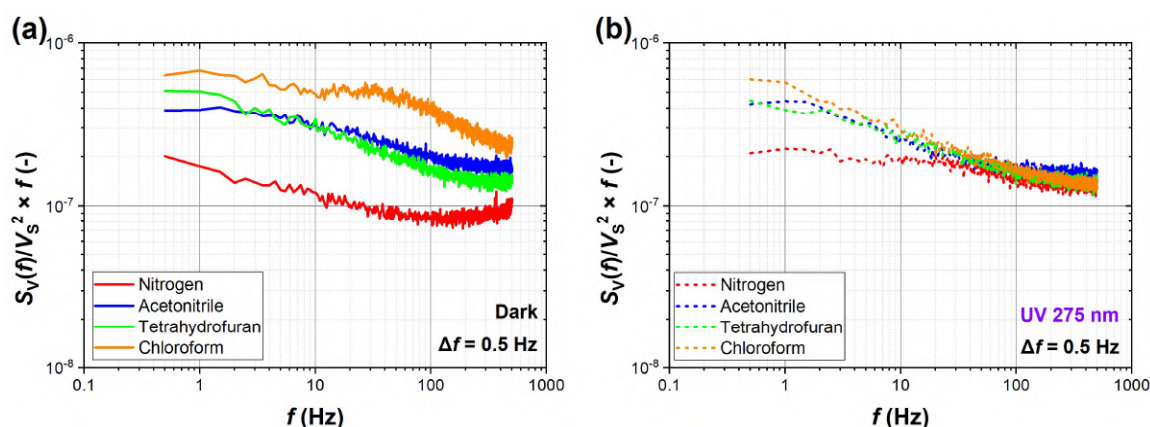


Figure 5.2 Power spectral density of voltage fluctuations $S_V(f)$ normalized to the voltage across the sensor squared V_S^2 and multiplied by frequency f for a GFET sensor. Plots (a) and (b) show the spectral range between 0.5 and 500 Hz with 0.5 Hz resolution in the dark and under UV irradiation, respectively.

The stability in time and reproducibility of responses to organic vapors were consecutive issues put under investigation, and the aging process of the GFET sensor was studied next. In between consecutive weeks of GFET measurements, the sample was annealed at 300°C for 30 minutes under a high vacuum (between 1×10^{-7} and 5×10^{-7} mbar). The procedure ensured the complete recovery to the sensor baseline resistance after consecutive detection cycles. Moreover, the graphene channel is prone to adsorb oxygen and humidity from ambient air when it is not constantly in an inert atmosphere. The aging process of the GFET sensor was studied for seven subsequent days of sensor exposure to chloroform in the dark and under UV light. The collected values of DC resistance R_S and normalized noise amplitude for the 60–90 Hz range are depicted in Figure 5.3. The lack of intermittent cleaning of the sensor surface with high temperature resulted in a shift in sensor baseline resistance from almost $10 \text{ k}\Omega$ on day 0 to ~ 5 – $6 \text{ k}\Omega$ for days 1–7 (in nitrogen as a reference), which affected the responsivity to chloroform. In the dark, a significant change in the sensor resistance was observed only on day 0 – the start of the measurement cycle. Simultaneously, higher changes in R_S with less variability during consecutive days are observed for chloroform introduction under UV light. No strict dependence

between the normalized noise and the number of days was observed – the product of frequency and normalized power spectral density of voltage fluctuations oscillated between 10^{-8} and 10^{-7} , both for dark conditions and UV light assistance.

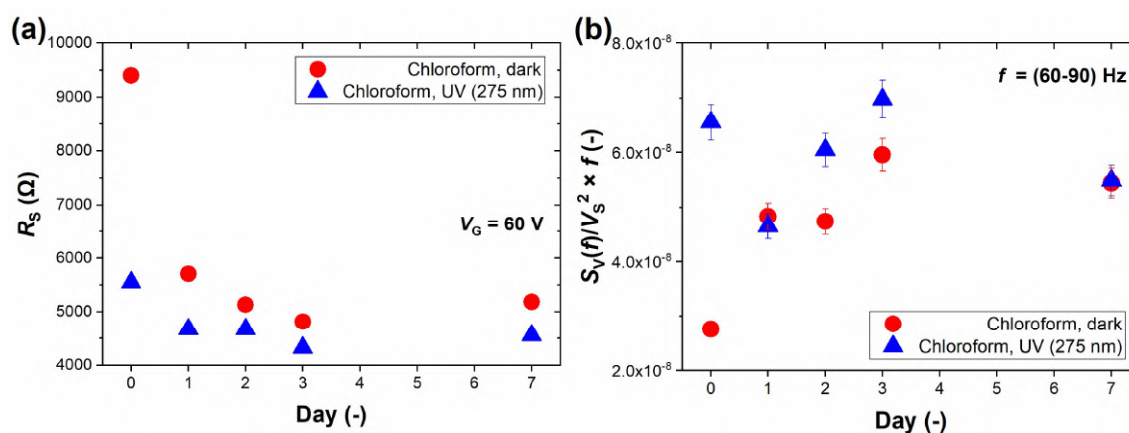


Figure 5.3 Results for a GFET sensor aging process of seven days of exposure to chloroform without intermittent cleaning of the sensing surface: **(a)** DC resistance R_s at gate voltage $V_G = 60$ V and **(b)** normalized power spectral density of voltage fluctuations ($S_V(f)/V_s^2 \times f$) as a mean value taken in the frequency range of 60–90 Hz. The error bars in **(b)** present the standard deviation from the mean value. Day 0 refers to measurements conducted for the sensor just after the cleaning at high temperature and under a high vacuum.

Additionally, restoring the sensor baseline only with UV irradiation was investigated and referred to as a refreshing process. In contrast to annealing at high-vacuum conditions, it requires a UV light source and nitrogen ambiance, so it is entirely a room-temperature operation. The refreshing process was conducted after seven days of the aging process of GFET in chloroform. Figure 5.4a depicts the transfer curves obtained for 100 minutes of sensor irradiation in an inert atmosphere. The process is relatively slow in time (the average change of ~ 11 Ω per minute), but it stabilizes after 90 minutes at ~ 5.5 kΩ. UV irradiation supports desorbing previously adsorbed species (oxygen species and chloroform residues), and nitrogen ambiance prevents the readsorption of atmospheric oxygen and humidity. Nevertheless, the results show that the cleaning procedure at elevated temperatures is much more effective in restoring the baseline resistance of graphene, while UV irradiation provides only partial recovery. Additionally, utilizing UV light does not affect the shape of the $1/f$ noise spectra, as demonstrated in Figure 5.4.b, which confirms that characteristic features observed in Figure 5.2 originate from the adsorption processes of the organic gases.

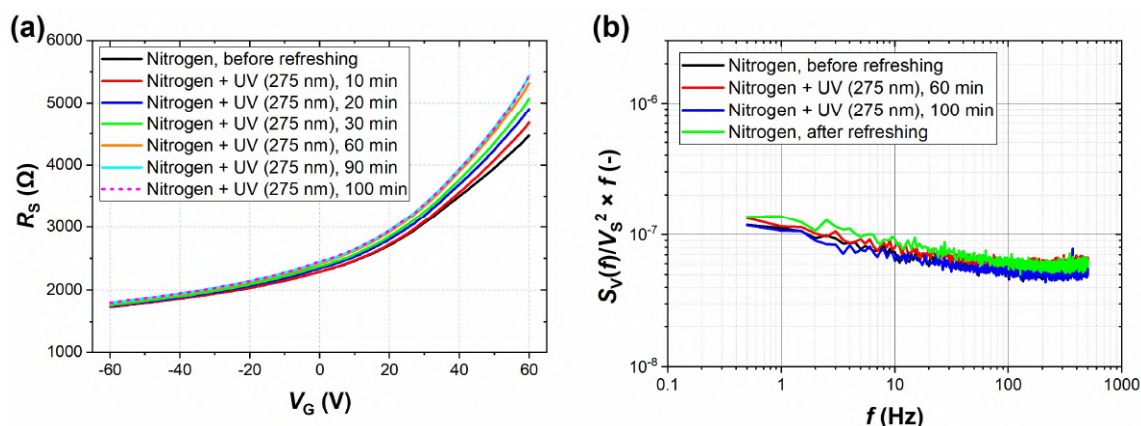


Figure 5.4 Results for a GFET refreshing process using UV irradiation under an inert N_2 atmosphere: (a) DC resistance R_S vs. gate voltage V_G for different times of continuous refreshing process and (b) normalized noise spectra multiplied by frequency ($S_V(f)/V_S^2 \times f$) collected before, during (60 minutes and 100 minutes), and after sensor refreshing.

The issue of graphene susceptibility to the ambience, resulting in the aging process and electrical properties drifting over time, encouraged the testing of graphene-based sensing devices in other configurations and using different substrates. The next tested device was a FET, which employed an epitaxially grown heterostructure of aluminum-doped and pristine gallium nitride (AlGaN/GaN) as a substrate instead of Si/SiO₂. The channel is then formed with two-dimensional electron gas (2DEG) at the AlGaN/GaN interface due to strong polarization effects (creating an *n*-type channel). Graphene utilized in the device served as the gate electrode and was deposited onto the GaN layer by the same CVD process as in the case of fabricating GFETs described earlier in Chapter 4.1. This way, the same type of graphene was tested in differently configured sensing devices. Moreover, a hybrid graphene-GaN device can combine both the high intrinsic sensitivity of graphene with the high thermal, mechanical, and chemical durability of GaN layers. The details of this study are demonstrated in the article: *Drozdowska, K. et al. (2023). The effects of gas exposure on the graphene/AlGaN/GaN heterostructure under UV irradiation. Sensors and Actuators B-Chemical, 381, 133430* [129] and respective Supplementary Material.

The graphene/AlGaN/GaN sensor was subjected to DC characteristics and low-frequency noise measurements under selected ambiances of inorganic (nitrogen dioxide, NO₂) and organic (tetrahydrofuran, C₄H₈O; acetone, C₃H₆O) target gases. The selection of target gases was adjusted to test the sensor responsivity to oxidizing and reducing agents and to compare the influence of tetrahydrofuran on graphene deposited on the GaN substrate. The measurements were conducted in the dark and under UV irradiation (wavelength of 275 nm, optical power density up to 1.59 mW/cm²). The UV light was observed to shift the drain-source current vs. gate voltage (I_{DS} - V_G) characteristics by reducing the FET ON/OFF ratio by a few orders of magnitude and shifting the threshold voltage from -3.45 V in the dark to -4.39 V under UV light. Moreover, the effect of oxygen and humidity from atmospheric air on the DC characteristics of the

graphene/AlGaIn/GaN device was minor. The sample was subjected to the cleaning procedure (annealing at 300 °C under pressure between 1.0×10^{-7} and 1.5×10^{-7} mbar) only once – prior to the sensing experiments, but it did not require intermittent cleaning between the measurements in contrast to graphene back-gated FET to regain its baseline. This observation was attributed to the difference in the substrate below the graphene layer and the use of the graphene as a gate instead of a channel.

Figure 5.5 depicts the effect of UV light and selected concentrations of NO₂ (oxidizing, inorganic gas) on DC characteristics of graphene/AlGaIn/GaN FET with a graphene layer of ~600 μm² surface area. The insets in Figure 5.5a show the magnifications of the transfer region between the OFF and ON states of the investigated FET and confirm that the characteristics shift toward positive gate voltage with increasing concentration of NO₂. Figure 5.5b confirms that the changes in I_{DS} with the gas concentration follow the negative linear dependence according to the R^2 figure of merit close to 1 (between 0.95 and 0.98 for selected voltage bias). Additionally, the UV irradiation reduced the detection limit (DL) for NO₂, but the estimated value depended on the voltage bias. The DL values are estimated as 3.89 ppm in the dark ($V_G = -3$ V) and 2.47 ppm under UV light ($V_G = -4$ V). The results show the possibility of tuning the gate voltage and using UV assistance to optimize the sensor performance. The time stability of the sensor was investigated by applying five consecutive cycles of NO₂ gas (concentration 5 ppm) introduction to the sensing surface. The results presented in Figure 5.6 show enhanced sensitivity to NO₂ under UV irradiation; however, the sensor exhibits short-time current drift regardless of the lighting conditions.

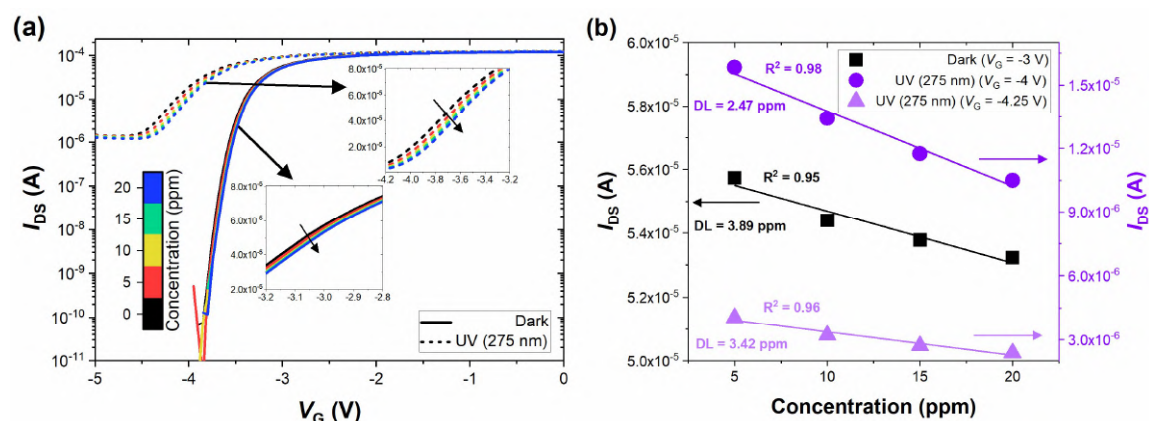


Figure 5.5 (a) Drain-source current I_{DS} vs. gate voltage V_G for selected concentrations of NO₂ in the dark (solid curves) and under UV (275 nm) irradiation (dashed curves), and **(b)** I_{DS} vs. NO₂ concentration showing the linearity of the response in the dark and under UV light. V_G was -3 V for the dark and -4 V or -4.25 V for the irradiated sensor.

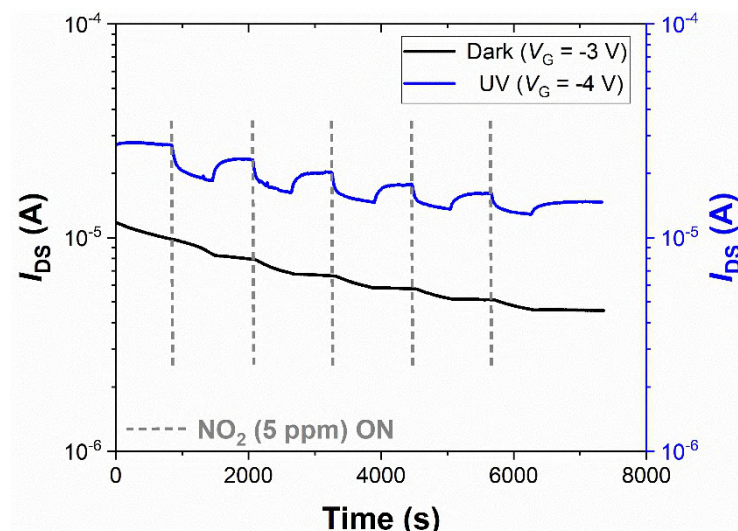


Figure 5.6 Drain-source current I_{DS} in time for five cycles of introducing NO_2 (5 ppm). The gate voltage V_G was set to -3 V and -4 V for dark and UV-enhanced conditions, respectively. Dashed lines indicate when the target gas was introduced to the sensing surface.

The effect of reducing gases on the graphene/AlGaIn/GaN sensor was tested using tetrahydrofuran (100 ppm) and acetone (110 ppm) vapors. Figure 5.7 shows I_{DS} - V_G curves obtained in the dark and under UV light for these two gases. Figure 5.8 demonstrates the transient curves for five repeatable cycles of organic gas detection. The DC characteristics confirm that the organic gases can be differentiated more easily under UV light than in the dark. Furthermore, acetone produces more pronounced and stable responses in time than THF. Overall, the irradiated sensor detects organic gases with reduced short-time drift.

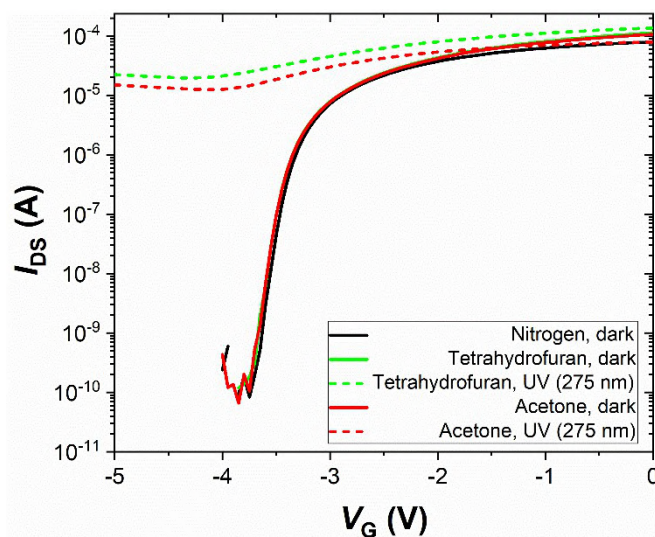


Figure 5.7 Drain-source current I_{DS} vs. gate voltage V_G for tetrahydrofuran (100 ppm) and acetone (110 ppm) in the dark and under UV (275 nm) irradiation.

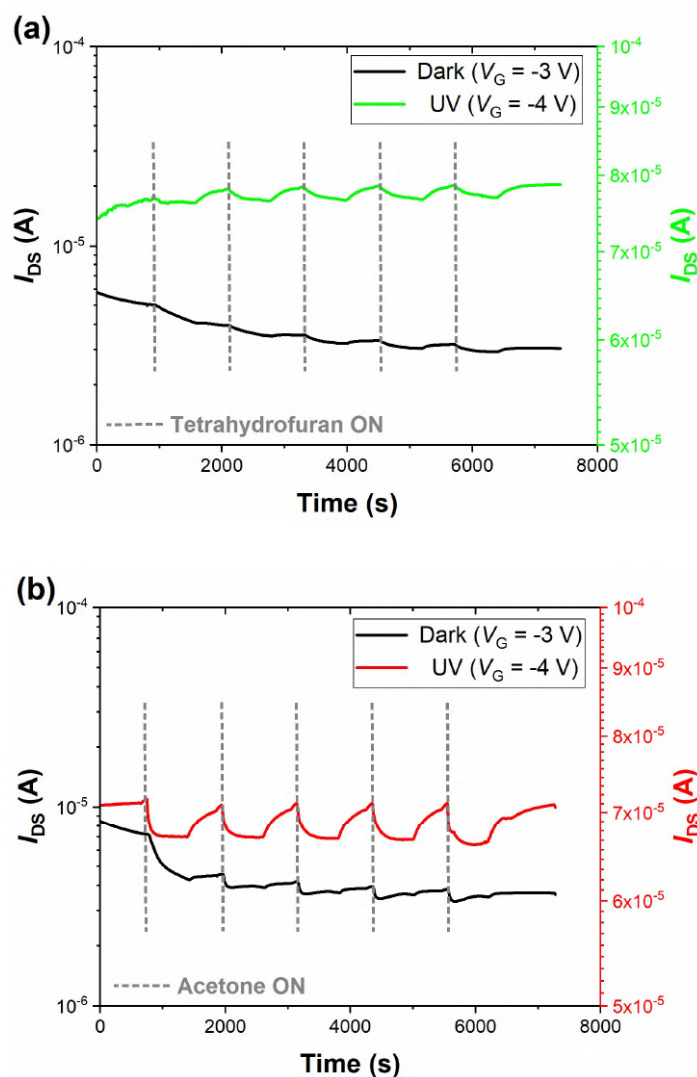


Figure 5.8 Drain-source current I_{DS} in time for five cycles of introducing (a) tetrahydrofuran (100 ppm) and (b) acetone (110 ppm). The gate voltage V_G was set to -3 V and -4 V for dark and UV-enhanced conditions, respectively. Dashed lines indicate when the target gas was introduced to the sensor.

Even though both organic species comprise the same elements (C, H, O), their geometrical configuration and polarity vary. Thus, their adsorption is expected to affect the electrical properties of the graphene-based FET differently. Compared to NO_2 , organic species usually bond weaker to the sensing surfaces, making them easier to desorb in the recovery phase. Thus, the desorption and the recovery process from strongly binding NO_2 molecules can be subjected to a more pronounced short-time drift of the current flowing through the channel.

The complimentary low-frequency noise measurements performed for graphene/AlGaIn/GaN sensor revealed the dominating effect of UV irradiation on fluctuations measured in the 1–500 Hz range. The quantitative detection for selected concentrations of NO_2 (5–20 ppm) was not possible in the dark, whereas minor changes in noise amplitude for different concentrations of NO_2 were observed for the lowest frequencies measured (~ 1 Hz) under UV

light. Similarly, in the case of organic vapors, the noise was not affected by these gases in the dark; however, the decrease in the normalized power spectral density of voltage fluctuations ($S_V(f)/V_S^2$) was observed under irradiation. The discussed results from $1/f$ noise studies are presented in Figure 5.9 (for NO_2) and Figure 5.10 (for tetrahydrofuran and acetone). UV irradiation clearly causes more intense fluctuations with emerging Lorentzian close to 10 Hz.

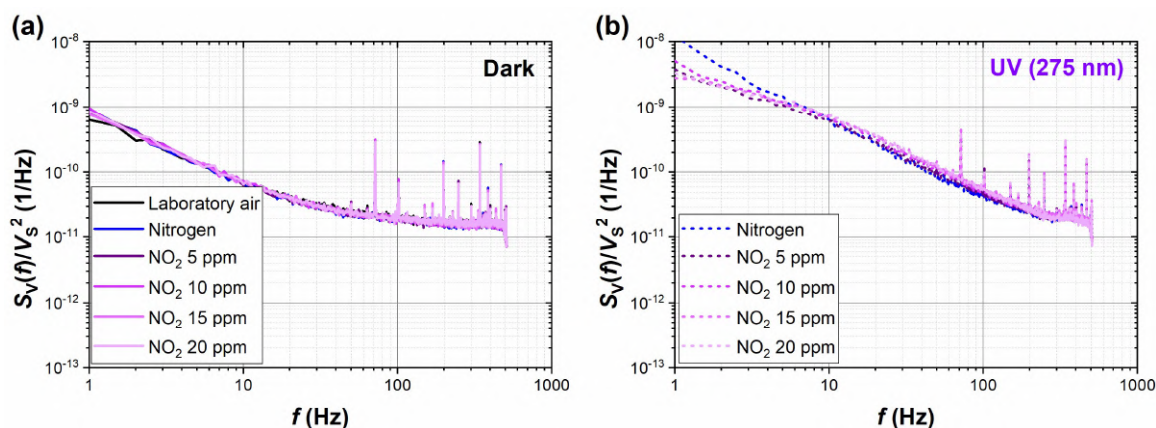


Figure 5.9 Power spectral density of voltage fluctuations $S_V(f)$ normalized to sensor DC voltage squared V_S^2 for selected concentrations of NO_2 (a) in the dark and (b) under UV irradiation.

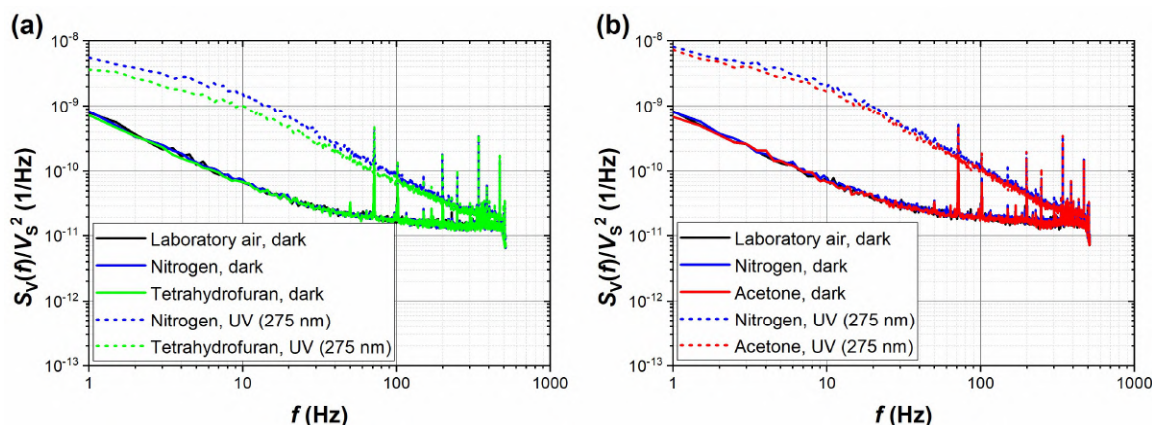


Figure 5.10 Power spectral density of voltage fluctuations $S_V(f)$ normalized to sensor DC voltage squared V_S^2 for (a) tetrahydrofuran (100 ppm) and (b) acetone (110 ppm) in the dark (solid curves) and under UV irradiation (dashed curves).

Figure 5.11 compares the product of $S_V(f)/V_S^2$ and frequency f for the investigated target gases and nitrogen as a reference atmosphere. The characteristic frequencies at which the maximum occurs (marked with dashed vertical lines on the graph) are 11 Hz, 12 Hz, 13 Hz, and 12 Hz for nitrogen, acetone, tetrahydrofuran, and nitrogen dioxide, respectively, so the shape of the spectrum is preserved regardless of the surrounding atmosphere with minor differences in the noise amplitude. The combination of DC response studies and $1/f$ noise measurements shows

a limitation of using graphene-based FETs with GaN substrates as highly sensitive and selective gas sensors.

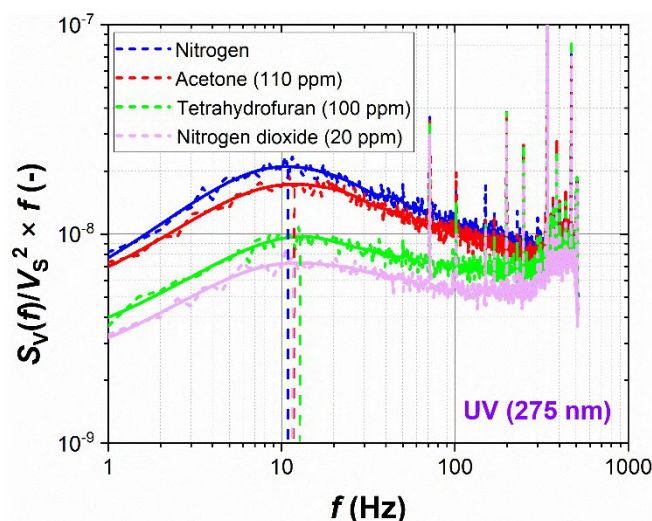


Figure 5.11 Noise spectra showing the multiplication product of power spectral density of voltage fluctuations $S_V(f)$ normalized to sensor DC voltage squared V_s^2 and frequency f for selected vapors. Dashed curves demonstrate experimental data, and solid lines correspond to polynomial fitted curves. Vertical dashed lines indicate the maximum noise values for fitted functions. Characteristic frequencies occur at 11, 12, 13, and 12 Hz for nitrogen, acetone, tetrahydrofuran, and nitrogen dioxide, respectively.

To conclude the observations from studying graphene-based FETs with two different substrates (Si/SiO₂ and AlGaIn/GaN) and varied configurations of graphene (channel or gate material), a few relevant points can be listed:

- back-gated GFET requires regular surface cleaning at high temperatures and under vacuum to regain its baseline resistance, whereas graphene/AlGaIn/GaN device recovers to its original baseline overnight;
- DC responses to the selected gases under UV light are higher for a back-gated GFET than graphene/AlGaIn/GaN sensor – for THF vapor, the relative resistive response is 100% at Dirac point for back-gated FET and only 8% in the transfer region of the I_{DS} - V_G curve for graphene/AlGaIn/GaN device;
- low-frequency noise studies of the graphene channel enable observing distinguishable features that can be ascribed to organic vapors, whereas for the device with a graphene gate, the characteristic Lorentzian appears at a similar frequency for all atmospheres and can be linked with the dominating effect of irradiating the structure;
- back-gated FETs utilizing large-area graphene as a channel (~ 0.2 mm² of active area) enable observing characteristic noise features in similar frequency ranges as FETs with graphene of more than a thousand times smaller surfaces, which confirms the first hypothesis of the dissertation that **low-frequency noise utilized for gas detection by**

back-gated graphene can be scaled up to larger surfaces, facilitating simpler gas sensor production;

- comparing two devices of distinct configurations of graphene and substrates shows that FET with graphene channel demonstrates higher sensitivity to selected gases, and FET with graphene gate exhibits higher stability of its baseline in time, which supports the second hypothesis of the dissertation that **the sensitivity and stability of the gas sensors based on two-dimensional materials can be improved by substrate selection.**

5.1.2 Graphene-Silicon Schottky diode

Another device was investigated to study further the possibility of enhancing the sensitivity and stability of light-assisted graphene-based gas sensors by substrate selection. As described above, FETs with graphene used as a channel or gate electrode produced distinct responses to organic and inorganic species that can be distinguished by DC characteristics and $1/f$ noise measurements. Another tested device with CVD-graphene grown on Cu foil as the main active component was prepared in the Schottky diode configuration. In this case, graphene was prepared *via* the scheme presented in Figure 4.1 with an additional step of selective etching of SiO_2 prior to transferring graphene directly onto the Si substrate. This way, the *n*-doped Si forms a Schottky junction with graphene of *p*-type semiconducting properties in ambient air, confirmed by DC characteristics. The research on graphene-silicon (G-Si) Schottky diodes was divided into two parts. The first one was devoted to studying DC characteristics of the junctions under oxidizing inorganic NO_2 and reducing organic THF using irradiation with selected LEDs. The second one focused on $1/f$ noise measurements and included the presentation of the possibility of decorating graphene with metallic nanoparticles. Similarly to GFET measurements, DC response studies were conducted according to the schematic from Figure 4.6 using the probe station as depicted in Figure 4.8b. The low-frequency fluctuations were measured employing the circuit illustrated in Figure 4.9. Details about methodology, including Schottky diodes fabrication and measurement procedures, are described in the articles *Drozdowska, K. et al., (2023). Enhanced gas sensing by graphene-silicon Schottky diodes under UV irradiation. Sensors and Actuators B-Chemical, 396, 134586* and *Smulko, J., et al., (2023). Low-frequency noise in Au-decorated graphene–Si Schottky barrier diode at selected ambient gases. Applied Physics Letters, 122, 211901* and attached Supplementary Materials [130,131]. The most important results from this research are discussed and concluded below.

The gas sensor in the Schottky diode configuration enables monitoring of current-voltage (*I-V*) characteristics in the forward bias at positive voltages (dominated by graphene resistance) and reverse bias at negative voltages (dominated by the Schottky barrier properties). Thus, DC characteristics were measured between -4 V and 4 V for the G-Si sensor with the Schottky junction area of $\sim 0.03\text{ mm}^2$ (width $W = 100\text{ }\mu\text{m}$, length $L = 250\text{ }\mu\text{m}$). The current I flowing through

the Schottky junction can be expressed with the following formula according to the thermionic emission model [64]:

$$I = I_0(e^{eV/\eta k_B T} - 1), \quad (5.1)$$

where e is the electronic charge, V is the applied voltage, η is the ideality factor, k_B is the Boltzmann constant, and T is the absolute temperature. The ideality factor informs about the degree of inhomogeneity at the interface of the two materials and the defectiveness of the junction and equals 1 for the ideal Schottky diode. Monitoring I - V dependence of the investigated G-Si junction at room temperature revealed the η factor of 3, suggesting that defects mediate the charge transport across the Schottky barrier. Additionally, the saturation current I_0 is defined as:

$$I_0 = AA^*T^2 e^{-e\phi_B/k_B T}, \quad (5.2)$$

where A is the Schottky barrier area, A^* is the Richardson's constant ($112 \text{ A}\cdot\text{cm}^{-2}\cdot\text{K}^{-2}$ for n -type Si), and ϕ_B is the Schottky barrier potential. The formulas (5.1) and (5.2) enable calculating the Schottky barrier height (SBH) $e\phi_B$ if the I - V characteristics are known. SBH reached 0.78 eV in the dark, and 0.55 eV and 0.64 eV under irradiation with blue LED (wavelength of 470 nm, optical power density up to 4.3 mW/cm^2) and UV LED (wavelength of 275 nm, optical power density up to 1.59 mW/cm^2), respectively. Moreover, the Schottky barrier properties were preserved in dry and humid air conditions, confirmed by comparing DC characteristics in dry synthetic air (S.A.) and laboratory air with relative humidity between 40–50%.

Qualitative and quantitative studies with oxidizing NO_2 and reducing THF as the target gases were conducted to evaluate the effect of irradiation on the G-Si junction current responses. Figure 5.12 shows time-evolved I - V characteristics for a constant value of NO_2 concentration (2 ppm diluted in dry S.A.), demonstrating a similar current response between 80% and 90% during the 1-hour introduction of the target gas to the sensing surface regardless of the used irradiation. However, the magnified regions close to 4 V bias show that the response saturates quicker for the irradiated sensor than in the dark, and the responses are higher for high positive voltage. The response Δ marked on the graphs signifies the percentage of the relative change in the current flowing through the diode I_{gas} in the target gas compared to the current in the reference atmosphere (S.A.) I_{air} , so $\Delta = (I_{\text{gas}} - I_{\text{air}})/I_{\text{air}}$. Since the forward regime of the I - V characteristic is dominated by the series resistance of the diode (mainly the resistance of the graphene layer), the shift caused by NO_2 adsorption in this region is linked to the change in graphene resistance. Since the current increases during gas detection, graphene resistance decreases, which agrees well with the oxidizing nature of NO_2 molecules and p -type semiconducting properties of the CVD-

grown graphene in the ambient air. On the other hand, the reverse regime of the characteristic is not influenced by the atmosphere, only by the incident light. Blue and UV light cause the growth of the reverse saturation current, and the effect is presumably correlated with the penetration depth and irradiation intensity. Blue light with a longer wavelength and more than 2.6 times higher optical power density shifts the characteristic and decreases the SBH slightly more than UV light. Quantitative measurements under UV light with the same sensor and NO₂ (Figure 5.13) demonstrate that the current increases gradually with increasing gas concentration (1–3 ppm). The data points derived from the *I*-*V* curve at 4 V were used to estimate the theoretical detection limit (DL) of the G-Si sensor equal to 75 ppb for NO₂ detection under UV light, which is comparable with the values reported for GFETs and graphene-suspended arrays demonstrated in Chapter 2 (Table 2.2). Additionally, the G-Si junction exhibited repeatable response/recovery cycles under NO₂ introduction, with the average response and recovery time estimated as 635 s and 1670 s for different gas concentrations, respectively. The adsorption/desorption pace demonstrated in Figure 5.14 is similar to that reported by other authors for graphene-silicon interfaces [65,66].

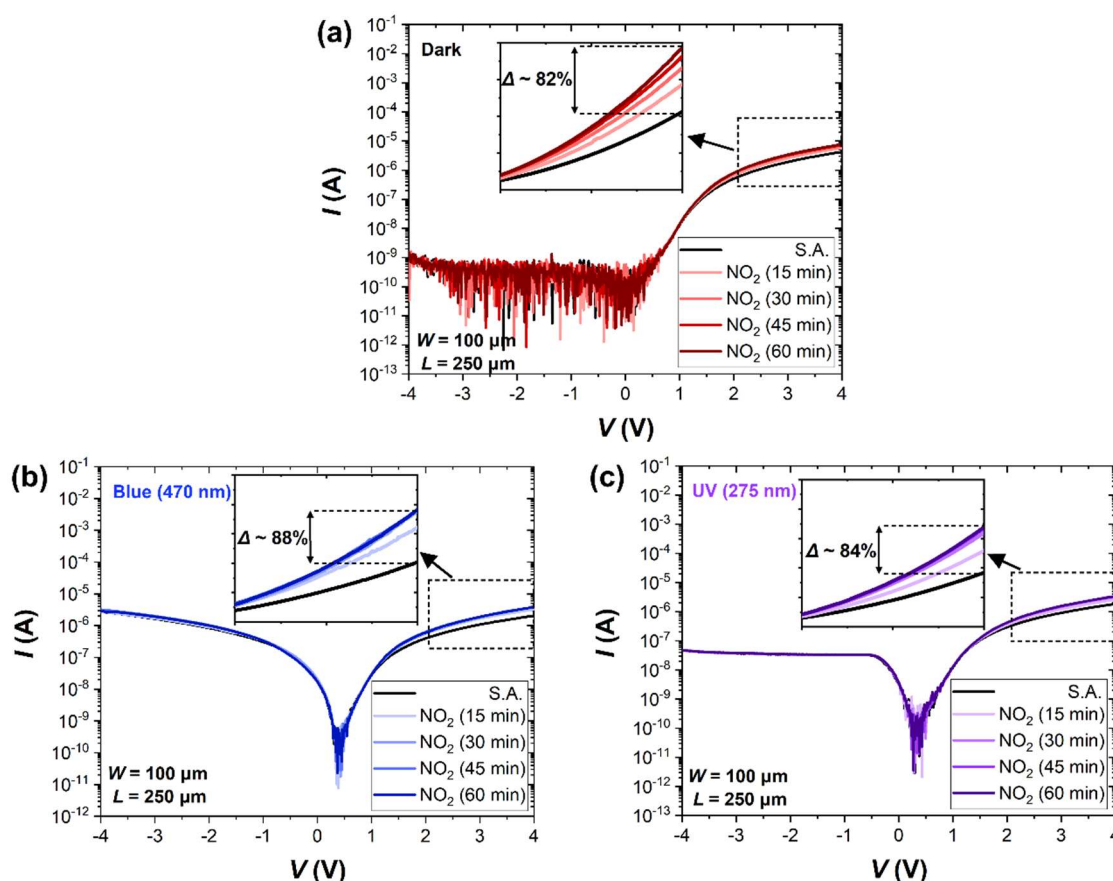


Figure 5.12 Current-voltage characteristics of the investigated G-Si Schottky diode ($W = 100 \mu\text{m}$, $L = 250 \mu\text{m}$) in an ambient atmosphere of NO₂ (2 ppm) collected (a) in the dark, (b) under blue LED (470 nm, 4.3 mW/cm²), and (c) UV LED (275 nm, 1.59 mW/cm²). The *I*-*V* characteristics were recorded at equal intervals of 15 minutes after introducing NO₂ gas.

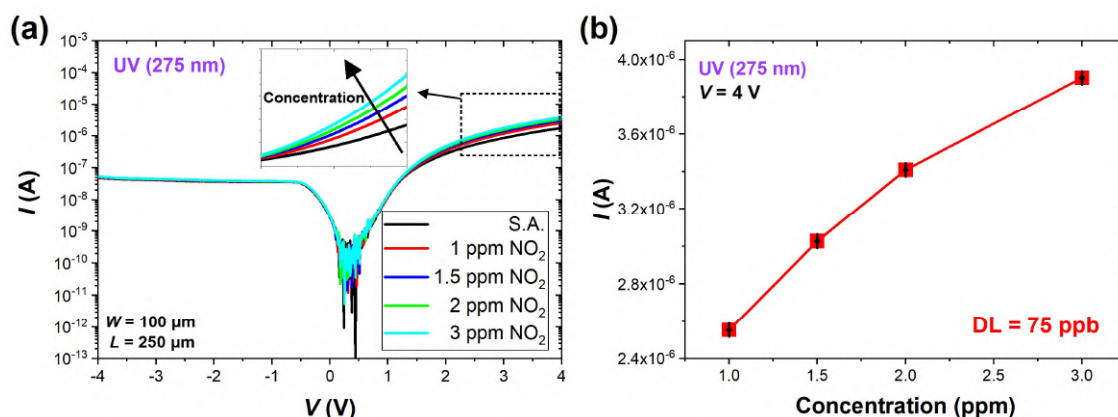


Figure 5.13 (a) Current-voltage characteristics of the investigated G-Si Schottky diode ($W = 100 \mu\text{m}$, $L = 250 \mu\text{m}$) for NO_2 (1–3 ppm) under UV light, (b) data points at 4 V bias (derived from I - V characteristics) for detection limit (DL) estimation. Black error bars represent the accuracy of the current measurements. Each characteristic was collected after 60 minutes of target gas introduction.

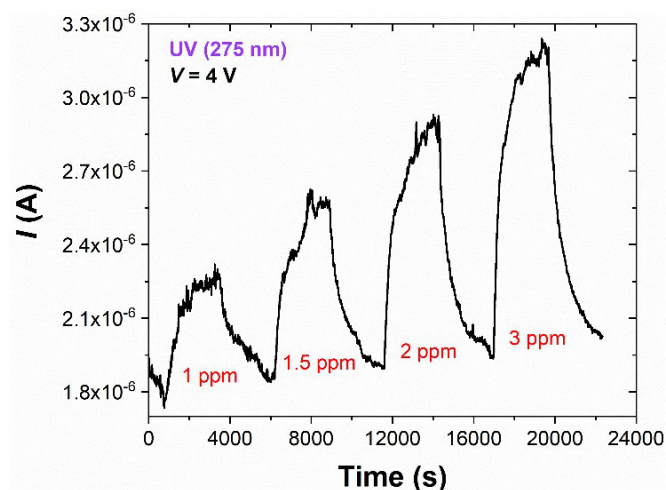


Figure 5.14 Time response of the G-Si Schottky diode ($W = 100 \mu\text{m}$, $L = 250 \mu\text{m}$) at 4 V bias for NO_2 (1–3 ppm) under UV irradiation. Each cycle consisted of 45 minutes of NO_2 flow and 45 minutes of recovery in S.A.

The following studies involved the detection of organic and reducing THF of different physicochemical properties than the NO_2 molecule. Based on the research on graphene-based FETs presented earlier in this chapter, it is evident that cyclic THF molecules interact strongly with the defective surface of Cu-grown graphene and shift its conductivity profile toward n -type semiconducting properties, especially under UV irradiation (tested wavelength = 275 nm). The accumulation of charges near the graphene interface and a strong photogating effect observed during UV-enhanced THF detection were expected to affect the G-Si Schottky junction properties, including the height of the barrier. Qualitative detection of THF (100 ppm) presented in Figure 5.15 revealed that THF induces the most pronounced changes in the I - V characteristic under UV irradiation with only a moderate downward shift in the forward regime and a more substantial

decrease of the current in the reverse bias (highlighted in the magnified region in Figure 5.15c). These observations suggest that THF induces changes in graphene resistance that are visible for positive voltage bias but also influences the Schottky barrier properties when applying UV light. The moderate decrease in the diode current confirms the *n*-type doping of graphene by THF, which donates electrons to the sensing surface.

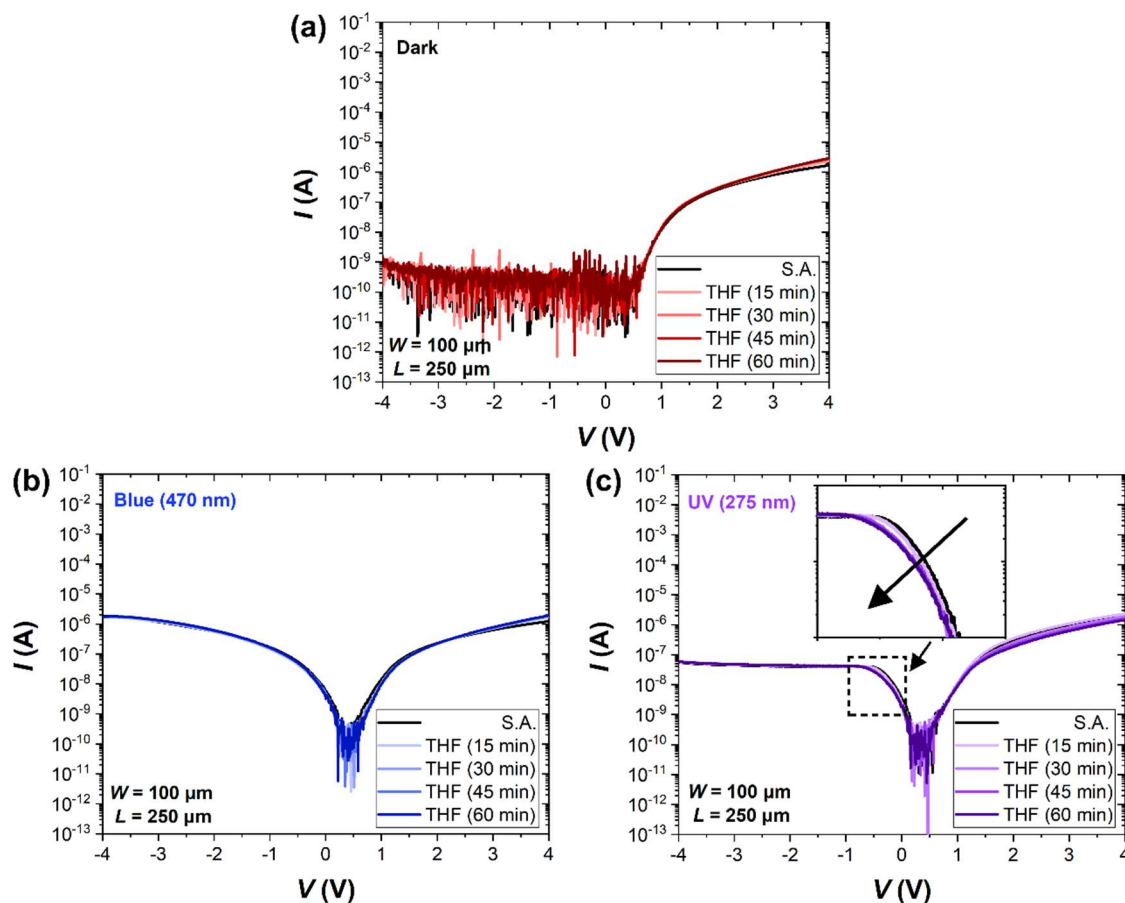


Figure 5.15 Current-voltage characteristics of the investigated G-Si Schottky diode ($W = 100 \mu\text{m}$, $L = 250 \mu\text{m}$) in an ambient atmosphere of 100 ppm of THF vapor operating (a) in the dark, (b) under blue LED (470 nm, 4.30 mW/cm^2), and (c) UV LED (275 nm, 1.59 mW/cm^2).

The differences in SBH after THF adsorption can be calculated based on formulas (5.1) and (5.2) for the diode current before (I_{air}) and after (I_{gas}) gas introduction and the change in SBH can then be reduced to a simple expression:

$$e\Delta\phi_B = -k_B T \ln\left(\frac{I_{\text{gas}}}{I_{\text{air}}}\right). \quad (5.3)$$

Based on this formula, the shift in SBH was calculated to be 16 meV for a 60-minute exposure to THF, and the average response and recovery times were estimated as 914 s and 997 s.

Supplementary measurements for varied concentrations of THF (50–200 ppm) at 4 V bias allowed the estimation of $DL = 31$ ppm for the tested organic vapor. Moreover, the analogous DC measurements for THF vapor under UV light with the Schottky junction of a bigger area (~ 0.07 mm²) showed that diodes exhibit similar junction properties regardless of their size (SBH of 0.64 eV and 0.63 eV for both samples) and minor differences in sensing responses can be ascribed to local variations in graphene defective morphology.

The second part of the investigation on G-Si junctions was devoted to studying low-frequency noise and the effect of decorating graphene surface with gold nanoparticles (AuNPs). Nanostructures act as additional elements bonded to the surface and the source of localized surface plasmon resonance (LSPR) induced with the incident light of wavelength correlated with the resonance peak of absorption for AuNPs. The Au nanoparticles were deposited onto graphene employing the Advanced Gas Deposition technique (AGD). AGD enables obtaining nanoparticles of log-normal size distribution. The average size of deposited Au nanoparticles was 8 nm, and they exhibited the maximum absorption at 586 nm (yellow light), corresponding to the resonance wavelength of the structures. The corresponding article collectively presents details of the fabrication process with structural and optical characterization [131]. The yellow LED (wavelength of 592 nm) was utilized in DC characteristics and $1/f$ noise measurements to induce LSPR and monitor the changes in the G-Si junction properties after inducing the plasmonic effect.

Since the yellow light is less energetic than blue or UV irradiation, and LSPR relates to the collective oscillations of charge within and beyond the volume of nanoparticles, the induction of plasmon resonance was expected to affect the noise spectra. To compare noise spectra with those obtained for GFETs, the experiments were conducted with two organic vapors of different physicochemical properties – tetrahydrofuran (THF) and chloroform (CHCl₃) that induced characteristic Lorentzians in the $1/f$ noise spectra of Cu-grown graphene. Figure 5.16 shows the DC characteristics for the selected vapors in the dark and under yellow light for the Au-decorated G-Si junction. The results in the logarithmic scale demonstrate the increase in the reverse saturation current by yellow light, and the linear scale exposes the minor changes in the current during THF adsorption (forward bias over 2 V). Since longer wavelengths do not activate the photocatalytic effect and acceleration of gas adsorption like UV irradiation, there is only a minor variation between sensing in the dark and under yellow light for THF and no change for CHCl₃. Moreover, there was no significant effect of gas adsorption and yellow LED irradiation for the non-decorated sample.

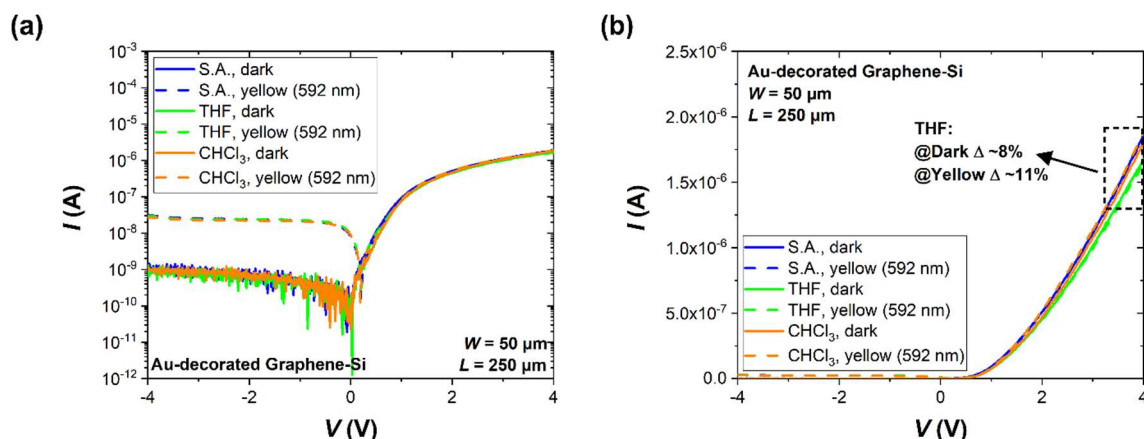


Figure 5.16 Current-voltage characteristics of the investigated G-Si Schottky diode ($W = 50 \mu\text{m}$, $L = 250 \mu\text{m}$) decorated with AuNPs in synthetic air (S.A.), 100 ppm of THF or 100 ppm of CHCl_3 (a) in logarithmic scale, (b) in linear scale with changes marked for THF ambience under forward bias. The solid curves correspond to dark conditions, and the dashed curves represent conditions with yellow LED (592 nm) irradiation.

The Au-decorated G-Si sample exhibited $1/f$ noise in the frequency range of 0.5–2000 Hz for voltage bias between 1.2 and 3.6 V (Figure 5.17a). The variation in the level of noise at 1 Hz is observed for the Schottky diode irradiated with yellow light, and there is a proportionality between the power spectral density of voltage fluctuations and voltage squared, meaning that the recorded noise is generated by the tested device and independent from the measurement setup. Supplementary measurements with the non-decorated G-Si diode showed that the noise level does not change with yellow LED irradiation. However, the overall noise intensity is around one order of magnitude higher than for the Au-decorated sample. For instance, at $V = 3.64 \text{ V}$ and $f_0 = 1 \text{ Hz}$, $S_V(f_0) = 2 \times 10^{-7} \text{ V}^2/\text{Hz}$ for the Au-decorated device and $S_V(f_0) = 3 \times 10^{-6} \text{ V}^2/\text{Hz}$ for the non-decorated one even if its volume was five times greater, and less intense flicker noise was expected according to the Hooge formula presented in equation 3.5 (Chapter 3). This shows that the excitation of plasmonic resonance in AuNPs suppresses low-frequency noise in the sensor. Such observation indicates that there is an energy transfer between the sensing material and nanoparticles, and resonating structures generate noise at higher frequencies compared to the observed range. The observed phenomenon indicates that decoration with plasmonic nanoparticles and creating or modulating surface defects can control the intensity of fluctuations generated in the graphene-based junctions.

Figure 5.18 demonstrates the results of utilizing the Au-decorated G-Si junction and FES method to differentiate between selected gases. The spectra of voltage fluctuations were converted into power spectral density of resistance fluctuations normalized to the dynamic resistance of the diode. Since the diode resistance depends on the voltage bias, the conversion required linearizing the Schottky diode by replacing it with the voltage source and serial resistance R_{Sdiff} being a differential of the I - V characteristic at $V = 3.64 \text{ V}$. This way, the presented resistance

fluctuations are independent of the measurement setup and biasing conditions. The $1/f$ noise measured under yellow light (Figure 5.18a) with the induced LSPR enabled simpler distinguishing between two organic vapors compared to blue light (Figure 5.18b). The noise level at 1 Hz differed by a factor of 2.8 under yellow light, and only 1.4 under blue light and 1.2 in the dark. Furthermore, no changes in the spectra shape for two organic vapors were observed, suggesting different noise generation mechanisms than in GFETs, even though the Schottky diode comprises the same type of graphene. The lack of characteristic Lorentzians suggests no dominant event of a particular lifetime when most of the graphene lies directly onto Si.

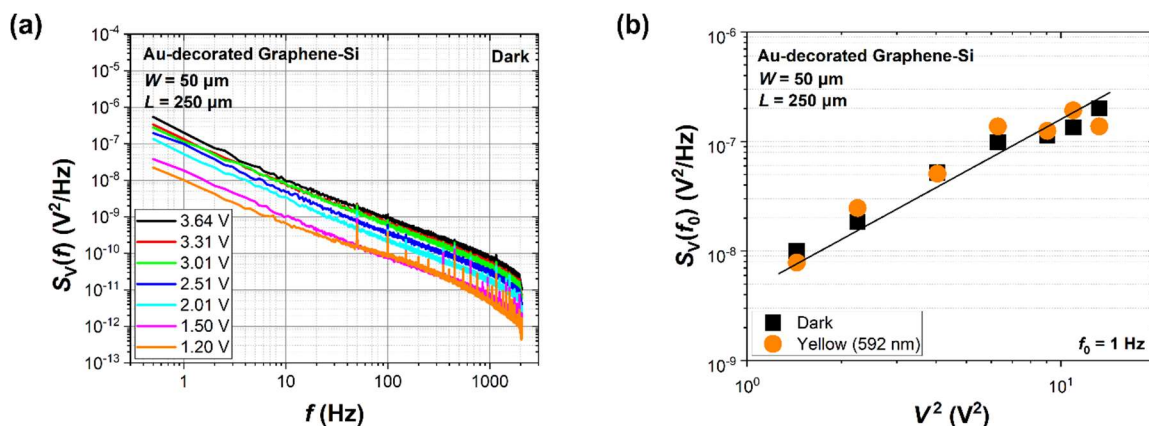


Figure 5.17 (a) Power spectral density of voltage fluctuations $S_V(f)$ generated in the Au-decorated G–Si Schottky diode under forward bias (1.20–3.64 V) in the dark and ambient air and (b) power spectral density of voltage fluctuations $S_V(f_0)$ at frequency $f_0 = 1$ Hz vs. bias voltage V across the diode, showing linear dependence as a function of V^2 in the dark and under yellow light (592 nm).

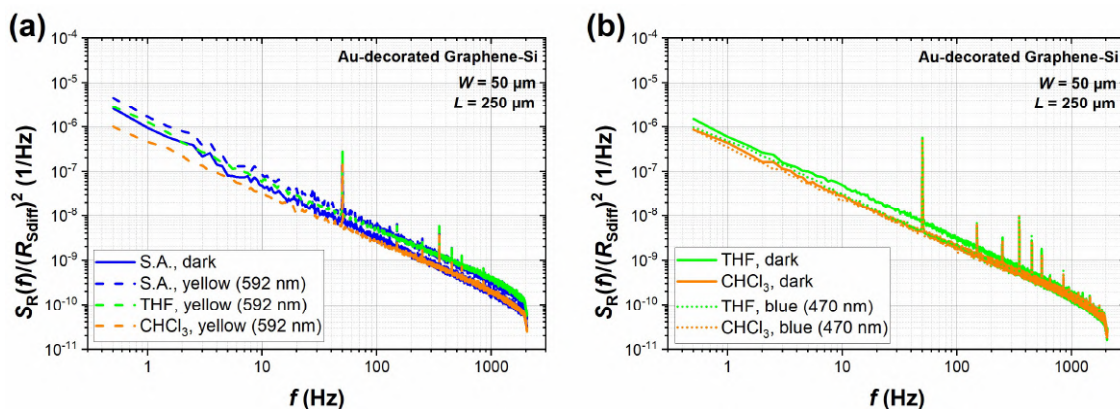


Figure 5.18 Power spectral density of resistance fluctuations $S_R(f)$ normalized to the square of dynamic resistance (differential resistance) R_{diff}^2 for a forward-biased Au-decorated G–Si Schottky diode at voltage bias $V = 3.64$ V in selected conditions: (a) in the dark and under yellow light (592 nm), (b) in the dark and under blue light (470 nm).

To conclude the results obtained from studying graphene-based Schottky diodes, a few observations can be highlighted:

- graphene deposited directly on *n*-doped Si provides the rectifying contact and Schottky junction, which allows observing resistive responses of tens of % for NO₂ and THF at relatively low voltage bias (4 V at maximum);
- 1/*f* noise is observed for the G-Si junctions, with its intensity changing under selected organic vapors and noise response enhancement by decorating graphene with gold nanoparticles, although no characteristic Lorentzians appear due to the presence of organic gases;
- compared to back-gated GFETs, high sensitivity of the Schottky diode sensors is obtained under lower voltage bias (maximum of 4 V) – GFETs required gate voltage biasing up to 60 V to observe responsivity up to tens of % or more for selected vapors, which suggests that low-power consumption sensors can be produced based on G-Si junction;
- fabrication of the Schottky junction enhanced the time stability of the sensor electrical properties, and the samples did not require high-temperature cleaning, enabling utterly room-temperature processing and operation;
- overall, the results confirm that the deposition of graphene directly on the Si rather than SiO₂ layer prevents graphene from fast aging while preserving the high sensitivity of the sensor at lower voltage bias, confirming the second hypothesis of the dissertation that **the sensitivity and stability of the gas sensors based on two-dimensional materials can be improved by substrate selection.**

5.1.3 Carbon nanotubes

The sensors based on thin layers of randomly oriented carbon nanotubes (CNTs) were investigated as supplementary to study another nanoscale-carbon form being a structural derivative of graphene. The initially studied CNT-based resistors with combined DC measurements and FES manifested their utility in NO₂ sensing enhanced by UV irradiation (wavelength of 365 nm or 275 nm) [132]. Whereas the CNT sensor exhibited resistance fluctuations following the carrier number model for dark conditions, the same assumptions could not be applied to the UV-assisted device, implying more complex fluctuations mechanisms under UV light. The following investigation on a series of samples exhibiting different CNT network densities and optical transmittance supported systematizing the possibilities of gas detection by light-assisted CNT resistors. The details on fabrication and structural, optical, electrical, and noise measurement procedures are provided in the article *Drozdowska, K. et al. (2023). Optimum Choice of Randomly Oriented Carbon Nanotube Networks for UV-Assisted Gas Sensing Applications. ACS Sensors, 8, 3547-3554* and corresponding Supplementary Material [122].

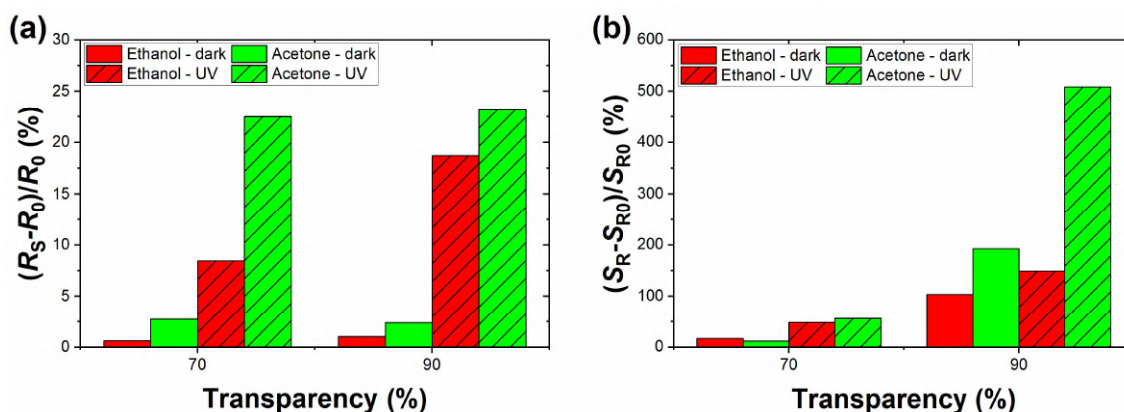


Figure 5.19 (a) Relative change in sensor resistance R_s and **(b)** power spectral density of resistance fluctuations $S_R(f)$ normalized to sensor resistance squared R_s^2 at $f_0 = 0.5$ Hz for ethanol (140 ppm) and acetone (110 ppm) in the dark and under UV 275 nm light for samples of 70 and 90% transparency. Reference resistance R_0 and reference power spectral density S_{R0} refer to synthetic air conditions.

The studies of optical and structural properties of the CNT sensors supported associating the density of carbon nanotube networks with their optical absorbance, which increased for denser layers. The optical absorbance or transmittance was correlated with the transparency (between 60–95%) of the structures related to the nitrocellulose filters used during the precipitation and deposition of the layers. The resistive measurements under irradiation of selected wavelengths (265–430 nm) showed that highly transparent samples exhibit higher photoresponse, which signals higher sensitivity to incoming irradiation and a possibility to employ it to enhance light-assisted gas sensing. Low-frequency noise studies of two representative samples (one with 70%-transparency representing high-density networks and the second with 90%-transparency representing low-density networks) revealed that both exhibit $1/f$ noise up to 100 Hz, and the noise of the 90%-sample is less intense when normalized to the sensor resistance and active area. Figure 5.19 summarizes the results of resistive and noise measurements for two representative sensors collected for ethanol (140 ppm) and acetone (110 ppm) in the dark and under UV light (wavelength of 275 nm, optical power density up to 1.59 mW/cm^2) when the sensor was biased with 0.1 V. The highest resistive and noise responses were obtained for the UV-assisted CNT sensor of 90% transparency. It can be ascribed to the higher porosity and a more significant number of binding sites for molecular adsorption of the thinner layer. Additionally, the relative change in the noise intensity of the same sample is around eight times higher than the resistive response for ethanol and around 22 times higher for acetone under UV light. This signals that fluctuations in the sensor are highly sensitive to surface processes, and the differences in the $1/f$ noise spectra can be easily observed under various atmospheres in CNT-based systems. A comparison of DL values estimated for 70% and 90% samples showed that the lower density of the CNT network and UV irradiation support achieving higher sensitivity to ethanol and acetone. DL was calculated as 0.89 ppm for ethanol and 0.48 ppm for acetone based on resistive responses collected during UV-assisted time

measurements. However, CNT-based sensors exhibited relatively lower resistive responses (up to ~20%) compared to graphene-based FETs and Schottky diodes (up to ~100%), showing that the structural configuration of the carbon atomic layer also guides the detection mechanisms.

5.2 Gas sensors based on 2D semiconducting materials

5.2.1 Molybdenum disulfide

The leading representative of the group of 2D semiconductors utilized for gas sensing is molybdenum disulfide (MoS_2). In electrical sensing devices, MoS_2 was often reported to be employed as high-quality single atomic layers of micrometer or submicrometer dimensions usually fabricated *via* CVD. To study the mechanisms of detection and noise generation and the possibilities of fabricating highly sensitive sensors through a simpler procedure, ink-printed MoS_2 resistors were considered for doctoral research.

The ink printing procedure of MoS_2 layers and measurement methodology are described in Chapter 4. The scheme of the fabrication process is illustrated in Figure 4.2. The initial results of structural and optical characterization of printed MoS_2 layers are shown in Figure 4.4. Additionally, the sensor was measured in the gas sensing chamber depicted in Figure 4.7b. The low-frequency noise of the ink-printed sample was measured according to the circuit presented in Figure 4.10 due to the high resistance of the material (up to ~1 G Ω). The responsivity of the MoS_2 sensor was tested under UV irradiation (wavelength of 275 nm, optical power density up to 1.59 mW/cm²), which assured the higher stability of the baseline, even though the time drift (short- and long-time) was observable during all measurements. The issue of drifting current was managed analytically by fitting and subtracting the exponential function from the sensor baseline. This way, the simple processing of sensing data enables obtaining stable and more reliable responses of the ink-printed MoS_2 device. The most significant results on the MoS_2 -based sensors are demonstrated and concluded below.

Figure 5.20 summarizes the photoresponsivity of the MoS_2 sensor. Stable *I*-*V* characteristics were collected up to *V* = 20 V and confirmed that the higher optical power density of the light source induces higher photocurrent. Thus, the UV LED operating at 1.59 mW/cm² of optical power density was selected for all gas sensing experiments. Additionally, since the semiconducting MoS_2 exhibits higher photoresponsivity at higher polarizing voltage, and the *I*-*V* characteristics were stable up to ~20 V, the voltage bias of 20 V was used in all time response measurements. Four consecutive cycles of irradiation showed that the sensor exhibits time drift. However, the response to UV light was repeatable in each cycle, yielding 18–20% of the peak-to-peak value for a 10-minute irradiation. The possible reason behind the observed drift is that the ink-printed sensing layer consists of multiple nanoflakes, so applying high voltage to such a structure can cause an elongated stabilization process when the individual flakes and boundaries contribute to the overall sensor resistance. Additionally, UV light activates surface

cleaning by removing oxygen and humidity from the surface, affecting the equilibrium of surface states.

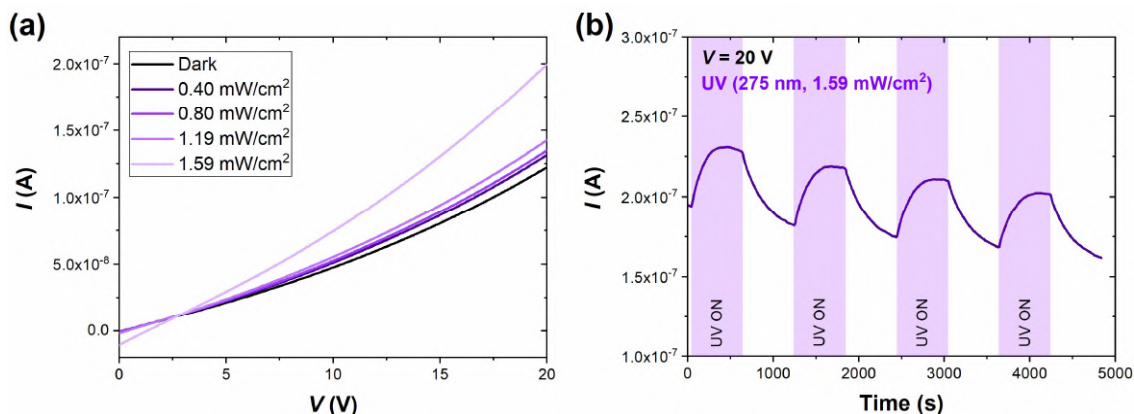
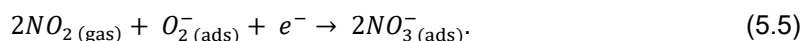


Figure 5.20 (a) Current-voltage characteristics of MoS₂ sensor in S.A. for selected optical power densities of the UV LED (275 nm), and (b) time response (current) of MoS₂ sensor to four consecutive cycles of UV light (275 nm, 1.59 mW/cm²) irradiation. Each irradiation and recovery cycle (in the dark) lasted 10 minutes. The bias voltage was set to 20 V for time-response measurements.

The gas sensing experiments were conducted for three gases of different physicochemical properties: nitrogen dioxide (NO₂), ammonia (NH₃), and acetone (C₃H₆O). NO₂ is an oxidizing inorganic gas, NH₃ is a reducing inorganic compound, and C₃H₆O is an organic nucleophilic species. Thus, the responsivity of ink-printed MoS₂ sensors to highly different species can be studied. Figure 5.21 demonstrates the qualitative and quantitative detection of NO₂. The subsequent cycles of introducing 5 ppm of the gas resulted in repeatable resistive responses (an average peak-to-peak value of 28%). Various concentrations of NO₂ caused the gradual increase in the sensor resistance, which agrees with the effect of electron-accepting NO₂ on an *n*-type semiconductor. Thus, all the following experiments employed UV light to obtain higher sensitivity. NO₂ is a highly electrophilic molecule, accepting electrons from the MoS₂, which results in a resistance increase:



Additionally, NO₂ molecules interact with oxygen adsorbed on the sensing surface if the sensor operates in the air:



Under UV light, oxygen photo ions participate in the reaction (5.5), and NO_2 ions easily replace them, increasing the response. Thus, the resistive response in the dark was only 4% but reached ~20% under UV light for a 15-minute exposure to NO_2 at $V = 20$ V.

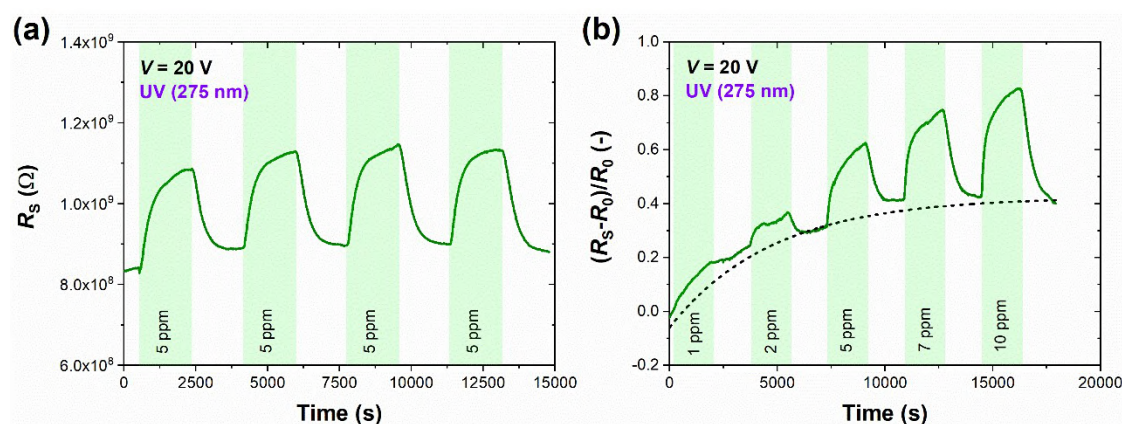
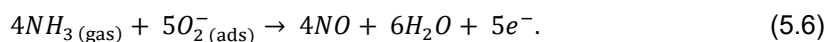


Figure 5.21 (a) Time response (resistance) of MoS_2 sensor to four consecutive cycles of NO_2 (5 ppm) introduction; and (b) time response (relative changes in sensor resistance) of MoS_2 sensor to five cycles of NO_2 introduction of selected concentrations (1–10 ppm) under UV light (275 nm). Each detection cycle consisted of a 30-minute response and 30-minute recovery in S.A. The bias voltage was set to 20 V.

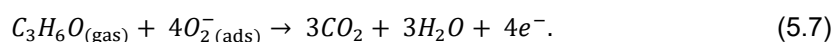
The black dashed exponential curve in (b) denotes the time drift present during detection.

The drift in the baseline resistance is observed to diminish in time, suggesting the longer process with a particular relaxation time, potentially of an exponential origin. Therefore, the exponential function with the general formula $S_R = S_0 + ae^{bt}$, where S_0 , a , and b are constants, S_R represents the resistive response, and t designates time was used to fit to the drifting baseline (black dashed curve in Figure 5.21) and was later used to estimate the detection limit for the sensing responses without the drift component. Figure 5.22 and Figure 5.23 present analogous DC characteristics for ammonia and acetone. Both gases exhibit electron-donating properties, which decrease the sensor resistance, and highly pronounced short-time drift marked with black dashed curves fitted to the experimental data. Comparing resistive responses to all three gases of the same concentration of 5 ppm (based on the last cycle as the most stable one), the sensor responds the strongest to NO_2 (0.26 of relative change in sensor resistance) compared to NH_3 (-0.04) or $\text{C}_3\text{H}_6\text{O}$ (-0.03). Ammonia and acetone decrease the sensor resistance; however, the direction of changes is disrupted with substantial drift, especially for acetone. Organic vapors usually exhibit relatively low adsorption energies and bind weakly to the sensing surfaces; thus, acetone produces lower responses than ammonia [127,133].

The sensor resistance decreases with increasing concentration of ammonia, which agrees with the reducing nature of this target gas. The donation of electrons by NH_3 during adsorption can be formulated *via* the reaction:



In this case, ammonia reacts with oxygen adsorbed on the surface, forming NO and H₂O and releasing electrons to MoS₂. Similarly to the NO₂ case, photoinduced oxygen ions can react with ammonia, producing an analogous electron-donating effect. Similarly, the sensor resistance decreases with increasing acetone concentration, suggesting that this nucleophilic gas has reducing properties toward *n*-type MoS₂. Compared to NO₂ and NH₃, the resistive responses to acetone are less stable, possibly due to the weak bonding of organic molecules to the sensing surface and weaker carrier exchange. The subtraction of the drifting baseline clearly exposes the direction of charge transfer, which drives gas detection for MoS₂ systems. Since the conductance of the sensor increases (resistance decreases), acetone adsorption is associated with electron transfer from the gas molecules to MoS₂. As the resistive responses are lower for acetone than for NO₂ or NH₃, the electron transfer is presumably quantitatively lower for this organic gas. Acetone molecules react with the adsorbed oxygen as follows:



The adsorption is accompanied by the release of electrons to the conduction band of MoS₂, causing a reducing effect similar to the one induced by NH₃.

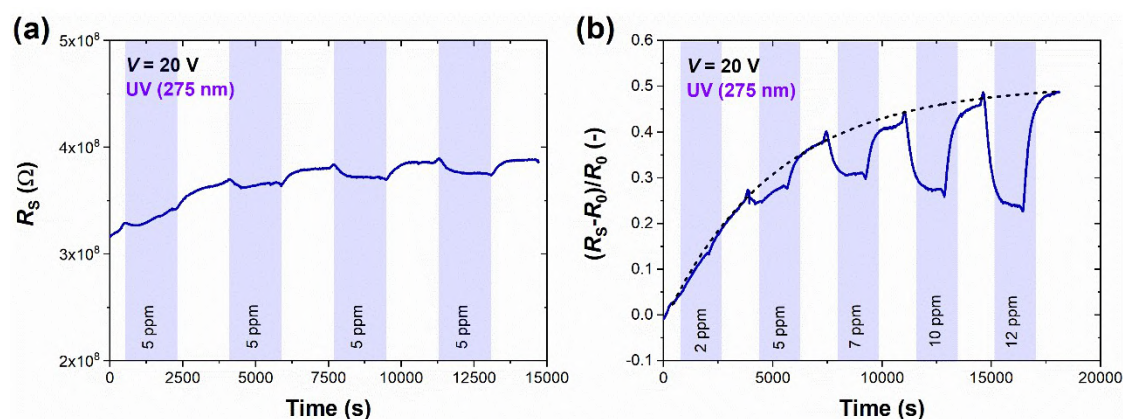


Figure 5.22 (a) Time response (resistance) of MoS₂ sensor to four consecutive cycles of NH₃ (5 ppm) introduction; and (b) time response (relative changes in sensor resistance) of MoS₂ sensor to five cycles of NH₃ introduction of selected concentrations (2–12 ppm) under UV light (275 nm). Each detection cycle consisted of a 30-minute response and 30-minute recovery in S.A. The bias voltage was set to 20 V.

The black dashed exponential curve in (b) denotes the time drift present during detection.

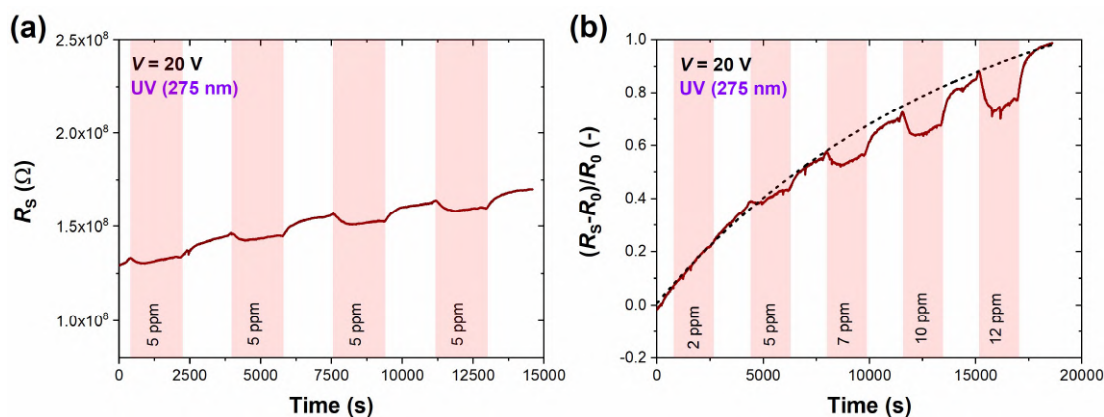


Figure 5.23 (a) Time response (resistance) of MoS₂ sensor to four consecutive cycles of C₃H₆O (5 ppm) introduction; and (b) time response (relative changes in sensor resistance) of MoS₂ sensor to five cycles of C₃H₆O introduction of selected concentrations (2–12 ppm) under UV light (275 nm). Each detection cycle consisted of a 30-minute response and 30-minute recovery in S.A. The bias voltage was set to 20 V. The black dashed exponential curve in (b) denotes the time drift present during detection.

Data processing and removing the drifting baseline are solutions to make the measured responses more apparent and easier to interpret regarding surface adsorption mechanisms, especially for weakly binding species. Thus, both raw and processed data points were used to calculate DL values for selected target gases. Figure 5.24 compares the sensor sensitivity before and after subtracting the drifting baseline, marked as “drift” and “subtracted drift”. The most significant observation is that for NO₂, data processing reduces the overall resistive responses because this gas produces the sensor resistance response in the same direction as the resistance drifts in time, making the raw responses slightly overestimated. In the case of NH₃ and C₃H₆O, it is visible that both gases reduce the resistance after drift removal. The raw responses are then underestimated for ammonia, and their sign is even changed completely for acetone. Additionally, ammonia induces higher changes in the sensor resistance for higher concentrations (10 and 12 ppm) than acetone. DL values highlighted in the figures indicate that simple data post-processing can improve DL by more than two times for NO₂ and four times for NH₃. In the case of acetone, DL was improved by less than 10% but remained at the sub-ppm level, which, compared to other literature reports, is a success for detecting organic vapors by pure MoS₂ [134]. Overall, the processed data reliably represents the adsorption process and the direction of charge transfer between MoS₂ flakes and selected inorganic and organic gases.

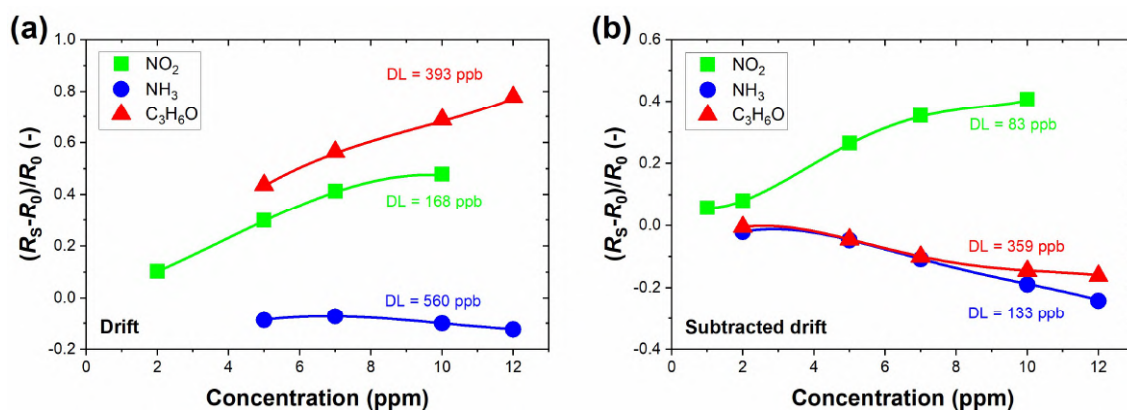


Figure 5.24 Relative changes in MoS_2 sensor resistance as a function of target gas concentration for NO_2 , NH_3 , and $\text{C}_3\text{H}_6\text{O}$ under UV light (275 nm) (a) before and (b) after subtraction of the drift baseline.

Theoretical detection limits established for NO_2 , NH_3 , and $\text{C}_3\text{H}_6\text{O}$ are marked on the graphs and are equal to 168 ppb, 560 ppb, 393 ppb (drift case), and 83 ppb, 133 ppb, and 359 ppb (subtracted drift case), respectively. Solid curves correspond to a third-order polynomial function fitted to the experimental points for DL estimation.

Supplementary low-frequency noise measurements of ink-printed MoS_2 sensor were devoted to studying the selectivity of the sensor and the possible mechanism of noise generation compared to graphene-based sensors (GFETs), presented earlier in this dissertation. Thus, the noise response to selected organic gases (chloroform, tetrahydrofuran, acetonitrile, and acetone) was studied as the power spectral density of current fluctuations vs. frequency between 0.1–500 Hz. Figure 5.25 summarizes the noise spectra generated in the sensor in the dark and under UV irradiation. It is visible that the presence of selected gases changes mainly the amplitude of noise in the dark, but it additionally affects the shape of the spectrum under UV light. Both the noise amplitude and slope are factors that support selective detection of gaseous compounds. Table 5.1 summarizes the noise features for the investigated conditions. The slope of the spectra for the frequencies below 10 Hz was estimated by fitting it as $S/f^2 \sim k/f^b$ where k is the proportionality factor, f is the frequency, and b designates the power of f that corresponds to the slope of the spectrum. Notably, the noise level increases significantly for acetonitrile (530% in the dark and 280% under UV irradiation at $f = 1$ Hz), whereas the slope of the spectrum changes in the most pronounced way for acetone under irradiation (the power of f changes from 1.00 to 1.59). The change in the slope of the $1/f$ dependence can signify the dominant source of the noise in the sample when the characteristic Lorentzian appears at a specific frequency. In the case of ink-printed MoS_2 , the dominant events seem to occur at the lowest frequencies measured and possibly lower than 0.1 Hz. This suggests the occurrence of fluctuations with long lifetimes during the adsorption of organic molecules on the investigated surface. For GFET tested under the same gas conditions, the Lorentzians appeared at ~ 1 Hz for most gases and at higher frequencies for chloroform in the dark. Interestingly, the single atomic layers of MoS_2 were not yet reported to exhibit the change in the slope of the $1/f$ spectrum, only the increase of the amplitude, e.g., for

acetonitrile like in the case of the investigated MoS₂ sensor [106,135]. The origin of noise for MoS₂ of a specific optical band gap is expected to be similar to the one proposed for semiconductors by McWhorter. The active surface states can participate in fluctuations in the number of charge carriers, being a dominant effect in noise generation. Nevertheless, the characteristic low-frequency Lorentzians can be distinguished in the structure of the overlapping MoS₂ flakes. It can relate to the specific structure of the ink-printed sensor but also longer processes occurring in the sample, such as long-term drift and aging, which are independent of the ambient atmospheres. Additionally, the differences in the noise induced by organic vapors can be ascribed to their physicochemical properties, including varied polar and structural properties, as in the case of graphene-based sensors.

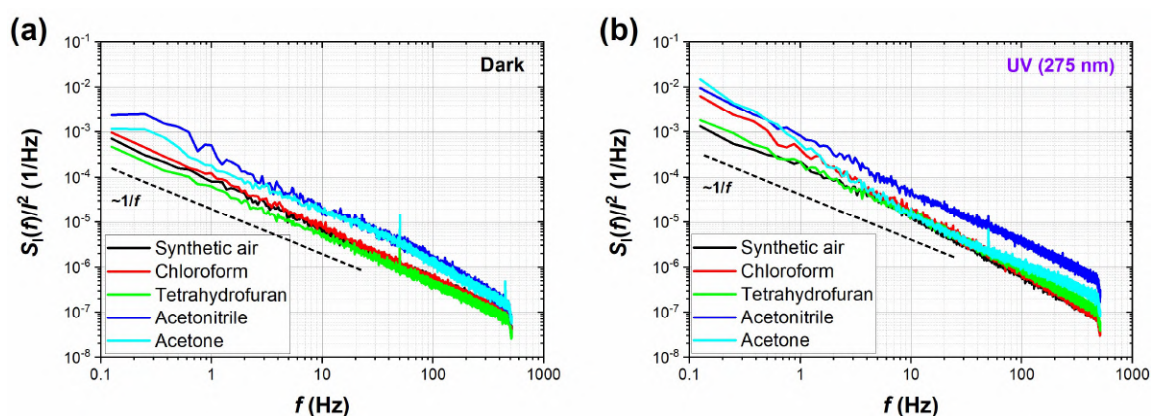


Figure 5.25 Power spectral density of current fluctuations $S(f)$ for the ink-printed MoS₂ sensor at different light and gas conditions: **(a)** in the dark and **(b)** under UV irradiation (275 nm, 1.59 mW/cm²).

The black dashed lines denote the $1/f$ noise shape.

Table 5.1 Noise features of the ink-printed MoS₂ sensor for selected organic vapors.

Gas	$S(f)/f^2$ at 1 Hz (1/Hz)		b up to 10 Hz (-)*	
	Dark	UV (275 nm)	Dark	UV (275 nm)
Synthetic air	8.00×10^{-5}	2.18×10^{-4}	1.04	1.00
Chloroform	1.23×10^{-4}	4.11×10^{-4}	1.08	1.33
Tetrahydrofuran	6.28×10^{-5}	2.17×10^{-4}	1.02	1.09
Acetonitrile	5.04×10^{-4}	8.23×10^{-4}	1.12	1.21
Acetone	1.85×10^{-4}	5.34×10^{-4}	1.11	1.59

*Parameter b denotes the power of frequency f in $1/f^b$ and describes the slope of the noise spectrum.

Despite the observed short- and long-term drift in the MoS₂ sensor, the resistive and noise responses can provide an efficient detection tool with specific data analysis. The most relevant conclusions from research on ink-printed MoS₂ sensors are:

- ink-printing allows obtaining sensors based on randomly oriented MoS₂ flakes that exhibit sensitivity up to 168, 560, and 393 ppb for UV-assisted detection of nitrogen dioxide, ammonia, and acetone without data post-processing, which confirms the third hypothesis of the dissertation, that **low-cost ink-printed molybdenum disulfide (MoS₂) flakes can detect selected gases at hundreds of ppb level;**
- data post-processing by fitting and subtracting the drifting baseline (resembling an exponential relaxation process) allows easier interpretation of the changes in the sensor resistance and direction of charge transfer between MoS₂ surface and ambient gas molecules;
- post-processed data allows obtaining reduced DL values up to 83, 133, and 359 ppb for nitrogen dioxide, ammonia, and acetone, respectively, suggesting an easy method to increase the sensitivity by data analysis;
- characteristic Lorentzians that appear below 1 Hz suggest fluctuations of longer lifetimes occurring during the detection of organic gases;
- the analysis of noise features (amplitude and slope) can be an efficient detection tool that enhances the selectivity of MoS₂ sensors, but it requires prolonged recording and data acquisition time.

5.2.2 Zirconium trisulfide

Zirconium trisulfide (ZrS₃), a transition metal trichalcogenide possessing semiconducting properties in bulk and as a monolayer, was studied to broaden the understanding of gas sensing by various 2D materials. The nanostructured ZrS₃ of *n*-type conductivity was tested in FET configuration with the ZrS₃ serving as a channel and sensing area of only 3 μm². Three LEDs (visible light) were applied to study the photoresponse of ZrS₃ (blue – 470 nm, 1.44 mW/cm², green – 515 nm, 4.05 mW/cm², and red – 700 nm, 0.91 mW/cm²). The gas sensing responses were studied *via* the transfer curves (*I*_{DS}-*V*_G) and time measurements in the nitrogen dioxide, ethanol, and acetone atmospheres. Details about ZrS₃-based sensors fabrication and testing procedures are described in the article *Drozdowska, K. et al. (2023). Study of ZrS₃-based field-effect transistors toward the understanding of the mechanisms of light-enhanced gas sensing by transition metal trichalcogenides. Materials Today Communications, 34, 105379* and corresponding Supplementary Material [136], and the most significant results are presented and discussed below. The supplementary noise measurements were realized according to the circuit scheme provided in Figure 4.10.

Figures 5.26a and 5.26b demonstrate the scheme and a microscopic photograph of the ZrS₃ layer (mechanically exfoliated from crystals) deposited between two gold electrodes operating in the FET configuration. Figures 5.26c and 5.26d show transfer and output characteristics for the device under selected lighting conditions, confirming that green and blue light induce the most significant photoresponse due to shorter wavelengths and higher optical

power density than red light. The FET characteristics measured in the reference atmosphere of S.A. confirm that nanostructured ZrS₃ exhibits *n*-type semiconducting properties. The wide hysteresis in the conducting profile is more pronounced under irradiation, which induces high photocurrent (blue and green light). Since the nanostructured ZrS₃ was observed to possess an indirect band gap of 1.8–1.9 eV, the material should strongly absorb wavelengths below ~690 nm. Longer wavelengths (e.g., 700 nm utilized in the experiments) can be absorbed if any discrete levels are below the conduction band, often observed in defective and doped semiconductors. Thus, the small impact of red irradiation can be explained by the presence of mid-gap energy levels in ZrS₃.

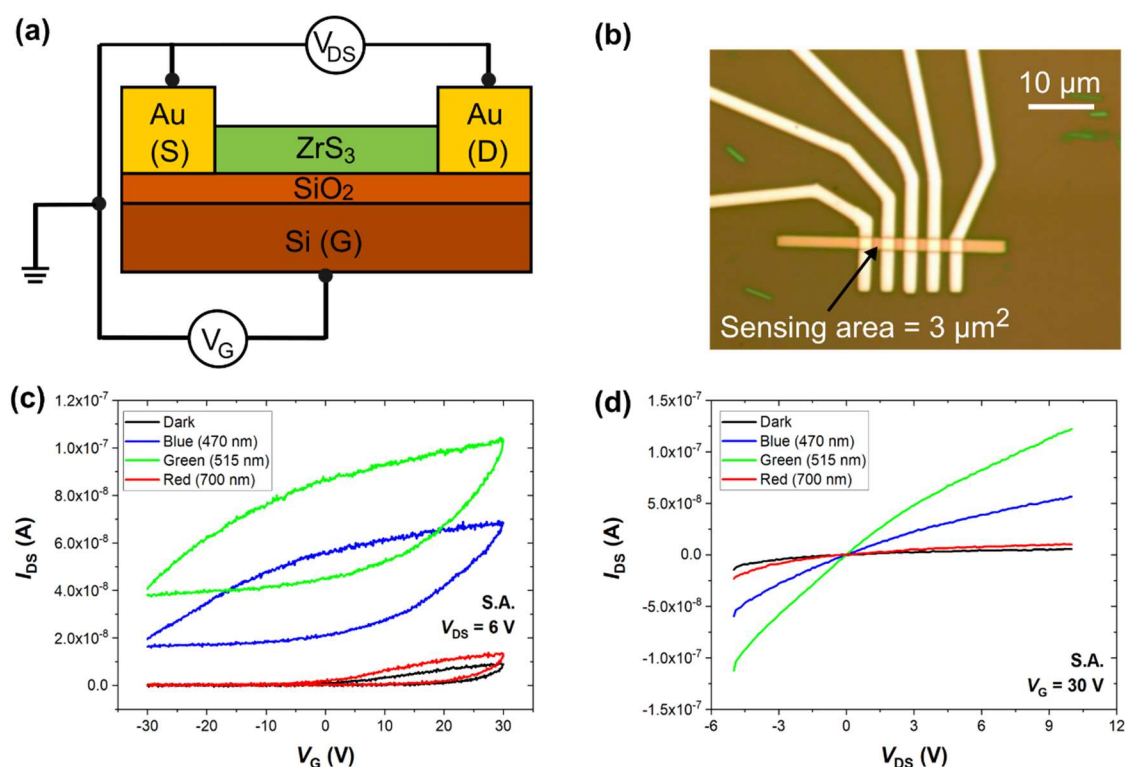


Figure 5.26 (a) Illustration of the ZrS₃-based FET sensor, and (b) microscopic image of the investigated sensing structure with a 3 μm^2 sensing area between each pair of electrodes;

(c) transfer curve (I_{DS} vs. V_G) with drain-source voltage (V_{DS}) biased to 6 V, and (d) output curve (I_{DS} vs. V_{DS}) with V_G biased to 30 V in the dark and under blue (470 nm, 1.44 mW/cm²), green (515 nm, 4.05 mW/cm²), and red (700 nm, 0.91 mW/cm²) irradiation. DC characteristics were measured in S.A.

The gas sensing experiments for the ZrS₃ FET sensor were conducted in inorganic (NO₂) and organic (ethanol, C₂H₆O; acetone, C₃H₆O) atmospheres at selected concentration ranges for each gas. Figure 5.27 depicts the transfer characteristics of the ZrS₃ sensor reacting to 4–16 ppm of NO₂ under different lighting conditions. In all cases, oxidizing molecules decrease the current flowing through the sensor, confirming the *n*-type character of the ZrS₃ FET. Blue and green light stabilize the sensing response due to induced photocurrent and provide measurable responses in tens or hundreds of nA. This way, irradiation facilitates room-temperature operation of the ZrS₃

FET sensor. The analogous DC measurements were conducted for ethanol and acetone, showing the opposite direction of changes induced by these two gases acting as reducing agents toward nanostructured ZrS_3 .

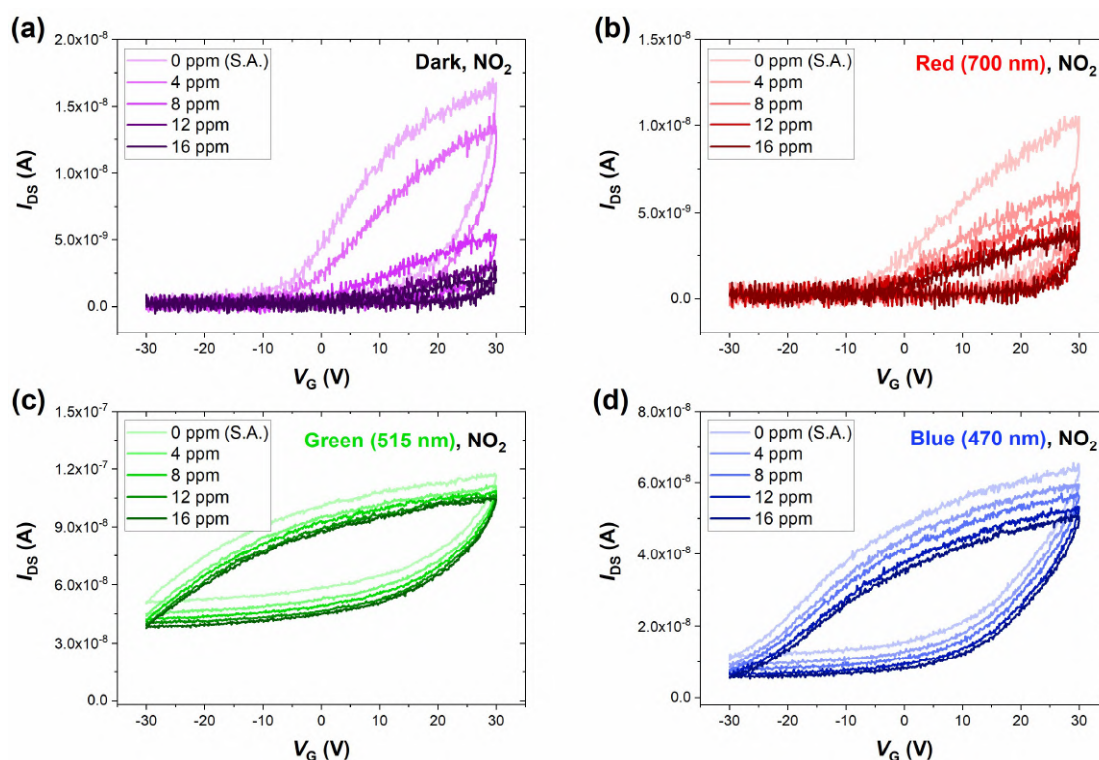


Figure 5.27 ZrS_3 sensor responses toward selected concentrations of NO_2 under different irradiation conditions: graphs (a)–(d) present drain-source current I_{DS} vs. gate voltage V_G for NO_2 detection in the dark and under red (700 nm, 0.91 mW/cm^2), green (515 nm, 4.05 mW/cm^2), and blue (470 nm, 1.44 mW/cm^2) light, respectively.

Figure 5.28 summarizes the current responses of the investigated sensor to three tested gases at $V_G = 30 \text{ V}$ and $V_{DS} = 6 \text{ V}$ in the selected concentration ranges. The R^2 parameter designated on the graphs for each lighting condition indicates the degree of linearity of the sensor responses ($R^2 = 1$ signifies the ideal linear dependence) and is evaluated during linear approximation of the analyzed data. Clearly, NO_2 can be easily differentiated from organic gases due to its oxidizing properties. However, the same concentration of reducing ethanol and acetone (30 ppm) can be distinguished, especially under blue irradiation. The relative change in the I_{DS} under green irradiation is 4.7% for 30 ppm of ethanol and 9.2% for 30 ppm of acetone. Under blue irradiation, the difference is more significant since the current responses are 2.8% for ethanol and 14% for acetone. The estimated responses show that blue light facilitates easier discrimination between two organic gases and enhances selectivity. Moreover, acetone molecules supposedly exhibit higher affinity to the ZrS_3 surface than ethanol molecules.

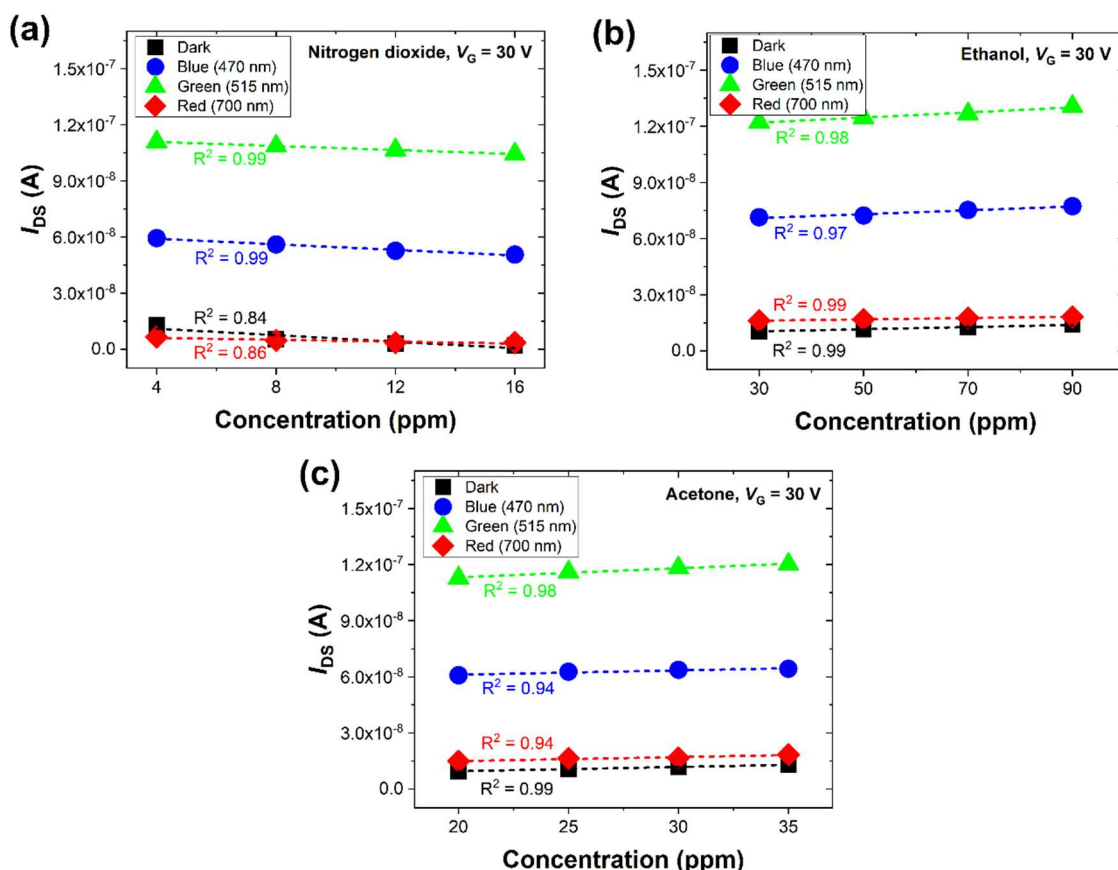


Figure 5.28 Comparison of ZrS_3 sensor responses toward different gases: drain-source current I_{DS} for selected concentrations of (a) nitrogen dioxide, (b) ethanol, and (c) acetone under selected irradiation conditions. I_{DS} values were derived from the transfer curves for $V_G = 30$ V. V_{DS} was biased to 6 V in all experiments. Dashed lines depict linear functions fitted to the experimental points, and parameter R^2 represents the quality of the linear fits.

Since there is a scarce number of reports discussing transition metal trichalcogenides for light-enhanced gas sensing, the discussion on possible mechanisms of gas detection by ZrS_3 was based on the knowledge on a leading representative of semiconducting metal sulfides – MoS_2 . Firstly, light excitation of the 2D sensing surfaces was earlier correlated with photoconductive and photogating effects (confirmed for GFETs). Secondly, UV-assisted gas detection by MoS_2 monolayers was reported to depend on changes in the concentration of carriers and changes in the mobility when the adsorbed molecules act as scattering centers for the carriers (including photocarriers). Charge transfer affects the sideways shift of the transfer curves, and mobility variations induce changes in the curve slope (these effects are depicted in Figure 2.6, Chapter 2.2). In the case of ZrS_3 , the change in the slope is visible mainly for gas detection in the dark and under red light. Under green and blue light, the gas detection does not affect the shape of the characteristics, implying that variations in carrier concentrations (pure charge transfer) mainly guide the sensing in such conditions. This observation can be connected with the high photoconductive effect induced for green and blue irradiation and a significant

number of photoinduced charge carriers participating in the surface adsorption processes. On the other hand, mobility variations are more pronounced when the photoconductive effect is weak (red light) or there is no such effect (dark), according to others [63]. Then, the scattering of the carriers on the adsorbed gas molecules results in a change in the hysteresis shape. The subsequent experiments were designed to test further the assumptions listed above, concentrating on the sensing enhanced by green and blue irradiation, as these conditions assure the most stable and easily measurable responses.

Figure 5.29 depicts the time measurements for a constant concentration of NO_2 (16 ppm). There are a few crucial observations based on time response studies. First, the sensor exhibits short-term stability with a stable baseline current and stable response to the target gas in consecutive detection cycles. Second, the studies confirm that optical power density affects the sensor baseline, so this property of the light source can be adjusted to modulate the baseline current to the desired and easily measurable values. Third, although the intensity of LEDs affects the baseline, the relative changes in I_{DS} remain similar regardless of the optical power density and equal 8.1%, 6.2%, 6.2%, and 7.1% in the consecutive cycles. According to [63], the constant or weak dependence between the light intensity and sensing response can be associated with the impact of mobility variation. Thus, despite the lack of change in the hysteresis shape due to NO_2 detection suggesting the dominant charge transfer mechanism, there still can be a weak influence of mobility fluctuations induced by the surface scattering of carriers. The coexistence of at least two phenomena connected with the trapping and de-trapping of carriers and scattering on surface defects and adsorbates is the most plausible explanation of gas detection mechanisms by nanostructured ZrS_3 . This assumption was additionally confirmed by the dependence between the sensor conductive response and NO_2 concentration (2–16 ppm) shown in Figure 5.30. The linear relationship between the inverse conductive response ($1/S_G$) and inverse gas concentration would imply the dominance of channel conductivity changes (pure charge transfer) with the negligible effect of other phenomena, as suggested elsewhere [63]. In the case of the results obtained for ZrS_3 , the deviation from the linearity ($R^2 = 0.86$) can suggest the occurrence of more than one mechanism during light-assisted detection. Additionally, the sensor response saturates for concentrations exceeding 8 ppm, which can be linked to the limit in coverage of the sensing surface by NO_2 molecules.

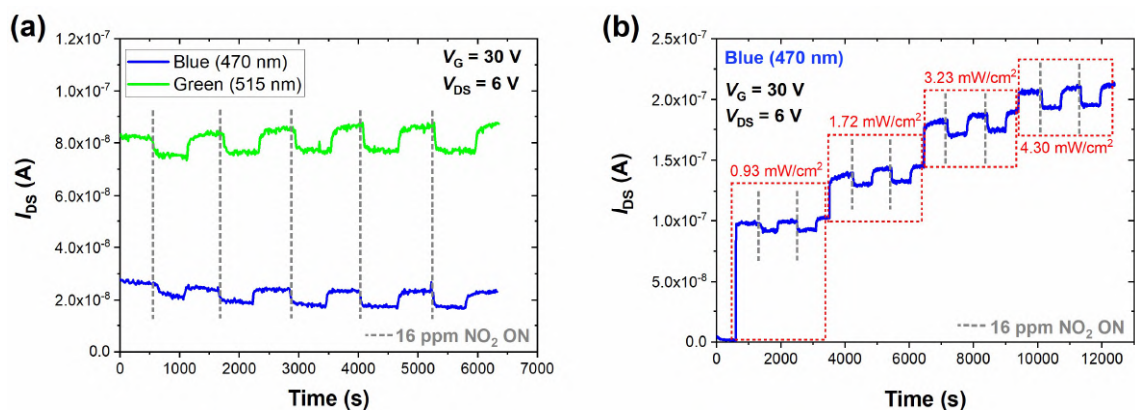


Figure 5.29 Time response studies of the ZrS₃ sensor for consecutive cycles of introducing 16 ppm of NO₂ (a) under continuous irradiation using green (515 nm, 4.05 mW/cm²) or blue (470 nm, 1.44 mW/cm²) light and (b) under continuous blue light (three LEDs connected in series) with optical power density between 0.93 mW/cm² and 4.30 mW/cm² (dashed red boxes indicate cycles of NO₂ detection for specific optical power densities with values marked above each box).

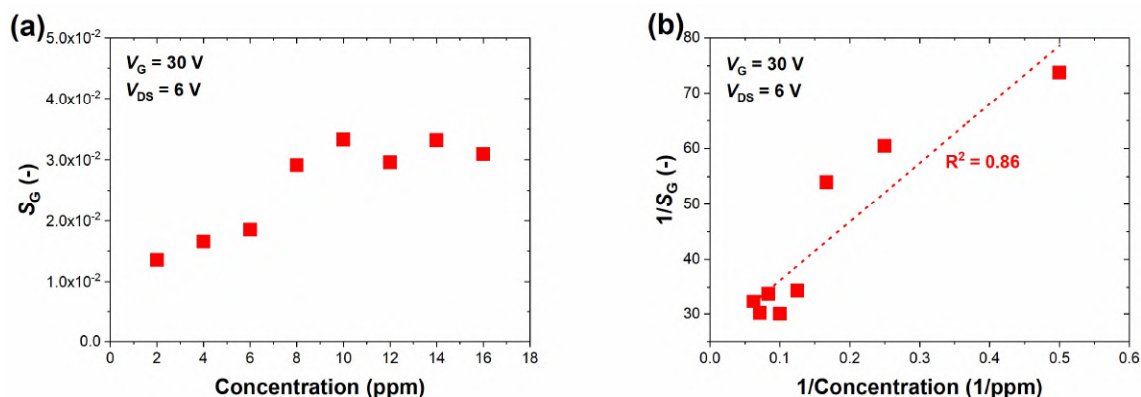


Figure 5.30 (a) ZrS₃ sensor response derived from the relative changes of conductance S_G vs. NO₂ concentration (2–16 ppm), and (b) the inverse conductive response vs. the inverse NO₂ concentration. Conductance G values were derived from the transfer curves for $V_G = 30$ V and V_{DS} biased to 6 V under blue irradiation of the highest optical power density (4.30 mW/cm²). S_G is then defined as $|G - G_0|/G_0$, where G_0 is the conductance in S.A.

The supplementary low-frequency noise measurements of ZrS₃ FET revealed that the sample exhibits $1/f$ noise between 0.1 and 10 Hz with minor variations for the lowest frequencies measured. Moreover, the noise intensity increases when detecting selected target gases under blue irradiation, as shown in Figure 5.31. The molecular adsorption and fluctuations of charge carrier number (dominant) and mobility (lower impact) increase the noise similarly for all three gases without the possibility for easy discrimination between gaseous species.

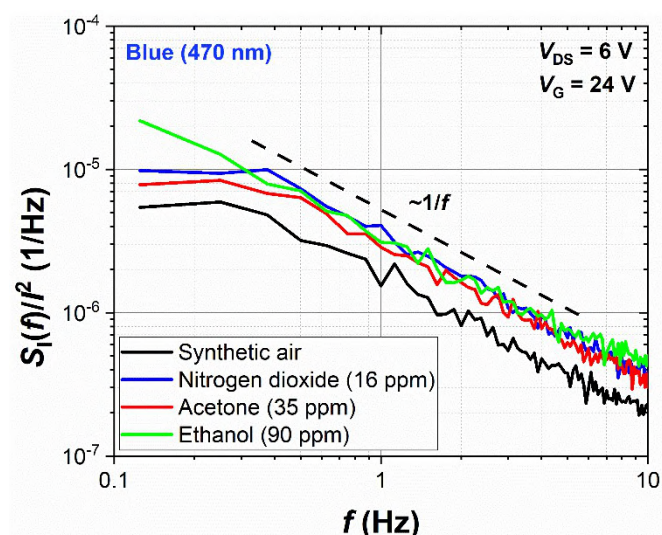


Figure 5.31 Power spectral density of current fluctuations $S_I(f)$ normalized to current squared I^2 for ZrS_3 sensor measured under blue light (470 nm, 4.30 mW/cm²) at $V_G = 24$ V and $V_{DS} = 6$ V in the atmospheres of selected target gases.

Overall, the studies on mechanically exfoliated, nanostructured ZrS_3 -based FET sensors complemented the research on 2D materials employed in light-assisted gas sensors. The most significant conclusions from the results described in this section are:

- green (515 nm) and blue (470 nm) irradiation enables stable and repeatable responses of the ZrS_3 -based sensor with gas detection guided by the photoconductive (dominant) and photogating effect;
- the probable explanation of the light-driven gas detection mechanism by ZrS_3 is the combination of charge transfer (change in the number of charge carriers) and mobility variations;
- the impact of scattering of carriers on defects and adsorbates is tentatively confirmed by the observed changes in the hysteresis shapes, weak dependence between the intensity of irradiation and sensing responses, and non-linear relationship between the inverse conductive response and inverse NO_2 concentration;
- light-assisted ZrS_3 sensor enables obtaining time responses of a more stable baseline than ink-printed MoS_2 sensor, possibly due to a much smaller active area; however, the detection mechanisms can still have the same origin for the group of different semiconducting metal sulfides.

6. CONCLUSIONS

The research presented in the doctoral dissertation aimed to propose gas sensors using 2D materials as active components. The objectives were to investigate possible structures and sensing components utilizing light enhancement and combining DC resistance and low-frequency noise measurements, as well as to study possible mechanisms guiding gas detection and origin of DC and noise responses, including noise generation mechanisms in low-dimensional materials. The research was divided into studying carbon-based sensors of relatively high electrical conductivity (graphene and carbon nanotubes) and 2D semiconductors with resistances up to G Ω (MoS₂ and ZrS₃). The results presented in Chapter 5 highlighted the most significant outcomes of the research that broadened the knowledge about mechanisms driving light-enhanced detection of inorganic and organic gases. The collected data allowed comparison between sensing devices of varying configuration (resistor, FET, Schottky diode), different placement of the sensing component (graphene as channel or gate in FET), and materials fabricated *via* different approaches (CVD-grown graphene, exfoliated ZrS₃ layers or solution-based ink-printed MoS₂). The gas detection mechanisms proposed in the dissertation for different sensors linked the fundamental knowledge on charge transfer in solid-state materials, surface science and molecular adsorption processes of species of different physicochemical properties, and basic noise generation models.

The research on the system of gas detection by 2D materials successfully confirmed the three hypotheses formulated in the dissertation, which constitute the original scientific achievements of the author of the thesis:

- I. **Low-frequency noise utilized for gas detection by back-gated graphene FET can be scaled up to larger surfaces, facilitating simpler gas sensor production (Chapter 5.1.1).**
- II. **The sensitivity and stability of the gas sensors based on two-dimensional materials can be improved by substrate selection (Chapter 5.1.1 and Chapter 5.1.2).**
- III. **Low-cost ink-printed molybdenum disulfide (MoS₂) flakes can detect selected gases at the ppb level (Chapter 5.2.1).**

Comparing the sensing features of all investigated samples led to highlighting other points that constitute additional significant research outcomes:

- Graphene utilized as a channel in FET or in the Schottky junction with silicon allows obtaining resistive responses of at least tens of %; however, the diode-configured device requires much lower input power to observe such high sensitivity (direction to highly sensitive low-consumption devices operating at RT).

- Employing GFETs enables observing characteristic low-frequency noise spectra with distinct shapes for organic vapors (increased selectivity), which is not observed for the graphene-silicon Schottky diodes.
- Decorating graphene-based Schottky diodes with gold nanoparticles improves gas sensing using the FES method when surface plasmon resonance is induced in the structure, showing the possibility of improving detection performance by controlling surface defectiveness.
- Ink printing constitutes an easy way to obtain sensitive layers from 2D MoS₂ flakes that exhibit resistive responses up to tens of % and noise responses in the form of distinct noise amplitude and slope; however, due to the structure consisting of overlapping flakes, the sensor exhibits lower stability and more intense time drift in contrary to mechanically exfoliated ZrS₃.
- The discourse on light-driven gas detection by MoS₂ and ZrS₃ indicates that possible detection mechanisms can be universal for novel materials that belong to the group of 2D or quasi-1D semiconductors.

Overall, based on the enlisted research outcomes, the aim of the doctoral dissertation to propose a system of gas detection using two-dimensional materials as active layers and to investigate, evaluate, and compare the gas-sensing performance of selected low-scale structures is achieved. Furthermore, the doctoral research initiated new directions worth investigating in terms of systems of gas detection by low-dimensional materials. Notably, the possibility of controlling the types of defects at the fabrication level (growth of defective 2D layer and nanoparticle decoration) and then preparing the sensing surface employing irradiation have the potential to produce highly efficient gas sensors. Methodology-wise, combining the DC resistance measurements with fluctuation-enhanced sensing proved to be an effective way to increase sensor sensitivity and selectivity. More elaborate studies on low-frequency noise generation in low-scale sensing structures also constitute the direction for future research, as connecting atomic-scale events responsible for resistance fluctuations were observed to influence the macroscopic features of the sensing devices directly. Thus, there are still plenty of possibilities for future studies and broadening the understanding of mechanisms involved in light-assisted gas sensors.

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8. LIST OF FIGURES

Figure 2.1 Examples of low-dimensional materials used in gas sensing devices. The class of 2D materials includes, for instance, graphene, transition metal di- or trichalcogenides (TMDCs or TMTCs) and their combinations [42]. 10

Figure 2.2 Top-view atomic structure and electronic band structure of 2D pristine (a) graphene, (b) molybdenum disulfide (MoS_2), and (c) zirconium trisulfide (ZrS_3). CB, VB, and E_G denote the conduction band, valence band, and band gap energy, respectively. E_G values marked on the scheme refer to direct optical band gaps. Grey, yellow, teal, and purple atoms represent carbon, sulfur, molybdenum, and zirconium. 12

Figure 2.3 Schematic representation of linear dispersion relation for pristine and p -doped graphene. The lower energy level of NO_2 leads to electron transfer from graphene Fermi level (E_F) to NO_2 LUMO, causing a change in material resistance R 14

Figure 2.4 Schematic of the transfer characteristic of graphene-based FET with Dirac point at $V_G = 0$ V and changes in Fermi level position for hole and electron regime. A negative V_G range indicates p -type conductivity and a positive V_G range corresponds to the n -type conductivity of graphene. 16

Figure 2.5 Schematic illustrations of the conductivity σ vs. applied gate voltage V_G and the corresponding physical phenomena for a GFET: (a) the lateral shift of charge neutrality point due to the charge transfer between a gas molecule and graphene, (b) the change in hole branch due to Coulomb interactions of the gas molecule with holes, (c) the change in electron branch due to Coulomb interactions of the gas molecule with electrons, (d) the vertical change in charge neutrality point position due to the modulated residual carrier concentration by gas molecule. Reprinted with permission from [62]. Copyright 2020 T. Hayasaka *et al.* 17

Figure 2.6 Theoretical graphs describing the changes in the transfer curve during NO_2 exposure under different irradiances: (a) charge-transfer model and (b) carrier-mobility modulation model. P_{L1} and P_{L2} denote different irradiances ($P_{L1} < P_{L2}$). The solid and dashed lines represent the characteristics before and after NO_2 detection. $I_{01(2)}$ and $\Delta I_{1(2)}$ are the initial current and change in current under an irradiance of $P_{L1(2)}$. V_{th} and g_m represent threshold voltage and transconductance. (c) Experimental characteristics measured before, during, and after exposure to 100 ppb NO_2 , and (d) the same transfer curves normalized for easier comparison. The solid and dotted curves are forward and reverse sweeps, respectively. Reprinted with permission from [63]. Copyright 2021 American Chemical Society. 18

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10. PUBLISHED PAPERS

The thesis was prepared based on six peer-reviewed papers enlisted below:

- I. **Drozdowska, K.**, Rehman, A., Sai, P., Stonio, B., Krajewska, A., Dub, M., Kacperski, J., Cywiński, G., Haras, M., Rumyantsev, S., Österlund, L., Smulko, J., & Kwiatkowski, A. (2022). Organic Vapor Sensing Mechanisms by Large-Area Graphene Back-Gated Field-Effect Transistors under UV Irradiation. *ACS Sensors*, 7, 3094-3101.

Contribution of the author of the thesis: *electrical and noise measurements of the sensors, structural characterization of the graphene layers, visualization of the research results, data curation, analysis and interpretation, writing of the original draft, and review and editing of the manuscript during the revision process.*

- II. **Drozdowska, K.**, Rumyantsev, S., Smulko, J., Kwiatkowski, A., Sai, P., Prystawko, P., Krajewska, A., & Cywiński, G. (2023). The effects of gas exposure on the graphene/AlGaIn/GaN heterostructure under UV irradiation. *Sensors and Actuators B-Chemical*, 381, 133430.

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- III. **Drozdowska, K.**, Rehman, A., Smulko, J., Rumyantsev, S., Stonio, B., Krajewska, A., Słowikowski, M., Filipiak, M., Sai, P., & Cywinski, G. (2023). Enhanced gas sensing by graphene-silicon Schottky diodes under UV irradiation. *Sensors and Actuators B-Chemical*, 396, 134586.

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- IV. Smulko, J., **Drozdowska, K.**, Rehman, A., Welearegay, T., Österlund, L., Rumyantsev, S., Cywiński, G., Stonio, B., Krajewska, A., Filipiak, M., & Sai, P. (2023). Low-frequency noise in Au-decorated graphene–Si Schottky barrier diode at selected ambient gases. *Applied Physics Letters*, 122, 211901.

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- V. **Drozdowska, K.**, Rehman, A., Smulko, J., Krajewska, A., Stonio, B., Sai, P., Przewłoka, A., Filipiak, M., Pavlov, K., Cywinski, G., Lyubchenko, D. V., & Rumyantsev, S. (2023). Optimum Choice of Randomly Oriented Carbon Nanotube Networks for UV-Assisted Gas Sensing Applications. *ACS Sensors*, 8, 3547-3554.

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- VI. **Drozdowska, K.**, Rehman, A., Rumyantsev, S., Wurch, M., Bartels, L., Balandin, A., Smulko, J., & Cywiński, G. (2023). Study of ZrS₃-based field-effect transistors toward the understanding of the mechanisms of light-enhanced gas sensing by transition metal trichalcogenides. *Materials Today Communications*, 34, 105379.

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