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Senzory plynů na bázi nanostruktur

Nanostructure based gas sensors

Diploma Thesis

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Poděkovaní

Tímto bych chtěl poděkovat mým rodičům, za celoživotní materiální i psychickou podporu v půběhu mého studia. Dále bych chtěl poděkovat panu Docentu Janu Vovsovi za vedení mojí práce a projevení důvěry, když mně umožnil pracovat v laboratoři nanolitografie na katedře mikroelektroniky. Díky patří také panu Ing. Alexandru Laposovi, který byl mým učitelem při řešení praktické části mojí diplomové práce v laboratoři a průvodcem problematio. Také bych chtěl poděkovat Jiřímu Šmarhákovi za zhotovení AFM scanů a Josefu Náhlíkovi, že jsem mohl použít jím napsané měřicí programy. V neposlední řadě bych chtěl poděkovat Martině Rohlíčkové za její neutuchající lásku a podporu a kolektivu kamarádů ze skupiny PID, za neustálou motivaci při přípravě této práce.

Anotace

Tato diplomová práce se zabývá přípravou sensorů plynů na bázi odporových vrstev s důrazem na použití technologie tzv. Inkjet tisku.

V teoretické části je popsán současný stav a trendy v oblasti detekce plynů, dále některé principy detekce pomocí změn elektrických parametrů, používané materiály, s důrazem na organické polovodiče, a způsoby depozice nanostruktur a tenkých vrstev obecně.

Součástí praktické části této práce je popis přípravy a následné charakterizace elektrických parametrů a měření odezvy připravených sensorů na přítomnost měřených plynů.

Klíčová slova

Sensory plynu, organické polovodiče, inkjet, tenké vrstvy

Abstract

This diploma thesis deals with preparation of chemoresistive type of gas sensors, with an emphasis on use of inkjet technology.

In theoretical part of this thesis, present situation and trend in gas sensing industry is review. Then principles of detection based on change of electrical parameters, together with typical materials and the possibilities of their deposition are described.

Practical part of this thesis is dedicated to description of preparation and characterization of those sensors with measurements of their response to target analytes.

Keywords

Gas sensors, organic semiconductors, inkjet, thin layers

Content

Introduction 1

1. Gas sensors: Present situation 2
   - 1.1. Present situation and prospects of gas sensing industry 2
   - 1.2. Overview on gas detection methods 3
     - 1.2.1. Chemoresistive 6
     - 1.2.2. Capacitive gas sensing 6
     - 1.2.3. Potentiometric and Amperometric 7
     - 1.2.4. Work function based gas sensors 8
   - 1.3. Materials used in Solid state gas sensors 11
     - 1.3.1. Organic sensitive materials 11
     - 1.3.2. Inorganic sensitive materials 13
     - 1.3.3. Composite materials 13
   - 1.4. Methods for thin films and nanostructures preparations 14
     - 1.4.1. Chemical vapour deposition 15
     - 1.4.2. Atomic layer deposition 16
     - 1.4.3. Thermal evaporation 17
     - 1.4.4. Sputter deposition 18
     - 1.4.5. Electrospinning 20
     - 1.4.6. Spin coating 21
     - 1.4.7. Inkjet printing 22
     - 1.4.8. Dip coating 24
     - 1.4.9. Doctor Blade 26
     - 1.4.10. Drop casting 27
   - 1.5. Sensor parameters 28
2. Methodology of gas sensors preparation and characterization 29
   - 2.1. Gas sensor preparation 29
     - 2.1.1. Inkjet printing process 29
     - 2.1.2. Spin coating process 32
     - 2.1.3. Sintering and annealing process in thermal oven 32
   - 2.2. Gas sensor characterization 33
     - 2.2.1. Devices for electrical characterization 33
     - 2.2.2. Response measurement aparature 33
3. Sensor preparations and characterization results 35

3.1. Sensitive layers 35
3.2. Gas sensors on prefabricated platform 37
3.2.1. Preparation process 37
3.2.2. Results of electrical and sensitivity characterisation 37
3.3. Gas sensors on PET foil 43
3.3.1. Preparation process 43
3.3.2. Results of electrical and sensitivity characterisation 45
4. Conclusions 52
References 53
Appendix A 56
Inkjet printing process 56
Golden IDE array on FR4 substrate .... **Chyba! Záložka není definována.**
Silver nanoparticle IDE array on PET foil 59

Abbreviations and symbols

AFM	atomic force microscopy
ALD	atomic layer deposition
ALE	atomic layer epitaxy
CNT	carbon nanotube
cp	centipoise
CT	Curing temperature
CVD	chemical vapour deposition
DDM	Dimatix drop manager
DoD	Drop on demand
HVAC	Heating, Ventilation, Air Conditioning
IC	Integrated circuit
LOD	limit of detection
MWCNT	multiwalled carbon nanotube
OFET	organic field effect transistor
OLED	organic led diodes
PAni	Polyaniline
PE-CVD	Plasma enhanced chemical vapor deposition
PET	poly (ethylene terephthalate)
PIJ	Piezoelectric inkjet printing
ppb	parts per billion
PPhV	phenylene vinylene
ppm	parts per million
PVD	physical vapour deposition
Rpm	rotation per minute
SWCNT	single walled carbon nanotube
TIJ	Thermal inkjet printing
UC	ultrasonic cleaner

Introduction

During last decades, there has been growing interest in a gas sensing technology from many areas including industrial, environmental, domestic, military etc. The ability to detect or monitor different gases became critical during some manufacture processes and in environmental issues, to avoid harmful effects causes by toxic gases. This demand accelerated research in gas sensor industry and different gas sensing techniques were proposed. There are two important groups of applications of these sensors. One group represents sensors with an ability to detect single gases like NO_X, O_3, NH_3, CO, H_2, etc. while the sensors from the other group can discriminate odours or changes in ambient in general[1][2]. The content of this thesis could be separated as follows:

In the first chapter, there is briefly discussed present situation in the gas sensing industry and given brief overview on the methods of detection, with emphasis on methods based on electrical variations. Then there is an overview about the materials, used as a sensitive layer in solid state gas sensors, and the methods of their deposition. Some of those techniques are introduced in this chapter. Last paragraph lists sensors parameters and their short definitions.

In the second chapter is description of used equipment during preparation process and the equipment used for characterisation of manufactured sensors.

Third chapter, contains results of the preparation and measured characteristics. The chapter is divided into two sections. First is dedicated to the prefabricated platforms with golden IDE arrays on FR4 substrate. The other one describes inkjet-printed silver IDE arrays on PET foil as a substrate.

The results of the measurements and preparations, including proposals for future development and activity are discussed in the chapter four.

1. Gas sensors: Present situation

1.1. Present situation and prospects of gas sensing industry

As mentioned above, gas sensors with ability to detect single gases or complex odours has been developed since there has been wide demand for both groups in various areas in our life. From single gas detecting systems in safety applications as a fire detectors to complex array sensors, so called e-noses, distinguishing quality of food. In the Table 1 there is a basic overview about the applications of gas sensors in different areas.

Table 1. *Fields of applications for gas sensors*

Sector	**Application**
Automotive	λ sensor Car ventilation control Gas leaking detection Exhaust gases analyser Combustion efficiency control Alcohol testers
Safety	Fire detection Leak detection
Environmental	Pollution monitoring
Food industry	Fermentation control Food quality control Packaging quality control
Healthcare	Breath analysis Respiratory control
Military	Toxic gases sensing
Industrial	Processing control
Aeronautical & Space	Launch vehicle safety application Fire detection Emission monitoring

Mainly due to possible miniaturization, allowed by MEMS industry, gas sensors market, according to recent analysis[3], has a potential to massively grow in next several years. This is caused by potential applications in consumer electronics such as smartphones and wearables, request for better quality air control from HVAC market as well as other fields of application mentioned in Table 1 like military or medical. Yole development's analysis says the market will grow from US$12 million in 2015 to more than US$95 million in 2021 [3]. Those facts together with increasing number of enforceable patents dedicated to miniaturized gas sensors, suggest the start of the market. In the Figure 1, we can see the optimistic scenario for volume production of gas sensors and its possible rapid increase over next few years.

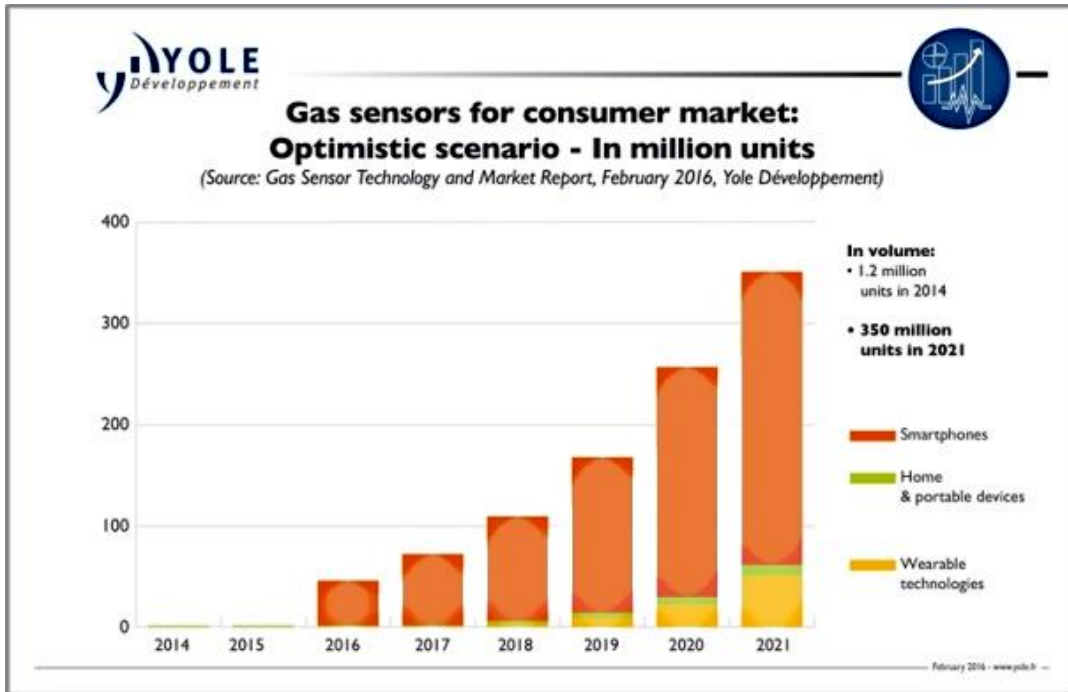

Figure 1. *Optimistic scenario for consumer gas sensor market growing volume production [3].*

1.2. Overview on gas detection methods

This chapter is dedicated to introduction of different techniques used for detecting various gases. The intention of this paper is not to give exhaustive review about all the existing gas sensing techniques, but to give a brief overview about the most important approaches used for detecting gases with attention to solid state semiconductor gas sensors based on electrical variations, which will be reviewed later in this chapter. Concretely, the sensors prepared in this thesis are chemoresistive type. There have been several physical principles applied in the gas sensing industry. The most common methods used for gas sensing is to detect the presence of the gas through electrical variation. Brief list of the most important techniques is given in the Table 2.

Table 2. *– brief distribution of the gas sensing methods according to the physical principle*

Gas sensors - physical principles			
Optical	**Thermal**	**Electrochemical**	**Gravimetric**
• Infrared • Colorimetric • Absorption • Gas chromatic • Photoionization • Surface Plasmon resonance	• Calorimetric • Catalytic • Thermoelectric • Thermal conductivity	• Chemoresistive • Functional (diodes, transistors) • Capacitive • Amperometric & Potentiometric	• Surface acoustic wave • Quartz crystal microbalance • Micromechanical resonator • Capacitive ultrasonic transducer • Film Bulk Acoustic Resonator

Gas response mechanism

It would be not correct to generalise response mechanism for all available and discovered gas sensitive materials. The interactions between the analytes and sensing materials are multiform, according to different analytes and different sensitive materials [4]. Though there can be some generally understood mechanism similar to most of the gas sensors. Most of metal oxides as well as conjugated polymers are formed of nanosized grains, that adhere partially to each other. This porous structure allows gas molecules, adsorbed on the surface, to penetrate into the bulk of the material, thus partly changing its physical parameters. This mechanism is shown on non-stochiometric SnO_2 which behaves like *n-type* semiconductor, due to oxygen vacancies in the crystal structure. When this material is exposed to the air, the oxygen in the ambient air adsorbs on the surface of the crystal grains. Each oxygen molecule then traps one electron. Electron trapping by oxygen depletes the surface of charge carriers, the depletion degree being maximal at the neck between two particles [5]. The mechanism described above creates potential barrier, which results in restrained electron transfer. The electrical resistance of such a sensor is given by potential barrier and can be expressed by equation 1.

$$R_{Air} = R_0 \frac{eV_{Air}}{k_B T} \qquad (1)$$

R_{air} represents resistivity of the sensor in ambient air, R_0 is a constant, e is elemental charge, V_{air} is a height of barrier in ambient air, k_b is a Boltzmann constant and T is absolute temperature. If reduced gas is presented in the air, it reacts with adsorbed oxygen on the surface of the substrate. Example of such chemical reaction is given in the Equation 2. This reaction cause that free electrons are released into the conduction band and inter grain potential barrier is decreased as can be seen in the Figure 2.

$$2CO + O_2^- \rightarrow CO_2 + e^- \qquad (2)$$

The resistivity upon this type of reducing reaction change with respect to the Equation 3.

$$R_{Gas} = R_0 \frac{eV_{Gas}}{k_B T} \qquad (3)$$

Where R_{gas} represents resistivity of the sensor in presence of gas and V_{gas} represents potential barrier height in gas environment, other variables are the same as in the Equation 1. Schematic diagram of reducing mechanism, with an influence on the energetic band formed in between two particles, is illustrated in the Figure 2.

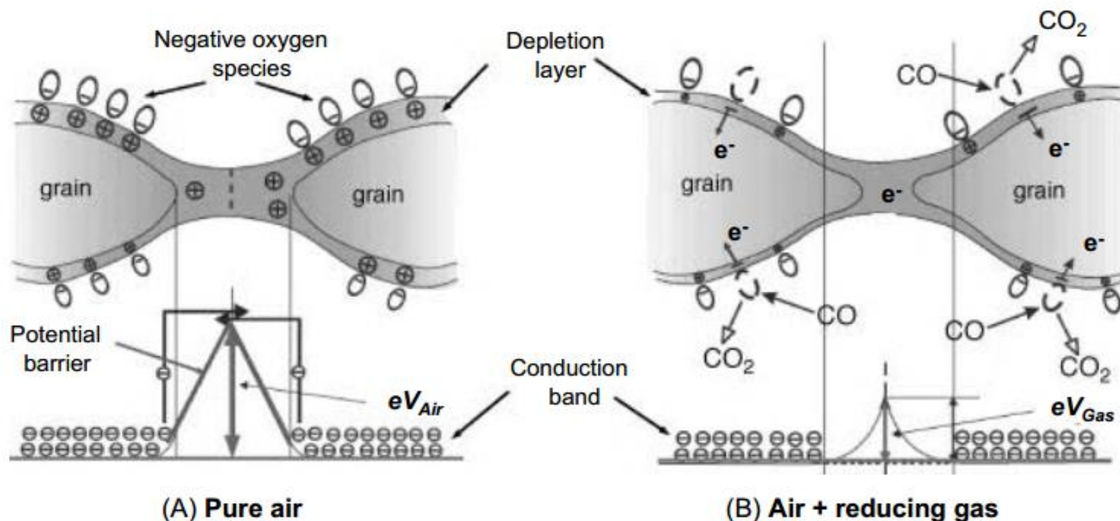

Figure 2. *Schematic diagram of porous semiconductive metal oxide.* ***A)*** *shows formation of charged oxygen layer by chemisorption and* ***B)*** *shows the effect of the reducing gas (CO)*[5].

Another example of mechanism which influence the resistance of sensitive layer, will be illustrated on Polyaniline. Polyaniline belongs to the family of conjugated polymers, although in this group of materials, it is exception because of the absence of strictly alternation single and double bonds. PAni is also special conducting polymer since its doped state can be controlled by acid/base reactions. This fact is widely used to detect acidic and basic gases. When it is exposed to ammonia gas, as it was in this thesis, PAni undergo dedoping by deprotonation [4]. The schematic illustration of this chemical reaction can be seen in the Figure 3.

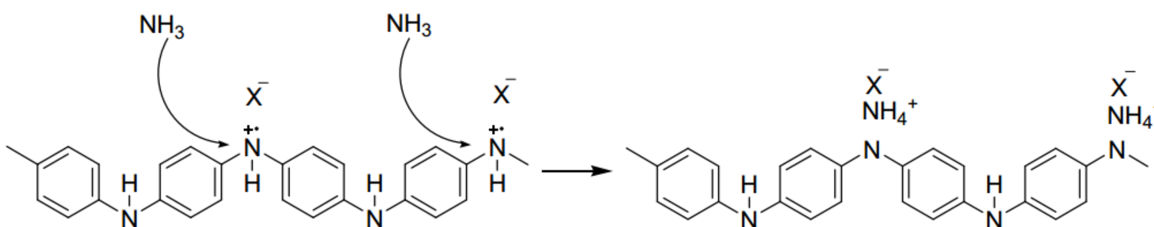

Figure 3. *Schematic diagram of chemical reaction of PAni with NH3 gas [4].*

The protons on –NH– groups were transferred to NH3 molecules to form ammonium ions while PAni itself turned into its base form. This process is reversible, and in fact, when ammonia atmosphere is removed, the ammonium ion can be decomposed to ammonia gas and proton. After reaction with acidic gases, such as HCl or H_2S PAni will be doped [4].

Methods based on electrical parameters variation

As written before, methods based on variation of electrical properties represents one of the most important and in praxis used approach for detecting gases, because of the ability to transform the concentration of desired analyte directly to electrical signal. Most important methods based on change of electrical properties are briefly introduced bellow.

1.2.1.Chemoresistive

Chemoresistors are most popular device configuration of gas sensors and many commercialised devices are based on this setup. This method is based on change of the resistance of sensing layer upon the exposure to selected analyte, which is about to be detected. In ideal case this reaction between the gas and the sensitive layer is fully reversible. In general, we can divide the detecting mechanism per the type of semiconductor, whether is n-type or p-type and according to the kind of gas, whether is oxidizing or reducing type of gas. In case of n-type semiconductor exposed to reducing gas, increase in conductivity can be observed, vice versa with the oxidizing gas, where there is decrease in conductivity. The p-type semiconductor exhibits opposite behaviour to the n-type in contact with the target gases. These phenomena result in change of current driven through the device, therefore reflecting the change of concentration of target gas. For this method, usually arrays composed of interdigitated electrodes (IDE) are used. Schematic representation of typical IDE array of chemoresistive type gas sensor can be seen in the Figure 4. In this Figure, there is a cross section of that type of sensor, the picture is not up to scale and it just illustrates the composition of the device.

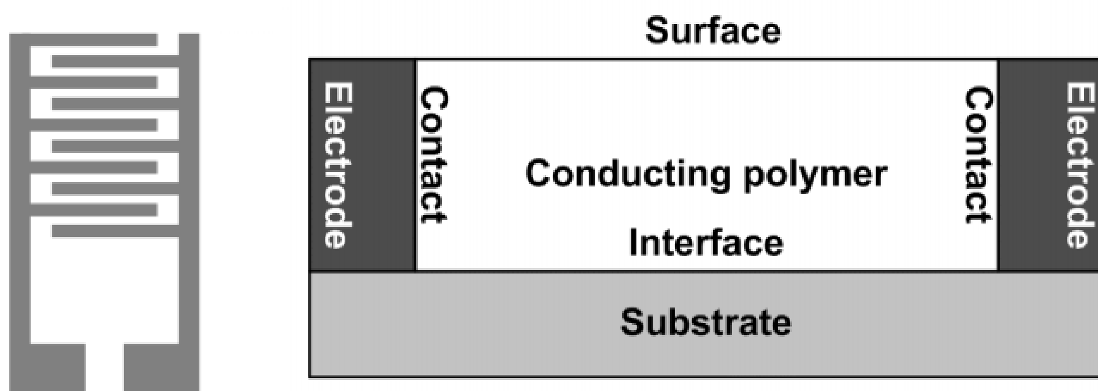

***Figure 4**. (left) Configuration of Chemiresistor with inter digitated electrodes (right) Cross section of Chemiresistor with conductive polymer as a sensitive layer [4].*

1.2.2.Capacitive gas sensing

This method is based on change of the sensors capacitance. This happens through the change in dielectric constant of the porous film in sensor, upon the interaction with the target gas. In general, two approaches can be used, but they both are based upon the change of capacitance of the device. One approach is measuring C-V curve shift, through sweeping DC bias voltage across the capacitor while measuring capacitance using a high frequency AC signal [6]. While the other approach is based on fact that whole device consists of differential layout, where one capacitor is covered with functionalized gas sensitive dielectric, while the other one remains uncovered [7]. In the Figure 5, we can see device with such a setup combined with Pt thermometer.

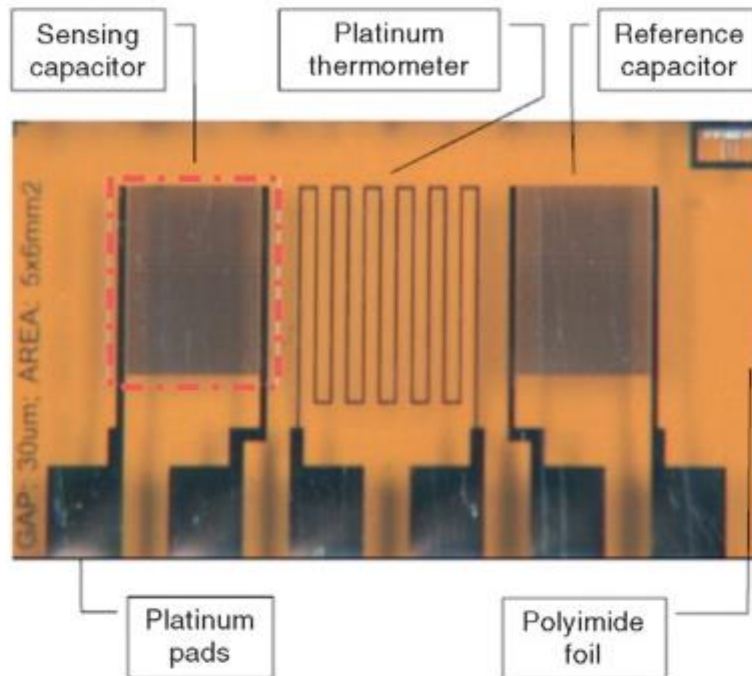

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Figure 5. *Inter digitated gas sensor based on differential setup together with a platinum resistance thermometer printed on polyimide foil [7]*

1.2.3. Potentiometric and Amperometric

These types of sensor allow gases to diffuse through the porous membrane to the electrode, where it is either reduced or oxidized depending on the character of target gas [8]. Electrical signal is generated by reaction of the target gas at the interface between an electronic /ionic conductor resulting in charge exchange. If the output is electromotive force (open circuit voltage), we talk about potentiometric type of gas sensors, whereas if the output is electrical current those sensors are called amperometric. One of the main composition of those kind of sensors consists of electrolyte, usually in solid or sometimes as well in liquid phase, separating the test and reference compartment and two porous metal electrodes. The basic setup of most typical potentiometric gas sensor, where the gas is converted into mobile ions in solid electrolyte is presented in the Figure 6. The potential difference is established between the two sides of the solid electrolyte and is dependent on the difference in activity across the solid electrolyte of the species that will equilibrate with the conduction ions in the solid electrolyte [9]. One example of this kind of potentiometric gas sensors based on YSZ (yttria-stabilized zirconia) represents the most used system for emission control at this time [1].

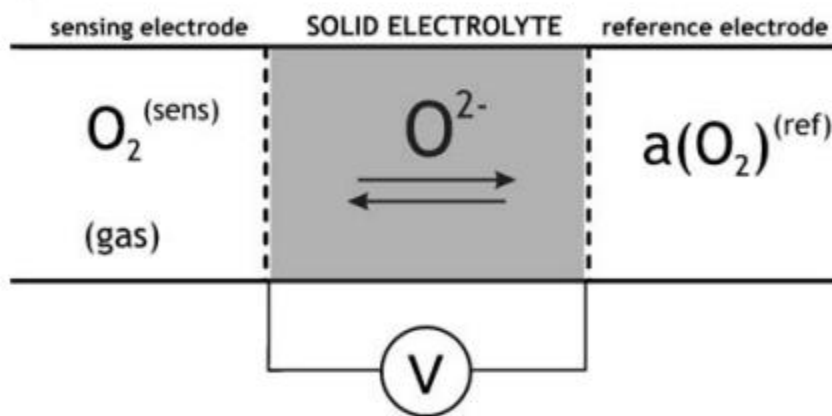


Figure 6. *Schematic diagram of the most conventional potentiometric type gas sensor [9].*

There are many different approaches of electrochemical gas sensors based on potentiometric or amperometric electrical variations and it is over the extend of this thesis to fully describe all of them.

1.2.4. Work function based gas sensors

The work function based gas sensors are generally composed on the metal/oxide/semiconductor (MOS) layers [10]. This group of gas sensors is usually divided into three major types according to the function. Schottky diode type and the Field Effect Transistor (FET). In comparison with Chemiresistor type of gas sensors, transistors and diodes types provide more parameters measurement, so they may give more detailed information about the conducting sensing film [4]

Schottky diode type

Schottky diode type gas sensors are typical sensors manufactured on the basis of standard semiconductors [11], although with the development in the field of organic semiconductors application of this type of sensor with a use of OSC have been investigated. Schematic diagram of this kind of Schottky diode type of gas sensor is illustrated in the Figure 7. Those sensors can operate both with forward and in reverse voltage. For standard semiconductors those kind of sensors are able to detect only H_2, while for porous semiconductor materials the possibility to detect NO, NO_2, humidity, vapours of acetone, propanol, methanol, CO and even CO_2 were observed [11]. The Schottky diode type of gas sensor is based on a device with an arrangement, in which the Schottky barrier is formed on the interface of inorganic/organic semiconductor and the metal/degenerated semiconductor.

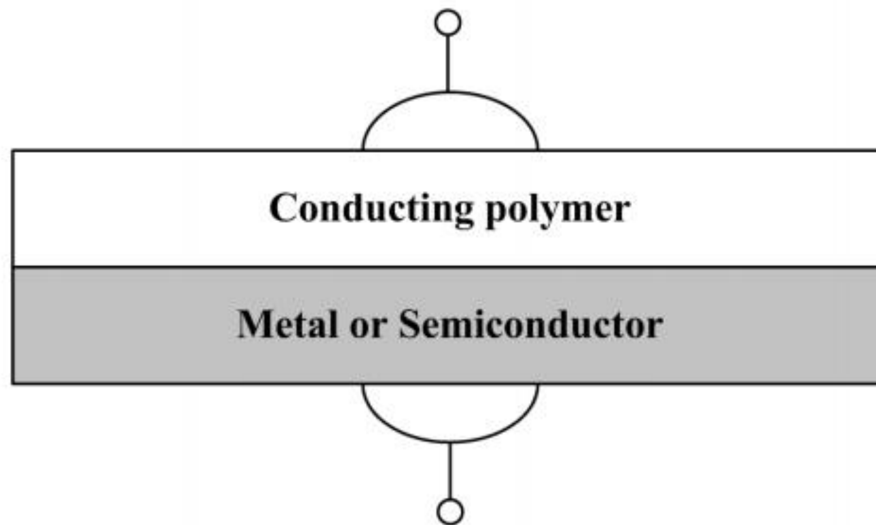


Figure 7. *Configuration of OSC type of Schottky diode type of gas senso*r [4].

Field effect transistor type

The configuration of those kind of sensors, are based on FET transistor setup. One of the advantages, as said before, is that more parameters are obtained using this device resulting in more detailed information to process. In case of FET transistors, this fact is caused by the possibility to amplify the signal, as well as the possibility to apply reverse voltage to the gate diode. There has been demonstrated that, field-effect transistors perform better than a conventional chemoresistors in terms of drift, sensitivity, signal-to-noise ratio, limit of detection, response time and life time [12].There are many different configurations of those sensors, regarding device configuration and different materials used in those devices. The most straightforward and basic division of those type of sensors can be made according to the type of material used as a semiconductive channel which is also an active sensing layer of the device. Whether the semiconductor is inorganic or organic, we call these type of devices MOSFET or OFET type of gas semsors respectively. There are many variations regarding the electrode and sensitive layer configuration, but also in the sense of the whole composition and combinations of materials used in those type devices. Common setup, consist of the transistor with the semiconductive channel acting also as a sensitive layer on top of the device. Since this is vast field under extensive research development and it is not the main topic of this diploma thesis, there is just brief description devoted to this topic. For illustration, examples of device setup of different types of OFET based devices are listed in the Figure 8. In this figure, are illustrated some modifications regarding device compositions

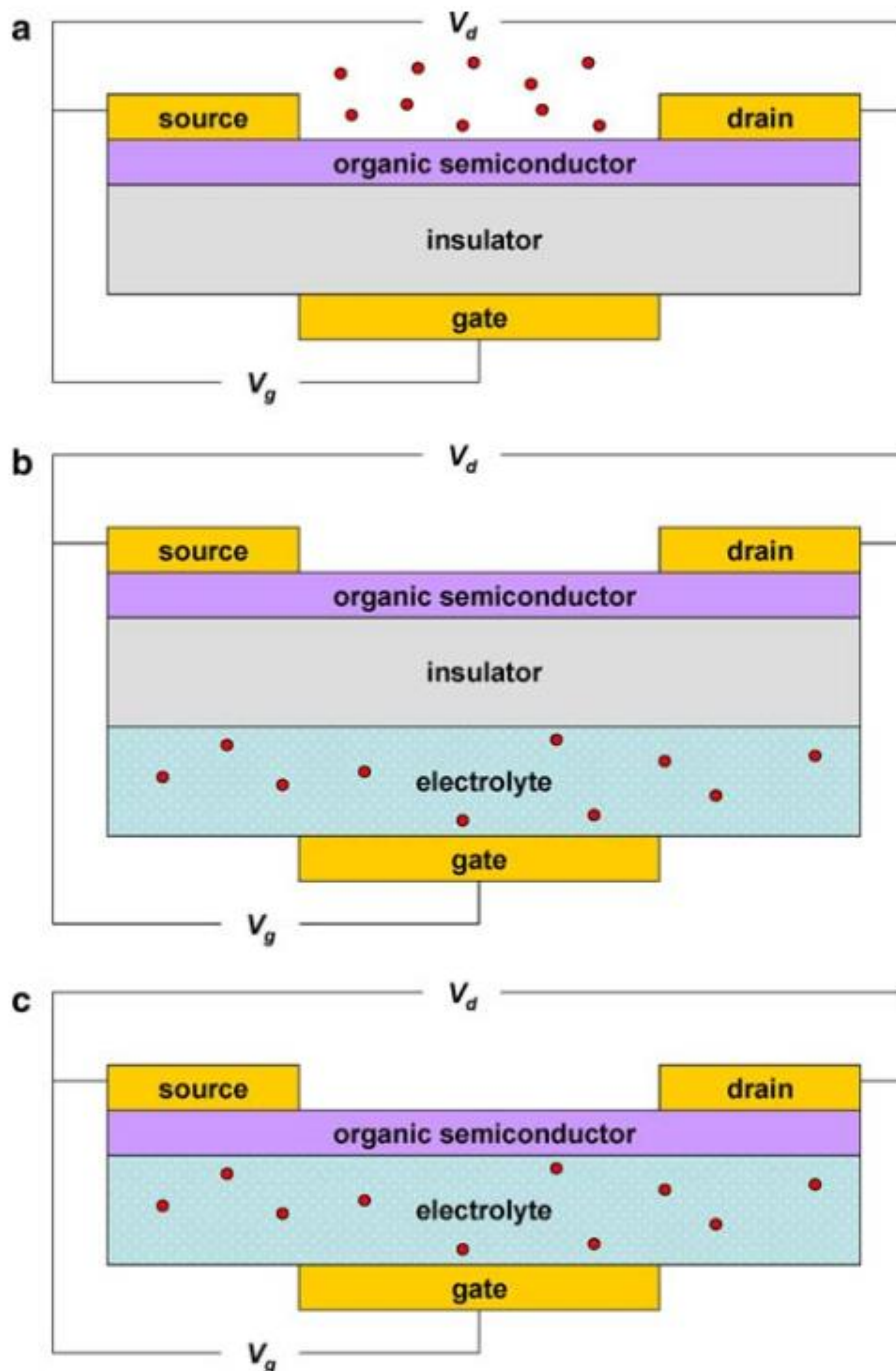


Figure 8. a *Schematic cross section of an organic field-effect transistor(OFET).* ***b*** *Schematic cross section of an ion-sensitive organic field effect transistor (ISOFET).* ***c*** *Schematic cross section of an organic electrochemical transistor (OECT). In each schematic, the analyte of interest is represented by solid red circles. The applied source-drain voltage V_d and gate voltage V_g are also shown [12].*

1.3. Materials used in Solid state gas sensors

Solid state gas sensor family is indeed one of the most important and promising. Its importance is rapidly growing with the development in microelectronics particularly in nanoelectronics that opened possibilities for using great amount of materials or nanostructures as a sensing material in those sensors. Those materials usually have behaving as a semiconductor. Another major influence for semiconductor solid state gas sensors represents micro machining, so called MEMS industry, which allowed miniaturization, that results in reducing power consumption, manufacture cost, improving response time, selectivity and sensitivity as well as possibility to implement the sensor with existing CMOS based silicon technology, therefore leading to another miniaturization caused by integration sensor itself with the electronics such as signal converter, signal amplifier, multiplexer, communication devices etc.. Mentioned above, allows possibility for batch production, thus resulting in reduction of the price of the sensor. The main characteristic of the solid-state gas sensors is reversible interaction of the gas with the surface of the sensitive layer of the sensor. This reaction can lead to change in conductivity, capacitance, work function, mass, optical characteristics etc. There have been many materials discovered and used for this purpose. Those materials can be divided to organic, inorganic and composite, that represents combination of different materials. Composite materials had recently gained a lot of attention from scientific field, because of their possibility to combine the advantageous properties of different materials. Brief description of above mentioned groups will be given bellow.

1.3.1. Organic sensitive materials

Those materials can be divided into conducting polymers, molecular semiconductors and carbon based nanostructures.

Organic semiconductors

The possibility, that organic materials could potentially carry electrical current, was indicated already in late of 19th century, when English chemist Henry Letheby obtained a partly conductive material by anodic oxidation of aniline in sulfuric acid. The material was probably polyaniline [13]. Although, real breakthrough came in 1977, when Prof. Alan J. Heeger, Prof. Alan G. MacDiarmid and Prof. Hideki Shirakawa discovered conducting polymers, for which they were awarded by Nobel prize in Chemistry in 2000 [13]. Their discovery changed the scientific point of view on such a common material as polymers, that were until then considered as an insulator. They managed to increase conductivity of polyacetylene by 10^9 orders by oxidizing with chlorine, bromine and iodine. As a parallel to doping process in classical semiconductors they called this polyacetylene as “doped” form [13]. The range of conductivity of conjugated polymers can be seen in the Figure 9.

This discovery lead to intensive research and new possibilities and prospects emerged based on this discovery. In recent years with the results from scientific research, whole novel group of so called organic electronics developed, based on the organic semiconductors discovery. As a typical example of success, in bringing this new technology to the market, represents OLED technology. Which characterize so far, the most novel display technology and is just in the beginning of its commercial application.

One of the advantages of organic semiconductors, over the inorganic ones, is the low-requirements for processing conditions, since the organic semiconducting materials does not require high purity crystalline substrates, high temperate and clean rooms to be deposited. Instead organic semiconductors are usually solution processable or can be deposited by thermal evaporation at room temperature, which enables usage of low cost and sometimes even flexible substrates like plastic, metal foil, paper or glass [14]. This makes use of organic semiconductors ideal low cost material, since the material itself,

manufacture process and substrates are relatively cheap compared to silicon inorganic counterparts. Another advantage is possibility to make transparent and flexible devices.

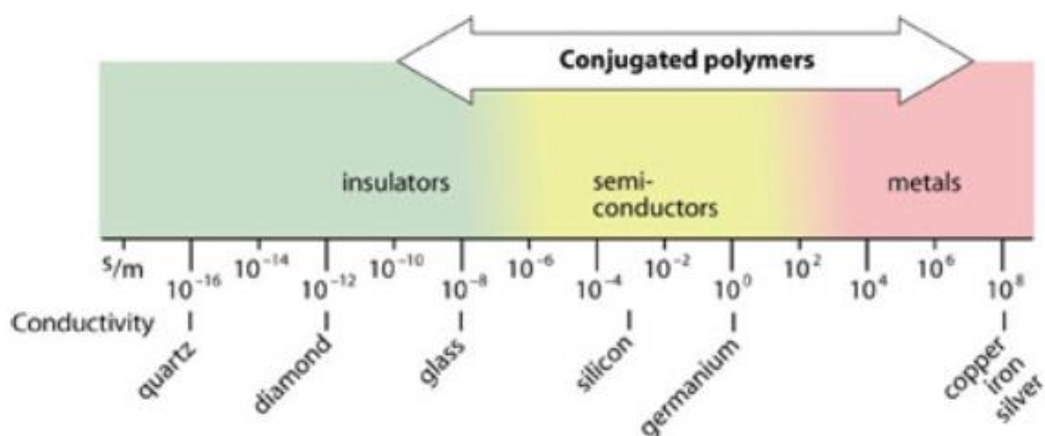
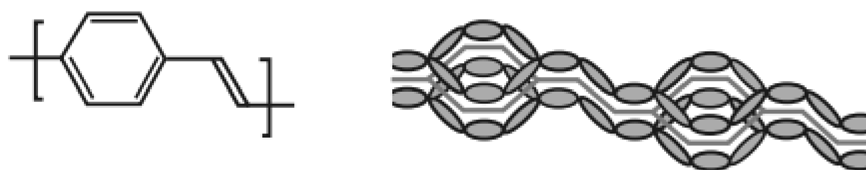


Figure 9. *The conductivity od Conjugated polymers compared to the other materials from quartz (insulator) to copper (conductor) [13].*

Those materials are also called conjugated polymers, because of the presence of conjugated double bonds in the polymer chain. Conjugated double bonds, are double bonds strictly alternating with single bonds that act collectively, knowing the next nearest bond is also a double bond [15]. Every bond contains a localised “sigma” (σ) bond which forms a strong chemical bond. In addition, every double bond also contains a less strongly localised “pi” (π) bond which is weaker [13]. In the Figure 10 can be seen the structure of PPhV conducting polymer and schematic representation of π clouds and σ sigma bonds. The only exception which belong in this group, despite the absence of strictly alternating double bonds, represents polyaniline, where are nitrogen atoms with an extra electron pair between the benzene rings and the conjugation passes through this extra pair. Because of those alternating single and double bonds, there is a gap in electronic density of states. All states bellow this gap are occupied and form the valence band, the states above the gap are empty and form the conduction band [15]. In case of organic semiconductors those bands are called HOMO (highest occupied molecular orbit) which is parallel to top of valence band in classical semiconductors and LUMO (lowest unoccupied molecular orbit) which is parallel to bottom of the conduction band



The Figure 10. *On the left is structure unit of PPhV. On the right are clouds of π electrons (in grey shapes) above and under C-C backbone of the unit and σ bonds connecting carbon atoms (grey lines) [16].*

Between organic semiconductors belongs conducting polymers and molecular semiconductors such as porphyrins and pthalocyanines

Many of those materials possess interesting and promising abilities to interact with different compounds of air, therefore makes them suitable material for use in gas sensors. These phenomena can be partly explained through interaction of the gas molecules with the "pi" (π) bond of the organic semiconductors which results in alternating its electrical behaviour like mobility, etc.

The main advantage of organic semiconductors, used as a sensing layer in gas sensors, is their ability to detect gas in ambient environment temperature, without necessity of using heater to promote detection mechanism, thus resulting in reduced power consumption of such a device.

Carbon based materials

Another group of organic materials, where the gas sensing possibility have been discovered and intensive research is going on there, is based on organic carbon nanostructures. Between those structures belongs: Graphene, Diamond structures, carbon nanotubes (CNT), whose can be divided in to multiwall (MWCNT) and single wall carbon nanotubes (SWCNT), then very promising are carbon nanohornes, carbon nanorodes and other nanostructures based on modification of existing carbon structures.

1.3.2. Inorganic sensitive materials

Metal oxides - MOx

The structures from this class of materials were historically first, that were used in solid state gas sensing applications. These materials are deposited in form of thin or thick film as desired sensitive layer by different deposition techniques. Between those metal oxide materials used in solid state gas sensing belongs SnO_2; TiO_2; In_2O_3; WO_3; NiO; ZnO [1].

With the development in many interdisciplinary fields, novel forms of those traditional materials appeared in form of nanostructures like nanowires, nanoribbons and others [17]. Several theoretical and applied articles have shown the advantage of reducing the metal oxide grain size down to nanometre scale in order to improve the sensing properties (mainly sensitivity and selectivity) as well as stability over time of the oxide layer [1].

Disadvantage of the gas sensors based on metal oxides is necessity of higher operating temperature. It varies depending on specific target gas in ambient and on the selected sensor material. As this working temperature ranges usually from 200 to 400 °C, it is necessary to implement a heating element in sensor device [1].

1.3.3. Composite materials

The materials, attracting very high attention from scientific community as a new possible sensing layers, are composed by combination of the materials from the groups mentioned above. Those, so-called, hybrid materials are indeed most interesting, since they can combine desired properties of selected materials. As there are so many possibilities for combining different materials together, extensive research is taking place there. To name all the possible combination is above the context of this paper

and since the new combinations are continuously being discovered, it's also almost impossible to list all of them. In general, there can be combination of two metal oxide materials, metal oxide with organic semiconductor, carbon based structures with metal oxides or organic semiconductors. Review about Graphene hybrid material has been conducted by Latif et al. [18].

Conducting polymer composites

These materials contain an electrically insulating polymer, matrix loaded with a conductive filler. The often-used filler materials are metals (Cu, Pd, Au, Pt), carbon black and semiconducting metal-oxides (V_2O_3, TiO, etc.). The most important polymers that can be used as matrices are: polyethylene, polyimides, polyesters, poly(vinyl acetate) (PVAc), PTFE, polyurethane, poly(vinyl alcohol) (PVA), epoxies, acrylics, e.g. polymethyl methacrylate (PMMA), etc. [19]

1.4. Methods for thin films and nanostructures preparations

Because thin films or different 3D structures, ranging from micro to nanometre size like nanotubes, nanowires and others, are nowadays essential part of the solid-state gas sensors, methods for their preparation with different morphology and properties are important part during manufacturing such a sensor. With respect to the fact written above, short list and description of some of those techniques will be given later in this paragraph. To classify the difference between thin and thick film someone defines thin film as a film with thickness ranging from few nanometres to one micrometre, but in general there is no strict rule[20]. In this thesis, we talk about thin films, when at least one of its dimensions is very small compared to the others, so the surface to volume ration increases and at least some of the properties are no longer volume independent. Also the microstructure of thin film like texture or grain size can be different from the bulk material even if it's the same material. [20]

With the development of silicon industry of the integrated circuits, during last decades, many different techniques for depositing materials to desired substrates were developed or mastered for their use. Those techniques can be divided into different categories such as Physical vapour deposition (PVD), there belongs evaporation techniques or sputtering techniques. Another major family includes Chemical vapour deposition (CVD) with many different approaches and modifications. Major group of techniques for preparing thin films or transporting nanostructures represent coating techniques like spin coating, dip coating and drop casting. Another group with vast number of modification are printing techniques like screen printing, offset printing, inkjet printing, thermal laser printing etc. Other deposition process mentioned in this thesis is quite novel method called atomic layer epitaxy. To list and describe all techniques used in depositing thin films is over the scope of this thesis, so just the techniques, considered as a major or promising used in depositing thin films or nanostructures in solid state gas sensors will be reviewed. The choice of the deposition techniques can depend on many factors. In research field, availability can be one of them as it was in case of this paper. Other factors can be process ability of desired material by given technique, solubility of desired material, the particle size, required final form or attributes of final product as well as dependence on the properties of substrate which is about to be coated and many other factors. In next paragraphs, some of those deposition techniques will be briefly described.

1.4.1.Chemical vapour deposition

History of CVD

One of the earliest examples of the CVD of metals is the deposition of tungsten, reported as early as 1855 [21]. The first reports about the deposition of silicon by CVD by the hydrogen reduction of SiCl4 appear as early as 1909 and 1927 and the widespread use of thin silicon films in the electronics industry is anticipated by the CVD of Si-based photo cells and rectifiers just after World War II [21].

CVD mechanism

CVD is a basic tool for material processing. It's very versatile and common chemical process, mainly used for applying well defined and high quality thin film coatings to the substrates, but as well for production of high-purity bulk materials and powders. CVD can be used for depositing wide range of materials, since majority of elements in periodic table has been deposited by this method, in elemental or more often in compound form [22]. This method requires fine tuning and accurate conditions with extremely clean conditions during the process acquired by high vacuum or carrying gas (N_2 or H_2), but it is fundamentally simple set of steps. In the broadest sense chemical vapour deposition (CVD) involves the formation of a thin solid film on a substrate material by a chemical reaction of vapour-phase precursors [21].The object, which is about to be coated, is placed in the chamber, whose size defines the maximum dimensions of the final product. In case of thermal CVD, vapor precursor is transported by carrying gas and introduced into the chamber, where the chemical reaction occurs on and near the hot surfaces, resulting in the deposition of a thin film on the surface. During above described reaction many by-pass products emerge and they are exhausted out of the chamber along with unreacted precursor gases [22]. The chemical reactions of precursor species occur both in the gas phase and on the substrate. That's why the activation energy of reacting compounds should be high, so the precursors react minimally outside of the substrate. Schematic diagram of thermal CVD can be seen in the Figure 11.

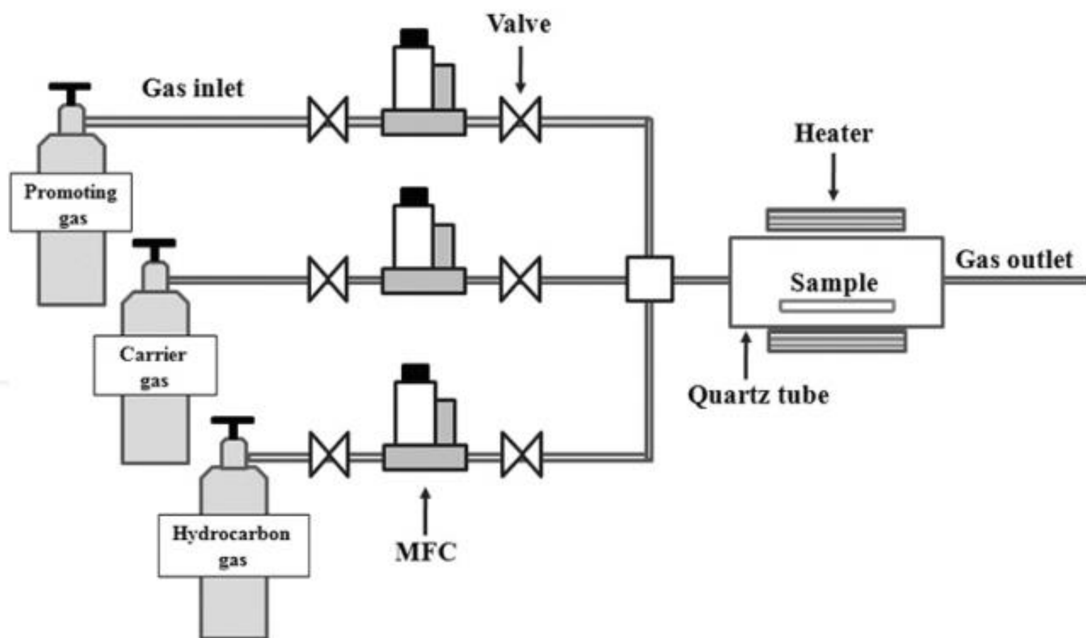


Figure 11. *Schematic diagram of tube furnace thermal CVD* [23].

CVD modifications

Reactions can be promoted or initiated by heat (thermal CVD), higher frequency radiation such as UV (photo-assisted CVD) or a plasma (plasma-enhanced CVD) [21]. The use of thermal CVD can, however, be disadvantageous. For example, heat input can result in damage to temperature-sensitive substrates

and so alternative forms of energy input have been developed which allow deposition at lower temperatures. One way of reducing growth temperatures is to use plasma-assisted or plasma-enhanced CVD(PECVD). Using this technique deposition can occur at very low temperatures, even close to ambient, since electrical energy rather than thermal energy is used to initiate homogeneous reactions for the production of chemically active ions and radicals that can participate in heterogeneous reactions[21]. Photo-assisted CVD has similar potential advantages to those of PECVD; namely, low temperature deposition, modifications of properties of grown layers, e.g. dopant incorporation, and independent control of substrate temperature and dissociation of precursor. There are other variations or modifications of CVD like a Metal-organic chemical vapour deposition (MOCVD) which is a specific type of CVD that utilizes metal-organic precursors. Metal-organic vapour phase epitaxy (MOVPE) or organometallic vapour phase epitaxy (OMVPE) is an MOCVD process that produces single crystal (i.e. epitaxial) films on single crystal substrates from metal-organic precursors. In MOCVD and MOVPE gas-phase reactions can sometimes play a significant role in the deposition chemistry [21]. Other modifications of CVD are according to the shape of chamber and furnace in the CVD method and other system parameters

1.4.2.Atomic layer deposition

History

Atomic layer epitaxy (ALE), now more generally often called atomic layer deposition (ALD) is a surface-controlled process for manufacture of thin films, formation of atomically controlled surfaces and for epitaxial growth of single crystals [24]. It is special modification of chemical vapour deposition method [25], and it was primarily developed for depositing compound materials such as compounds II-VI and III-V semiconductors, oxides and nitrides [24]. The history of Atomic layer deposition comes back to late part of 20th century and has been invented independently twice. Once in the Soviet Union in 1960's under the name "Molecular Layering" (ML) by Prof. Aleskovskii and Prof. Koltsov and the second time under the name "atomic layer epitaxy" (ALE) in 1974 in Finland by Dr. Tuomo Sutola and patented the same year [26]. Dr. Sutola's motivation to develop ALE was driven by need for the growth of zinc sulphide layer, the light-emitting material in electroluminescent thin film flat displays [26].

ALD mechanism

The ALE process can be carried out either in vacuum or in an inert gas atmosphere [24]. ALE can be performed in several modes of operation depending on the type of material to be grown and the type of reactants used in the process. In the beginning it has been developed for the compound materials, but with a certain restrictions it can be carried out using elemental materials as well [24]. During ALE process, the reactants are pulsed onto the substrate alternately one at a time, and between the reactant pulses the reactor is purged with an inert gas [25]. In the Figure 12, process of ALE mechanism, is illustrated for compound reactants, thought in principle for elemental materials its similar process as well. In first step, the first precursor of desired material is exposed to the surface of the substrate, where it chemisorbs on the substrate and after saturations creates perfect monolayer on the substrate. Next step consists of purging the excess molecules with an inert gas from the chamber. Subsequently next reactant is introduced into the chamber, where it aggressively reacts just with the monolayer of

the first reactant creating desired thin film and by-pass gaseous products, that are purged out of the chamber of the system.

Compared to CVD, the activation energy of reactants is low, i.e. on the surface of the substrate they exhibit high reactivity, which supports quicker and stronger film formation. The high reactivity is not obstacle since the gas phase reactions are eliminated by sequencing gaseous reactants [24].

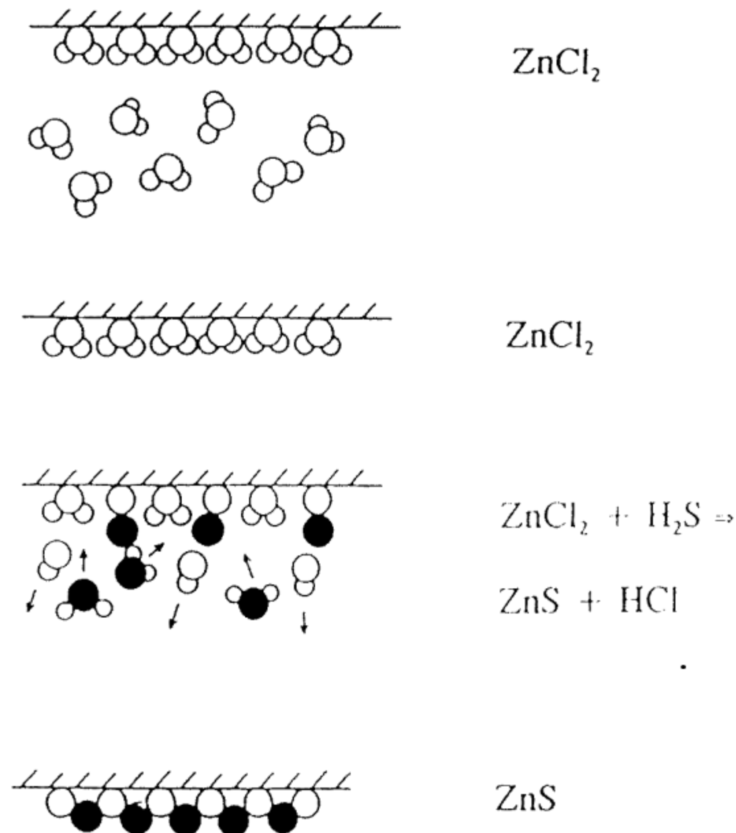


Figure 12. *Schematic diagram of principle mechanism of the ALE for growing of ZnS film* [25]

1.4.3.Thermal evaporation

Thermal evaporation belongs to the family of physical vapour deposition methods and is one of its simplest representative. Thermal evaporation is a process where solid material, evaporant, is evaporated by thermal energy. There are different sources to produce energy required for thermal process. It doesn't matter whether, the energy supplied to evaporant come from electrons or photons , the vaporizing mechanism can still be thermal [20]. However, typical laboratory setup is the system, where vaporization is achieved by heating the material electrically. This setup consists of the evaporation source, vacuum chamber and hemispherical, where the substrate is located. In the Figure 13, we can see schematic diagram of thermal evaporation system using electrical heater. Between basic requirements for evaporation source belongs supporting evaporant, provide it with thermal energy and as a critical requirement there can't be any alloying or chemical reaction between evaporation source and evaporant. The evaporation source is typically resistive type and is heated by passed electric current, usually made from metal wire, foil or boat. Vacuum better than 0.013 Pa, should be achieved in the evaporation chamber, so that evaporant atoms can reach the substrate without colliding, as they

travel from the source to the substrate. To obtain high purity films, the pressure in the chamber should be reduced to the level of 1.33 x 10^{-7} to 1.33 x 10^{-9} [20]. Substrate is rotated, to achieve uniform deposition of desired material. Often, physical masks are used to interrupt the flux of evaporated atoms and to produce defined pattern on the substrate [20].

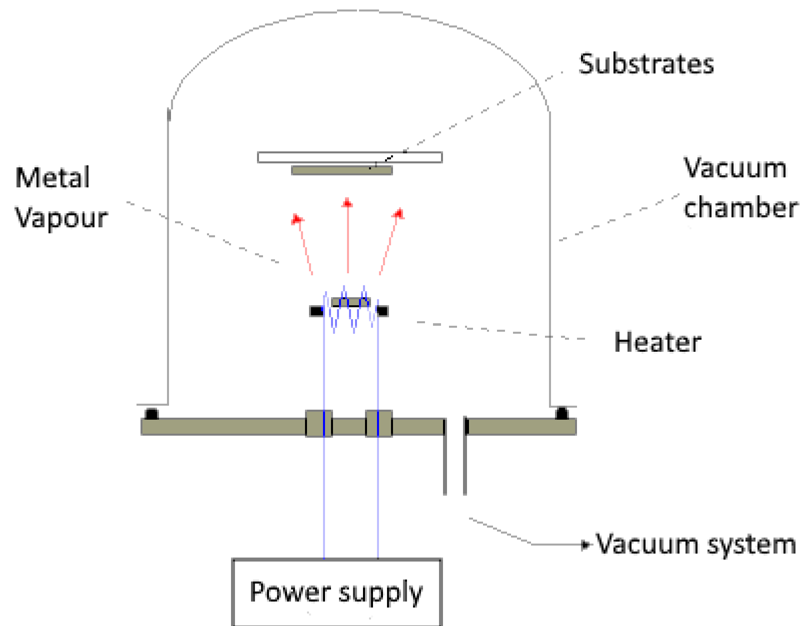


Figure 13. *Schematic diagram of thermal evaporation system, using electrical heater.*

1.4.4.Sputter deposition

This technique, as well as above mentioned process, thermal evaporation, belongs to family of physical vapour deposition, since the sputtering is purely physical process [27]. During sputtering process the particles are ejected from solid, or sometimes liquid target source, by bombardment of energetic particles, mostly ions, recoil atoms or energetic neutrals [28]. This process takes place under vacuum or inert gas environment. In the Figure 14, is schematic diagram of the collision sequence and the possible scenarios in behaving of the involved particles. Depending on the source of the energetic particles, used environment and surrounding condition, there are different modification of sputter deposition. One of the most popular type of sputtering technique is called magnetron sputtering.

Magnetron sputtering deposition

The most common approach for growing thin films by sputter deposition is the use of a magnetron source in which positive ions, present in the plasma of a magnetically enhanced glow discharge, bombard the target resulting in sputtered atoms that covers the substrate. The target can be powered in different ways, ranging from dc for conductive targets, to rf for nonconductive targets [27]. Schematic diagram of the magnetron DC powered sputtering can be seen in the Figure 15.

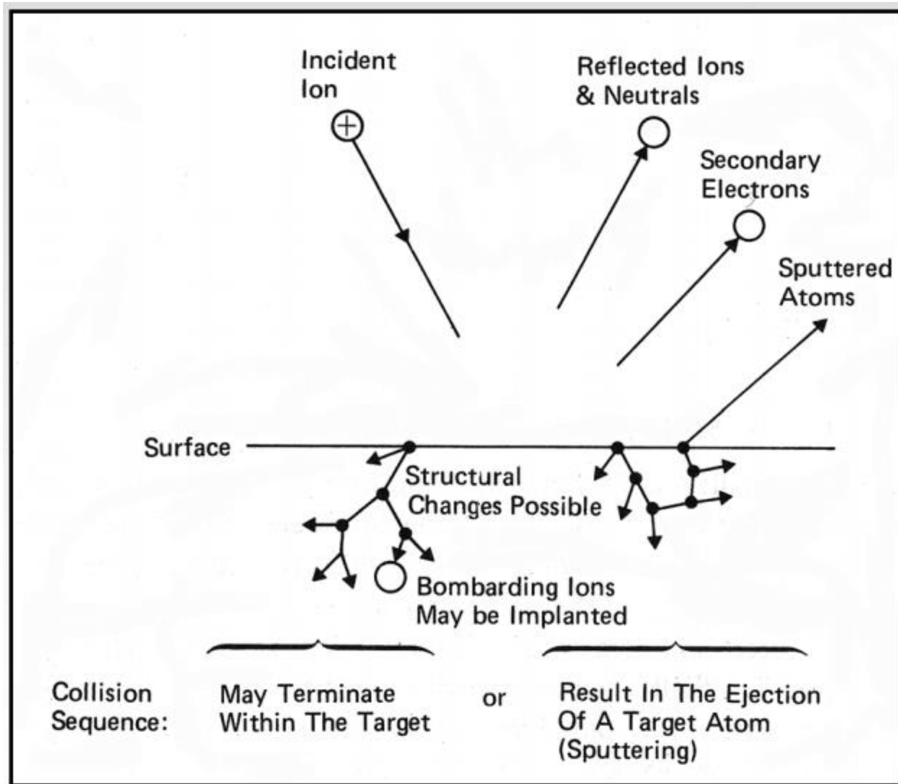


Figure 14. *Schematic diagram of incident of ion on the target during sputtering deposition* [29].

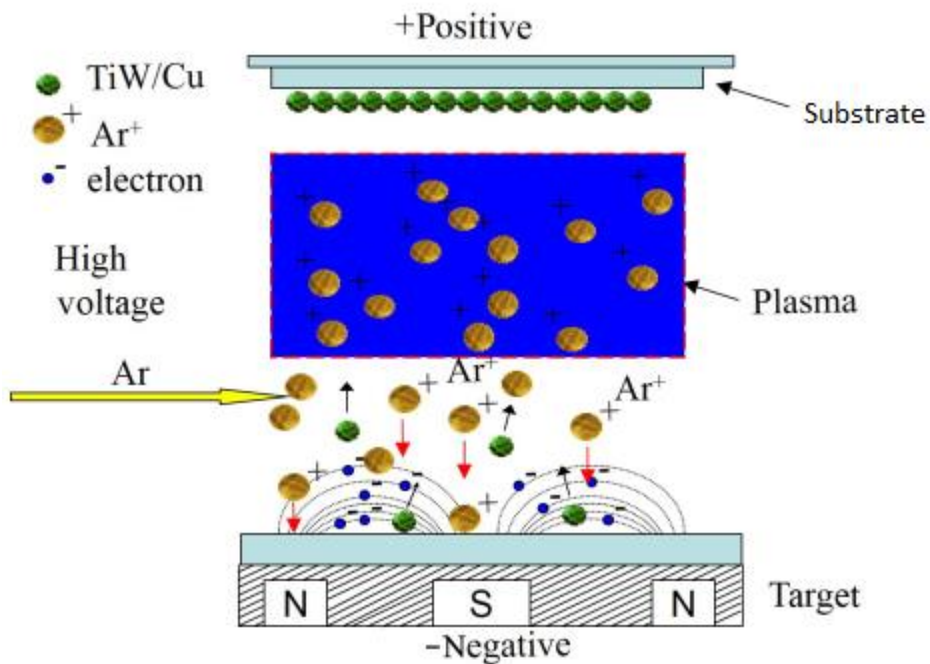


Figure 15. *Schematic diagram of magnetron sputtering process* [30].

Reactive sputtering

We talk about reactive sputtering, when the reactive gas is introduced into the chamber and sputtered particles undergo chemical reaction with the compounds of reactive gas before coating the substrate. The result of adding non-inert gas into the chamber is that the final deposited film is different from the target material. Common added gases are oxygen and nitrogen which together with use of a silicon target, can be used to produce silicon oxide or silicon nitride film respectively. Another advantages, other than that it gives new possibilities, are controlled stoichiometry at high deposition rate and that elemental targets can be very pure and easy to produce [29].

1.4.5. Electrospinning

Although electrospinning belongs between the novel methods for fabrication of nanofibers with the diameter ranging from submicron down to nanometre, history of this method comes back to 1902, when two patents involving electrospinning were issued by Cooley and Morton [31]. Reason, this method wasn't very popular and didn't draw much attention until mid-1990s, is because of its relative slow production rate compare to industrial fibre spinning processes which can have yarn rate ranging up from 200 to 1500 $m.min^{-1}$, compared to electrospinning, where the fibre yield is about 30 $m.min^{-1}$ [31]. With the development in the field of nanoscience and nanotechnology, the research community started to realize huge potential of this method for the fabrication of nanofibers and nanowires. The advantage of electrospinning, compared to existing methods that can be used for producing nanofibers, is in its flexibility, versatility and ease of production. The typical set-up consists of high voltage power supply, pump, syringe, flat tip needle and collector, usually grounded. In the Figure 16, we can see schematic set up for this manufacturing tool. There has been many variation of this setup regarding differences in high voltage power supply, which can be AC or DC, different collector design or polarity etc. Though it is beyond the content of this paper to try to fully describe all the possible configurations. As said above, electrospinning is flexible tool, because wide variety of materials can be processed using this method. The most typical materials used for nanofiber production are polymers, composites, semiconductors and ceramics[31]. One of the most important advantage of electrospinning, over the other existing methods for nanofiber manufacturing, is the ability to fabricate various nanofiber assemblies *in situ.*

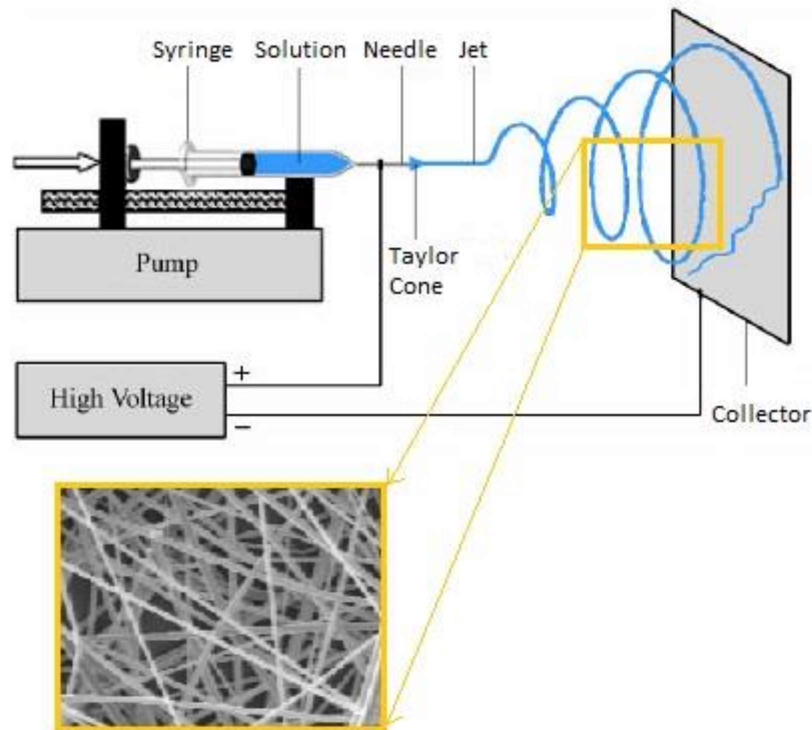


Figure 16. *Schematic setup of electrospinning tool – modified picture from* [32]

During the electrospinning process, solution is being pumped into the needle at the end of syringe and kept at the tip of needle by surface tension. Then high electric field, generated by high voltage power supply, is induced between the needle containing the solution and the collector. The charge is induced on the surface of the solution by electromagnetic field and mutual charge repulsion creates the force of opposite direction to the surface tension. With increasing intensity of the electromagnetic field, hemispherical surface of the solution, at the end of tip of the needle, elongates forming conical shape known as Taylor cone. When the intensity of electromagnetic field reaches the critical value, during which repulsive force overcomes the surface tension of the solution, charged jet of the solution is ejected from the tip of the needle. The formation of nanofibers happens as the jet flies in the air as a result of uniaxial stretching of viscoelastic solution and the solvent evaporation [31], [32].

1.4.6.Spin coating

For decades, spin coating is one of the most common techniques used for depositing thin films to desired flat surfaces. Using spin coating, even layers ranging from few nm to few um can be deposited onto the substrate. It can be also used for depositing desired micro or nanomaterial in solvent as an ink.

The general description of the process consists of few steps. In the first step the substrate is dispensed with desired fluid or ink and then rotated at high speed. Centripetal force caused by rotation, spreads the fluid or ink over the entire surface of the substrate. In this step the thickness of the final film is determined. In the last step, the substrate with the deposited layer is dried by exhausting the fumes in the spin coater chamber to remove extensive solvent from the substrate surface. Below main parameters determining the quality of the layer deposited by spin coating technique will be described, with the main differences and effects on the final product.

In general, we can distinguish between two major spin coating methods depending on the dispense procedure. In the following paragraphs the major differences and advantages/disadvantages between the dynamic and static dispense spin coating methods will be discussed.

Dynamic Dispense Spin Coating Technique

Generally, dynamic dispense approach is more common method. In this method, an ink is deposited in the centre of the substrate, when it is already rotating at low speed usually about 500 rpm. After the dispense substrate is accelerated to high rotation from about 1500 to 6000 rpm. This helps in spreading the fluid over the whole area of the substrate. This step can last from tens of seconds up to several minutes [33]. One of the advantage of dynamic dispense spin coating is that it offers higher controllability, which leads to better substrate to substrate variation. It is caused by fact that the solvent has less time to evaporate during the process, thus the dispense time is less critical during this process. Another advantage is that it usually uses less ink for the coating. Dynamic dispense technique in general uses rotation speeds above 1000 rpm.

Static Dispense Spin Coating Technique

Sometimes it is required, due to some special circumstances, to drop the rotations under 1000 rpm. It can be caused for example by the fact that better crystallization of desired nanomaterial happens during low speed spinning or because used fluid/ink doesn't have desired parameters for higher spin speed. In that case, static dispense is used, because with the rotations under 700 rpm it usually gives better results and higher quality films [34]. During static dispense, the ink is deposited in the centre or as close as possible to the centre of the substrate or all the active area of the substrate is covered by the ink before starting the rotation. One of the most important issue for static dispense represents evaporation of the solvent in an ink. This can be problem for high pressure solvents, because the time between the dispensing and starting rotation can be critical for the thickness and quality of the final film thus influencing the substrate to substrate variation. This is main purpose why, if it is possible, dynamic dispense approach is recommended.

Spin speed

The rotation speed defines the layer thickness and it ranges from around 600 rpm to 6000 rpm although there are some specialist spin coaters with even higher rotation. There has been relationship between the rotation speed and thickness of the layer that can be expressed by so called spin coating thickness equation, where the thickness is proportional to the inverse of the spin speed squared, as we can see in equation below. Where t is the thickness of the layer and ω is angular velocity.

$$t \approx \frac{1}{\sqrt{\omega}}$$

1.4.7. Inkjet printing

The inkjet printing is not just an important tool in colour documentation printing, but as well powerful tool used in printed electronics. It is non-impact printing technology which reproduces digital pattern to the various substrates (paper, foil, etc.). The non-impact ability to print is one of the main benefit as well as reduced consumption of the material, because there is almost no waste of material.

History and main characteristics of inkjet

Inkjet printing roots comes back to the middle of 19th century, where the first inkjet-like device for automated recording of telegraph messages has been developed by William Thompson, later Lord

Kelvin, and patented in 1867(UK Patent 2147/1867) [35]. This machine used siphon to produce continuous stream of an ink onto moving paper and driving signal moved the siphon to successfully record the message. Thought rapid development of inkjet technology started in late fifties, when first practical continuous inkjet technology was patented by Elmqvist in 1951. Generally, there are two main categories of inkjet printing, continuous and drop on demand principle. The main difference is already mentioned in the names of the stated technologies, where continuous inkjet printing represents continuous flow of droplets. Droplets are electrostatically charged and as they move through an electrostatic field between electrostatic deflection plates they are directed toward the substrate. In case of Drop on demand principle, the droplets of an ink are ejected only when needed. In the Figure 17, there is main classification of the inkjet printing techniques and drop formation mechanisms. In this thesis, brief description of thermal and piezoelectric printing will be presented, since they have biggest impact on the printing industry.

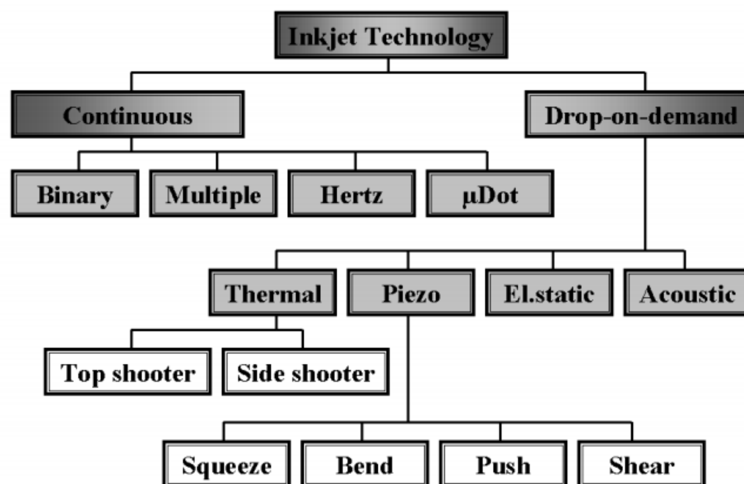


Figure 17. *Classification of inkjet printing technologies* [35]

Thermal inkjet printing

The technology of drop on demand (DoD) thermal inkjet (TIJ) device was first patented in 1965, but no further developed into commercial product, then in 1979 Endo and Hara from Canon reinvented the inkjet printing head using thermal energy to eject ink drops, called bubblejet, which resulted in manufactured printer in 1981. The first real world application of thermal inkjet was developed by HP and lead to first successful low cost inkjet printer in 1984. Historically, main advantage of TIJ compared to piezoelectric inkjet was ease of miniaturisation of the device, since the thermal transducer of the device could consist of simple resistor, which is cheap and easy to miniaturize. Also, the IC manufacturing process, at that time already developed, allowed the TIJ to be mass produced, leading to reduction of the nozzle's coast. The mechanism of ejecting drops from the nozzle of thermal inkjet printer is essentially conducted by pressure pulses, made by collapse of the small bubbles generated by heating element inside the head of cartridge

Piezoelectric inkjet printing

The development of piezoelectric inkjet printing comes back to the 1970s where three patents involving piezoelectric inkjet action have been issued and the first piezoelectric DoD inkjet printer, to reach the market, has been developed by Siemens in 1977 [35]. DoD piezoelectric inkjet represents low cost research tool for mask-less deposition of liquid phase materials[36]. The materials are dissolved in a solvent, to form ink with specific parameters which makes it suitable for printing. The process of printing consists of few steps. First the chamber of the fixed volume in the head of cartridge is filled with an ink. Then the volume of the chamber is suddenly decreased via piezoelectric action of a membrane and the droplet of an ink is formed through the nozzle. This is achieved by applied external voltage to piezoelectric membrane in the chamber of MEMS device in the head of cartridge. By means of gravity and influenced by air resistance, the ejected droplet falls through the air until it hits the surface of the substrate. Droplet then dries through the evaporation of solvent, whose parameters are the key for successful printing and have underlying influence on droplet formation. Schematic diagram of inkjet process and the droplet formation is presented in the Figure 18. Viscosity is one of the most important factor in behaving of the drop on the surface of the substrate. It is also the main parameter that influences jetting ability of the ink, as well as, spreading and the final shape of the printed droplet. Other important characteristics of the fluid are surface tension and used solvent.

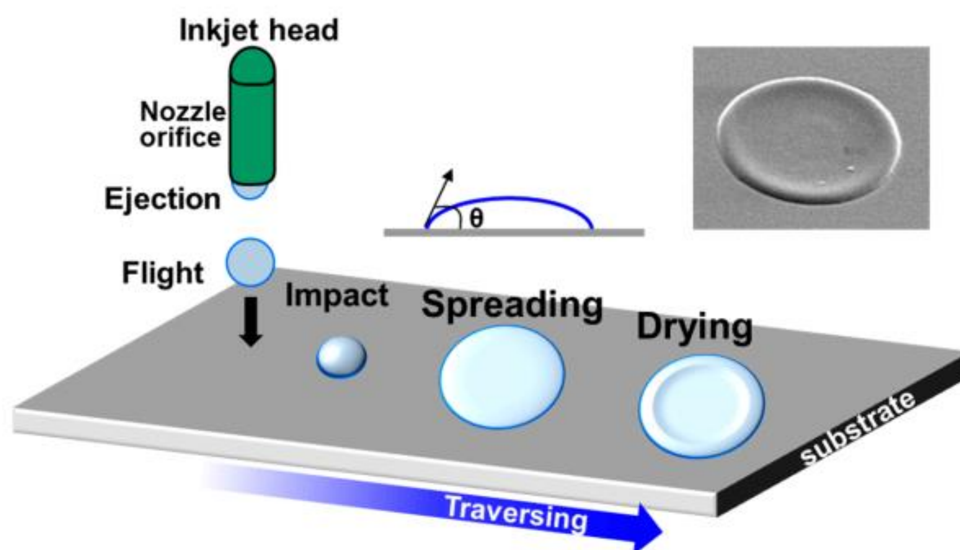


Figure 18. *Schematic diagram showing inkjet printing process. Right/Top inlet presents SEM image of PEDOT:PSS ink droplet. Copyright 2013 American Chemical Societ*y.[37]

1.4.8. Dip coating

Like some of the methods mentioned in this chapter, dip coating is also the method for deposition films from the solution, so called wet chemical thin film deposition. It's the oldest commercially applied process from those techniques. The history of dip coating comes back to 1939, when first patent was issued to Jenaer Glaswerk from Schott & Gen. for sol-gel derived silica films [38]. Its setup and technical process is very simple. The process of dip coating can be separated into three stages. First the substrate

is immersed into the precursor solution at a constant speed and dwelled in solution reservoir for certain time to allow defined interaction time between the substrate and the solution to take place. After dwelling, substrate is again at the constant speed pulled out of the solution and the thin layer on the substrate is deposited. Excess liquid drain out of substrate to the solution reservoir. Last step consists of evaporation of the solvent from the solution, thus formation of final thin film on the substrate. This step can be promoted by ventilation or heating. Under general description it seems this method is rather simple, though there are many factors influencing thickness and other properties of deposited thin film.

Classical Dip Coating

During classical dip coating process, substrate is pulled out vertically from the liquid reservoir at a constant speed U_0. Moving substrate cause streamlines in the solution, to illustrate behaving of the fluid regarding pulling substrate, we can see the drawing of the stream lines in the Figure 19 [38]. In there we can see that as the substrate is pulled out of reservoir, it causes flux, at the surface of the reservoir, divides into two streams at the point called stagnation point, one caused by capillary force points up with the moving substrate, while the other stream returns back into the reservoir

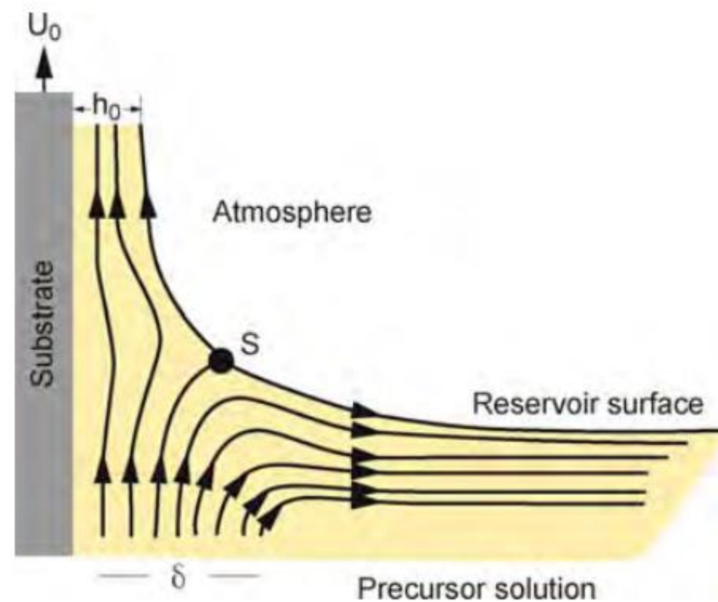


Figure 19. *Schematic drawing of streamlines during classical dip coating process. U_0 is speed, S is so called stagnation point, h_0 is thickness of the pulled liquid film on the substrate and δ is the boundary layer.* [38]

Angle dependent dip coating

In this dip coating modification, the substrate is pulled out, from the solution reservoir, under variable angle. The outcome of this approach is different film thickness on each side, resulting in thicker film on upper side and thinner film on bottom side, as we can see in the Figure 20. Thickness variation depends on the inclination angle between the substrate and the surface of the fluid in the reservoir and the pulling speed as well as viscosity and other properties of deposited solution. The operation range is limited to angle of inclination lower than 60° and withdrawal speed up to 10 mm/s [38].

Figure 20. *Schematic drawing of ADDC (Angle dependent dip coating) process* [38].

1.4.9. Doctor Blade

As well as dip coating, doctor blade technique (also called tape casting) is too widely used industrial technique for depositing thin films from solution. It was originally developed in 1940 to from thin sheets of piezoelectric materials and capacitors [39]. It has gained its place in industrial area, because of its ability to cover large area surfaces with a reasonable speed up to several meters per minute. Thickness of the deposited wet material ranges twenty to several hundred micrometres [39]. Doctor blade technique can be divided into two subgroups, regarding the shape and the way of transferring the solution on the substrate, doctor blade (or frame) and spiral film applicator.

Doctor Blade

In this group of doctor blade coating, there are two main approaches. In one kind of device the frame with a solution is moving along the substrate as it is illustrated in the Figure 21, while in the latter device the substrate is moving and the blade with a reservoir is static. Controlling thickness is done simply by adjusting the gas between the blade and the substrate.

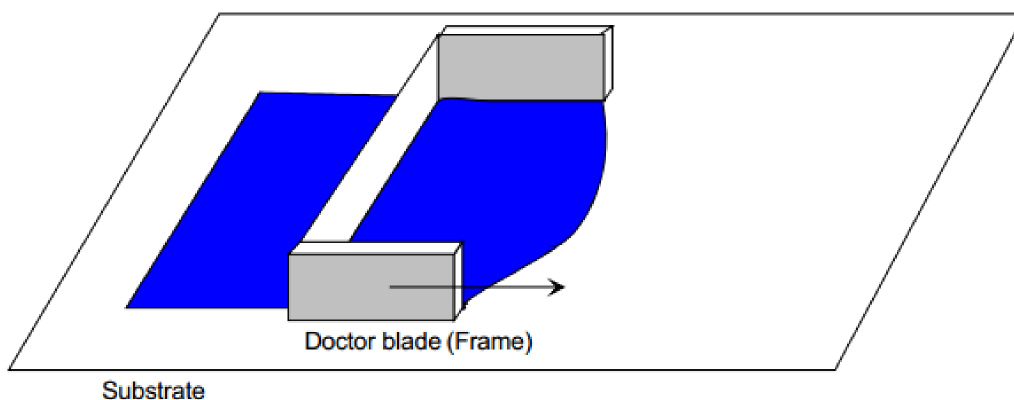


Figure 21. *Doctor blade technique in configuration with a moving blade across the substrate*

Spiral film applicator

This modification of doctor blading use the spiral to spread the solution over the substrate. It is used usually for coating foils, textiles, leather or any other flexible substrate with uneven surface, since the ability of spiral film applicator is to press down and flatten. Schematic drawing can be seen in the Figure 22.

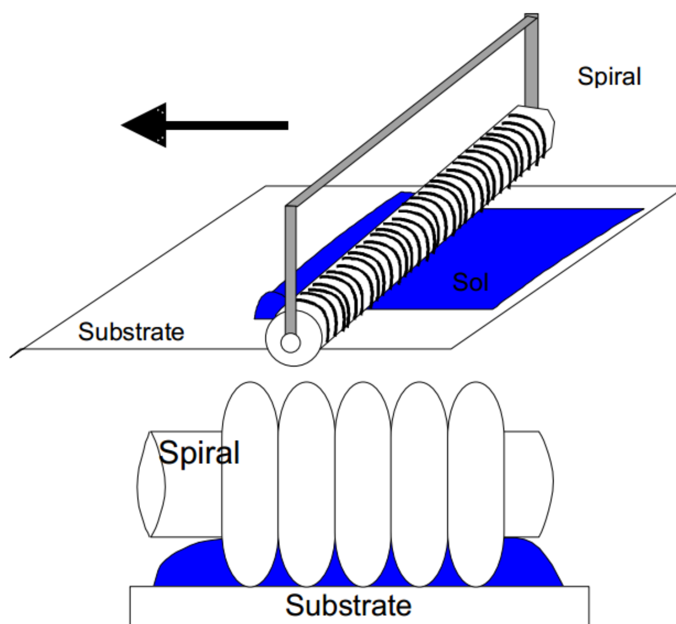


Figure 22. *Schematic drawing of doctor blade technique with spiral film applicator*[39]

1.4.10. Drop casting

Drop casting represents one of the simplest method for depositing desired material in a form of solution. In the Figure 23, we can see the drop casting procedure, where defined volume of solution is dropped by pipette and then evaporated under specific or ambient condition. Evaporation conditions as well as type of used solvent are the main parameters influencing the morphology of manufactured film. Between the advantages of this method belongs mentioned simplicity and as well there is no waste of material. One of drop casting disadvantages is limitation in size of produced film, the other disadvantages are poor film uniformity and difficulty in controlling the thickness of desired film.

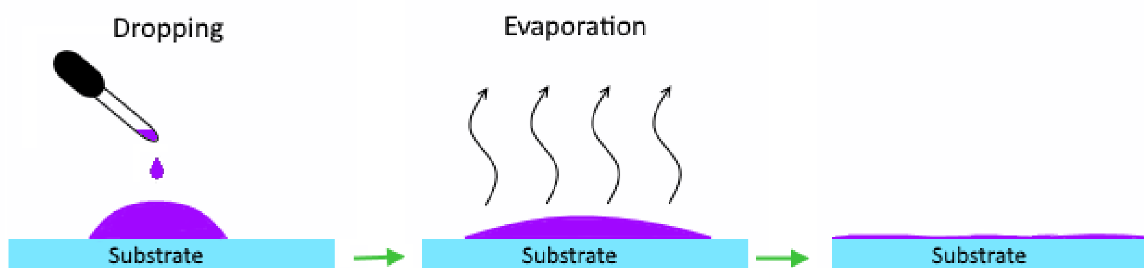


Figure 23. *Schematic of drop casting film procedure*

1.5. Sensor parameters

As every electronic device, also gas sensors have some key parameters which characterize the function and the performance of the device. Brief description of most important parameters is given below, in order with respect to their importance.

Sensitivity

This parameter defines the response of measured signal of the sensor per unit concentration of the target gas concentration. Sensitivity is one of the key parameters for gas sensor [40].

Selectivity

Characterize the sensors ability to selectively respond to the group of analytes or specifically to one desired analyte.

Limit of detection (LOD)

Is the lowest concentration of the target gas, which is possible to detect with selected device.

Response time

Describe how fast can sensor respond to the step change in the concentration of the analyte gas. This parameter usually defines the time, when the response from the sensor reaches 90% of the total response to the given concentration of the gas and is usually marked as τ_{90}.

Recovery time

This parameter is the opposite to the *response time* and it characterizes the response from the sensor to the step change in the concentration of the analyte from certain value to zero.

Stability

Defines the ability of the sensor to maintain its functional parameters over the long-term period. By functional parameters, is understood parameters mentioned in this chapter.

Resolution

Is the lowest difference in concentration which is possible to detect.

Linearity

Describes the deviation of the output signal from the sensor to ideal straight line.

Life cycle

Life cycle defines the period of time, that the sensor is able to continuously operate.

2. Methodology of gas sensors preparation and characterization

In this chapter will be reviewed the techniques and equipment used in manufacturing process of, developed solid state gas sensor and their respective measuring under the exposition to different analytes.

2.1. Gas sensor preparation

Sensors prepared as a part of this thesis were chemoresistive type of gas sensors. During the process, different approaches of depositing thin film were considered and compared. As a pattern platform for testing and comparison of results was used prefabricated platform from FR4 substrate, with deposited interdigitated array of golden electrodes. Other platforms of interdigitated arrays have been fabricated by piezoelectric inkjet printer Dimatix Fujifilm DMP-2831. Description and the parameters of this device will be given bellow in separate paragraph. Different techniques, were used for deposition of the sensing thin films. This includes, simple drop casting method using labopette pipettes with defined volume of the drops, deposition by spin coater Polos MCD200 and by Dimatix DMP 2831 inkjet printer.

2.1.1.Inkjet printing process

Inkjet printing of desired materials and structures has been conducted by Fujifilm Dimatix DMP 2831 inkjet printer. DMP 2831 is a DoD piezoelectric inkjet printer designed as a laboratory and a limited scale production tool. It enables researchers to rapidly prototype and proof concepts of ink jetting technology. It's a complex tool, which enables extensive optimization of the process, thanks to PC controlled operation with a possibility to visually observe drop formation and jetting, as well as inspect printed pattern through fiducial camera. User fillable cartridge are compatible with most of the solvents. Main components and parameters will be briefly discussed in paragraphs below.

DMP 2831 general description and system identification

As said before, DMP 2831 is a PC controlled DoD IJP printer. The PC with a controlling software comes together with a printer. Controlling software, Dimatix drop manager (DDM) is a GUI application software allowing extensive optimization of the printing process, together with the cartridge cleaning process and printed pattern inspection. The schematic diagram of main components of DMP 2831 printer is in the Figure 24. The printer consist of print carriage, which is *x,y,z* adjustable and carry and operate the cartridge. Another main component is platen, with embedded heater and vacuum holder for supporting the substrate. The platen temperature can be controlled in a range from ambient to 60°C. The angle of the platen is also adjustable and it can hold the substrate 210 x 315 mm in size. On the left side, inside the working area of the printer, there is a maintenance blotting pad for execution of the cleaning cycles of the cartridge.

On the opposite side is placed build-in drop jetting observation system, called the drop watcher. This system allows direct viewing of the nozzle and actual jetting of the fluid. It's used for controlling the jetting performance, like a drop speed, shape observation and direction and correction of formation of unwanted effects during jetting like satellite drops. The capture of jetting process during the printing process of this thesis can be seen in Appendix in the Figures 53 and 54.

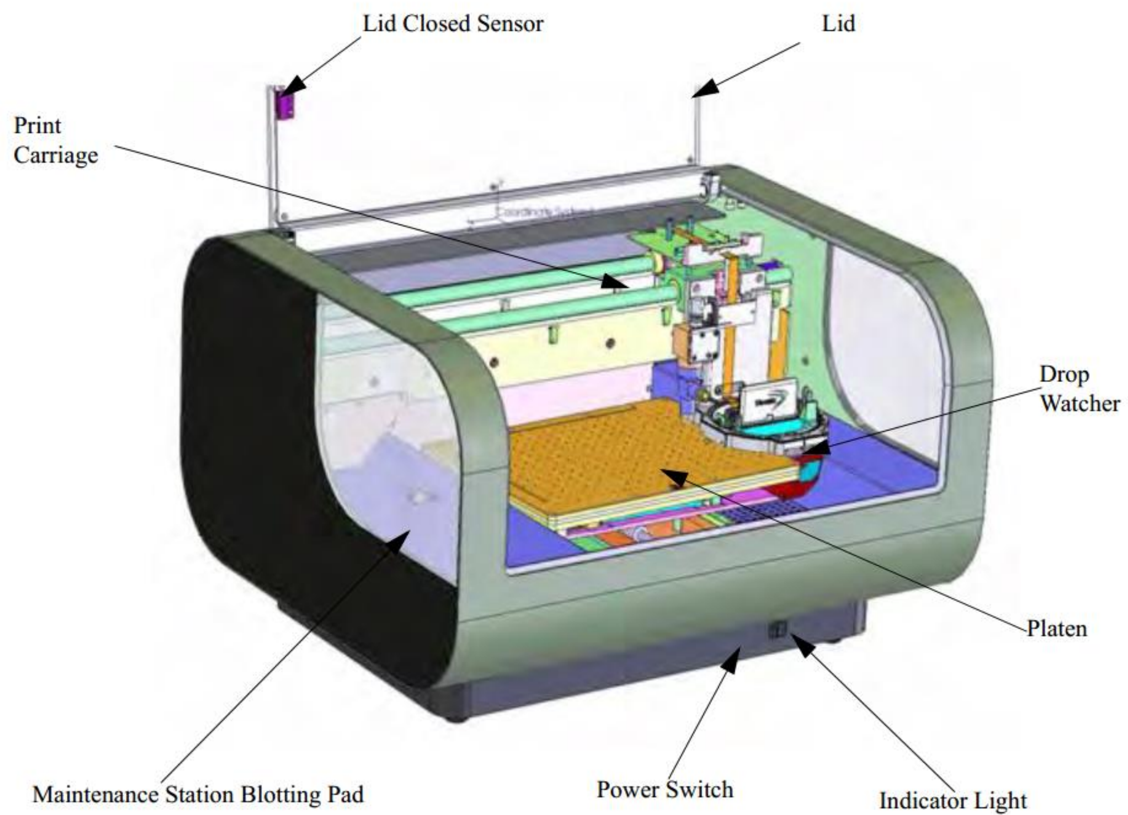


Figure 24. *Schematic diagram of Dimatix DMP 2831* [41].

Print carriage

Function of print carriage is to move the print head and it's a place where the cartridge is located. The main components of the cartridge carriage can be seen in the Figure 25 [41]. It has embedded so called fiducial camera, whose functions are to inspect the printed pattern, set precisely the print origin as well as align the substrate and align additional printed layer with the layers already printed. In the fiducial camera mode, it is also possible to do basic dimension measurements of the printed patterns. The fiducial camera operates in two modes of illumination, dark field or bright field. There are two light sources in the head carriage, that can be selected by switch on the cartridge head. By using dark field, it is possible to view clear fluid on highly reflective substrate. The intensity of the source can be also adjusted by the slider in the Dimatix Drop Manager. In bright field mode device works in same principle as a regular microscope, as the light shines on the substrate and is directly reflected into the objective. On the print carriage, there is also possible to adjust the angle of the cartridge. This angle is calculated by the system, depending on the drop spacing specified in the pattern. With this angle, it is possible to adjust drop spacing in the axis *y*.

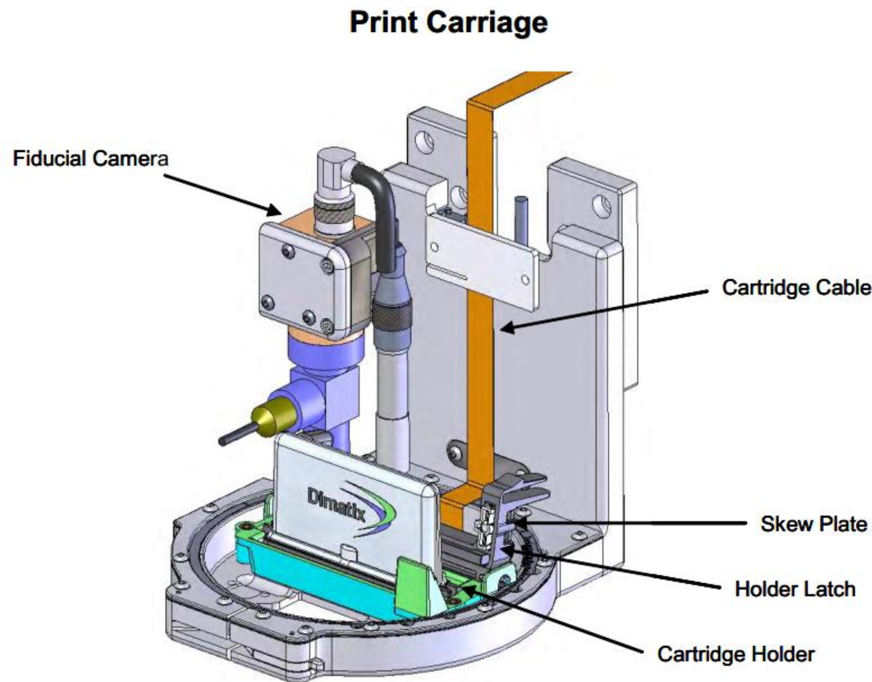


Figure 25. *Schematic diagram of the major component of print carriage* [41]

Dimatix drop manager

As meant before, Dimatix drop manager is used to control the DMP 2831 printer. This software allows.

To clean the cartridge, user can define cleaning cycles, in cleaning cycle editor, during and in between each printing process. There are three main approaches to clean the cartridge. They can be used solo or their combination can be configured as well as duration of each individual approach. Spit cycle refers to jetting the nozzles at certain frequency at given time. Next option, which can be used for cleaning is so called Purge. This option refers to pushing the liquid through the jetting device with a pressure. It is usually used to get rid of the air in the cartridge. Last cleaning process Blot, refers to cartridge simply coming down to make a contact with a cleaning pad for a given time. Because the nozzles are recessed into the cartridge they don't come in contact with a cleaning pad, but still the cleaning pad absorbs residual fluid from the nozzle plate.

Very important part in Dimatix drop manager is a drop watcher. With this tool, it's possible to set the parameters for the whole cartridge and some parameters for each individual nozzle. In the waveform editor under drop watcher, the waveform driving the piezoelectric membrane in the chamber of the cartridge head can be modified to achieve the best possible result with used ink. The waveform consists of jetting and non-jetting stage, each of them can be divided into many stages. Jetting part of waveform is responsible for successful ejecting the drop from the nozzle, meanwhile non-jetting stage maintain the nozzle and the fluid inside the chamber in jet-able form, while the nozzle doesn't perform jetting. In waveform editor, it is also possible to adjust the cartridge temperature and the driving voltage separately for each nozzle. This allows to correct different drop speed from each nozzle, so all the nozzles jet the fluid at almost same speed. Another parameter, which is possible to adjust under the drop manager window or cartridge settings is a jetting frequency of the nozzles.

Print cartridge

One of the essential part of the DMP 2831 printer represents the print head cartridge. It is one time use and user fillable cartridge. The cartridge reservoir can hold up to 1.5 ml of the fluid and the minimal volume for successful printing is 0.2 ml. In the head of cartridge, there is a MEMS structure with 16 in line nozzles connected to pumps driven by piezoelectric actuating membranes, whose driving electrical signal can be adjusted through included software. The nozzle to nozzle spacing is 254 µm and its silicon orifice diameter is about 21.5 µm. The cartridge also allows heating of the fluid, to lower its viscosity, with embedded heater. The maximum temperature is 70°C.

DMP-2831 Printer parameters

Dimatix DoD IJP is a material printer with a possibility to print wide range of materials from aqueous and solvent-based fluids, solutions and particle suspensions. There are some limitations with regards to viscosity and surface tension. The particles in the solution or dispersions should not settle or aggregate, since there is danger of clogging the jet of the cartridge. The fluid jettable viscosity range is listed as 2 - 30 cp, though recommended value is in between 10 to 12 cp. The surface tension of used fluid

2.1.2.Spin coating process

The spin coating of desired sensitive layer has been tested by Polos MCD200 single substrate spin processor. This device is designed for R&D typically low volume applications like cleaning, rinse/dry, coating and developing. This spin coater represents manual chemical dispense (MCD) system and it can handle substrates ranging from small fragments up to 200mm diameter with vacuum or mechanical chuck. The model in laboratory is designed as stand-alone table- top device with integrated keyboard. The gloved-finger friendly panel with backlit display allows easy programming of time, acceleration (adjustable in 1 rpm/sec.) and spin speed, ranging from 1 to 10.000rpm (spin speed accuracy 0.1rpm) [42].

2.1.3.Sintering and annealing process in thermal oven

Thermal oven has been used for sintering process of nanoparticle silver ink, used for IDE array printing, as well as for drying process of deposited organic layers. For this purpose, has been used universal thermal oven UF 30plus by Memmert. This device allows control of sintering process with regards to precise temperature, length of process and fanout setting. UF 30 plus is universal thermal oven with natural convention or forced ventilation and with ability to operate in range from +30 °C up to +300 °C. Although temperatures above +50 °C are recommended. To maintain homogenous temperature field, the system is controlled through PID microprocessor with integrated auto-diagnostic system and incoming air is preheated as can be seen in the Figure 26. The process control is conducted through twin TFT touch screen display [43].

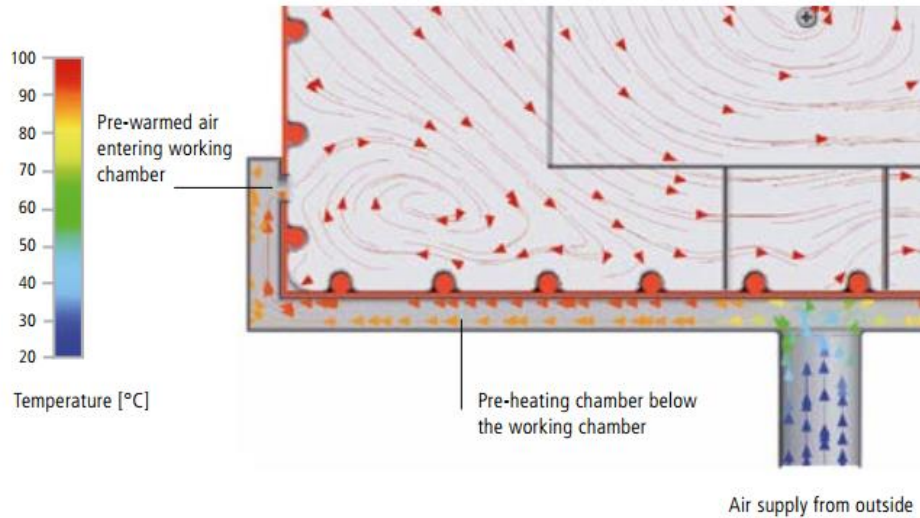


Figure 26. *The air preheating mechanism used in Memmert UF30plus Universal thermal oven* [43]

2.2. Gas sensor characterization

Electrical parameters have been measured using 4-point probe station Cascade Microtech m-150 and Precision semiconductor parameter analyzer Agilent 4156C. Response of manufactured sensors, to different gases have been measured in a testing chamber assembled at the department of microelectronics at Faculty of electrical engineering at CTU in Prague. This sophisticated measuring setup including mass flow meters, precision meters etc. and will be reviewed later in this thesis. The morphology of deposited silver IDE array was investigated using Atomic force microscope NT-MDT. The same device was used to scan the surface of deposited PAni thin film.

2.2.1. Devices for electrical characterization

The VA characteristic were examined using probe station to reach stabile contact and Agilent semiconductor analyser connected to PC and operated by program in LabVIEW to obtain requested data.

Cascade Microtech M-150 probe station

To be able to measure the VA characteristics, it was necessary to obtain precise and non-destructive contact with measured IDE platform, Cascade Microtech m-150 probe station have been used for this purpose. It has support that can hold up substrate up to 150 mm. The measured device is kept in place by vacuum holder. M-150 probe station is designed for measuring small structure on wafer, integrated circuits, IC packages, MEMS and even biological structures [44].

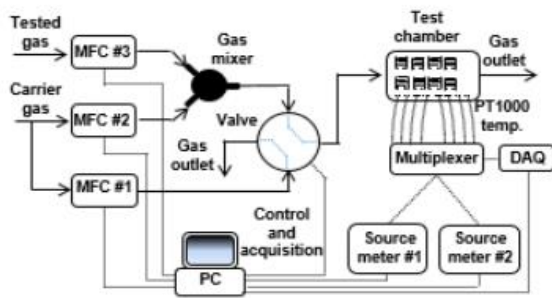
Precision semiconductor parameter analyzer Agilent 4156C

This device has been used to obtain VA characteristics of prepared sensors.

2.2.2. Response measurement setup

The response of prepared solid state gas sensors to the target analytes were analysed on the laboratory setup. In the Figure 27, we can see schematic diagram of the laboratory setup and the photo of attached sensor array in the socket of the gas chamber. The schematic diagram and photo of the measuring equipment can be seen in the Appendix in the Figures 61 and 62, respectively. As a gas

source were used steel bottles with pressured gases of N_2, NH_3, CO and NO_2. The pressure from the bottles was reduced in reduction valves. To properly set the desired gas concentration, three Low-ΔP-Flow mass flow meters by Bronkhorst were used. The volume of the gas flow was set in LabVIEW program through PC. The detection and cleaning stage of the measurements were cycled using two-way four inputs/output valve driven by VICI universal valve actuator controlled by the same LabVIEW program via serial port. Prepared gas sensors were power supplied by Keithley 2230-1-1 triple channel DC power supply and the change in resistance was measured by Keithley 2401 Source meter. This whole setup allowed me to conduct repeatable measurements and data acquisitions.



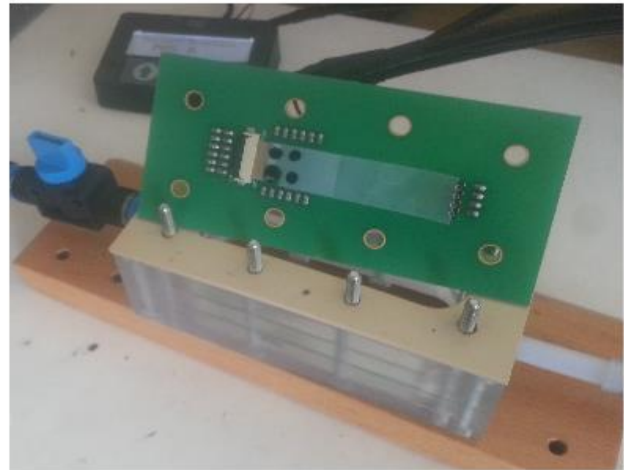


Figure 27. *(left) Laboratory setup for measuring response to the target analyte. (right) Inkjet-printed gas sensor plugged to the socket in the gas chamber.*

3. Results of sensor preparations and characterization

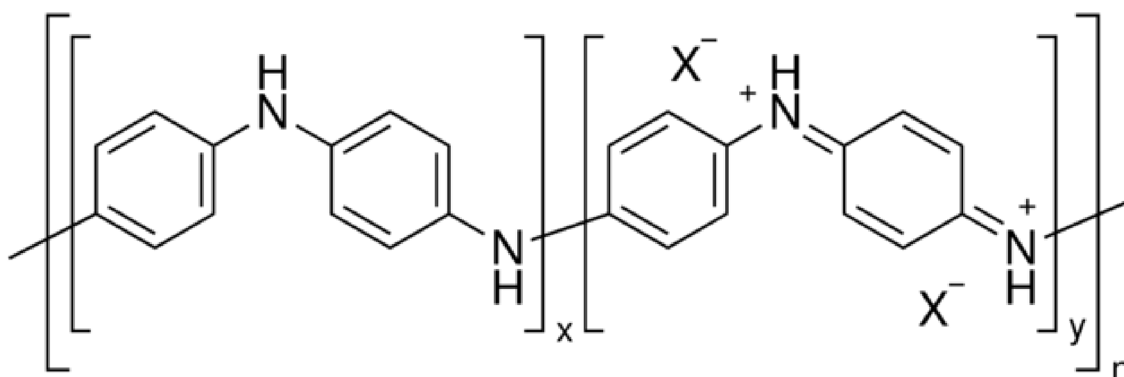
Sensor preparation can be divided into the two major steps. The first step was preparing IDE arrays, the base of chemoresistive type of gas sensor and the second step consisted of depositing sensitive thin films on IDE arrays. As a reference platform, prefabricated golden IDE array on FR4 substrate has been used. To be able to compare measured results, silver IDE with same dimensions was designed in AutoCAD and fabricated using inkjet printer. For deposition of sensitive thin films several approaches had been proposed, investigated and tested. Those techniques were, Spin coating, Inkjet printing and Drop casting deposition methods. Unfortunately, only valid results were obtained using drop casting method. There was an effort to prepare platform with Ag IDE on ceramic substrate using IJP Dimatix Printer to have the possibility to deposit materials with elevated annealing temperature. Used substrate has been 97% Al2O3, corundum. Unfortunately, this was not successful due to XXXXX. The images of those

3.1. Sensitive layers

Several available materials have been considered as a sensitive layer in prepared gas sensors. After examining those materials, the biggest obstacle appeared to be their curing temperature, since both substrates of used platforms had low thermal stability under high temperatures. FR4 and PET substrates cannot withstand temperatures above 120 or 150 °C, respectively. Thus all the samples have been prepared with Polyaniline or PEDOT:PSS organic sensitive layers, because of their ability of deposition under low temperature., with different modifications during processing and deposition. There has been effort to print IDEs on ceramics IDE

Polyaniline (emeraldine salt)

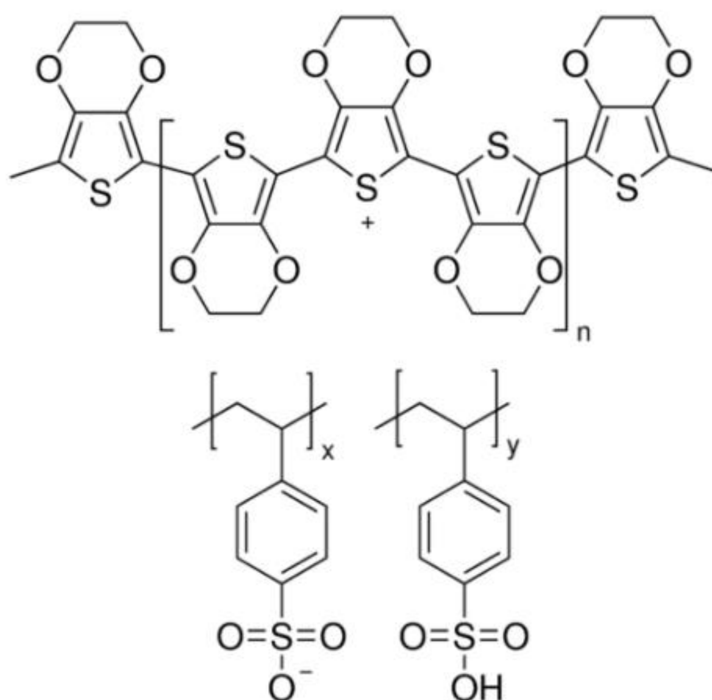
Polyaniline in form of emeraldine salt is doped conjugated polymer, with high mobility. It has been obtained from Sigma Aldrich in form of the powder. It is non-soluble chain of small molecules, with a possibility to be dispersed in different solutions. The dispersion of polyaniline was conducted first in demineralized water, with different mix ratios. Better results were obtained after dispensing in xylene. The dispersion of polyaniline in both liquids was conducted in ultra-sonic cleaner under different temperatures with different process duration. Chemical formula of PAni in form of emeraldine salt can be seen in the Figure 28.



The Figure 28. *Chemical formula of polyaniline in form of emeraldine salt.(source: Sigma Aldrich)*

PEDOT:PSS

Is a polymer mixture of two ionomers. One component is made up of sodium polystyrene sulfonate. Part of the sulfonyl groups are deprotonated and carry a negative charge. The other component poly(3,4-ethylenedioxythiophene) or PEDOT is a conjugated polymer and carries positive charges and is based on polythiophene. Together the charged macromolecules form a macromolecular salt. In this thesis has been used 0.8% PEDOT:PSS dispersion in H_20 from Sigma Aldrich. Chemical formula of PEDOT:PSS can be seen in the Figure 29.



The Figure 29. *Chemical formula of PEDOT:PSS. (source: Sigma Aldrich)*

Table 3. *Table of listed samples and parameters during preparation*

No	Substrate	Sensitive layer	Deposition	Annealing
12	FR4	PEDOT:PSS	Drop Coat 5µl	Hotplate 20m@60°C
25	PET	PAni 2% wt in DEMI H2O (sonicated 40m@50C)	Drop Coat 3µl	Hotplate 20m@60°C
27	PET	PAni 5% wt in xylene (sonicated 10m@30°C)	Drop Coat 3µl	Hotplate 2m@60°C
33	FR4	PAni 5% wt in xylene (sonicated 10m@30°C)	Drop Coat 3µl	Hotplate 2m@60°C
35	PET	PAni 5% wt in xylene (sonicated 10m@30°C)	Drop Coat 3µl	No
37	PET	PAni 5% wt in xylene (sonicated 2h@60°C)	Drop Coat 2µl	No

3.2. Gas sensors on prefabricated platform

Those sensors consisted of Au IDE array on FR4 substrate, with deposited sensitive layers. Several modifications of sensitive layer have been deposited during this process.

3.2.1. Preparation process

During the preparation process of IDE array there has been no work, since the platform has been already designed on department of microelectronics on FEE at CTU and manufactured at Pragoboard s.r.o. In the Figure 30, we can see microscope image of the whole platform and detail of single IDE with marked dimensions. The main object of this thesis has been to develop IJP sensor arrays, so the sensors on the prefabricated platform served rather to compare the results with printed sensors. There have been several modifications of the deposited layers with regards to the method of deposition, conditions during deposition and annealing and material used for final thin film. Materials used during the deposition were, Polyaniline in form of emeraldine salt and PEDOT:PSS. One dispersion of the PAni powder was conducted in demineralised water with concentration of 2% wt. and the other dispersion was 5% wt. of PAni in Xylene. Drop casting has been used as a method for deposition of thin films with an adjustment of drop volume and annealing after the process.

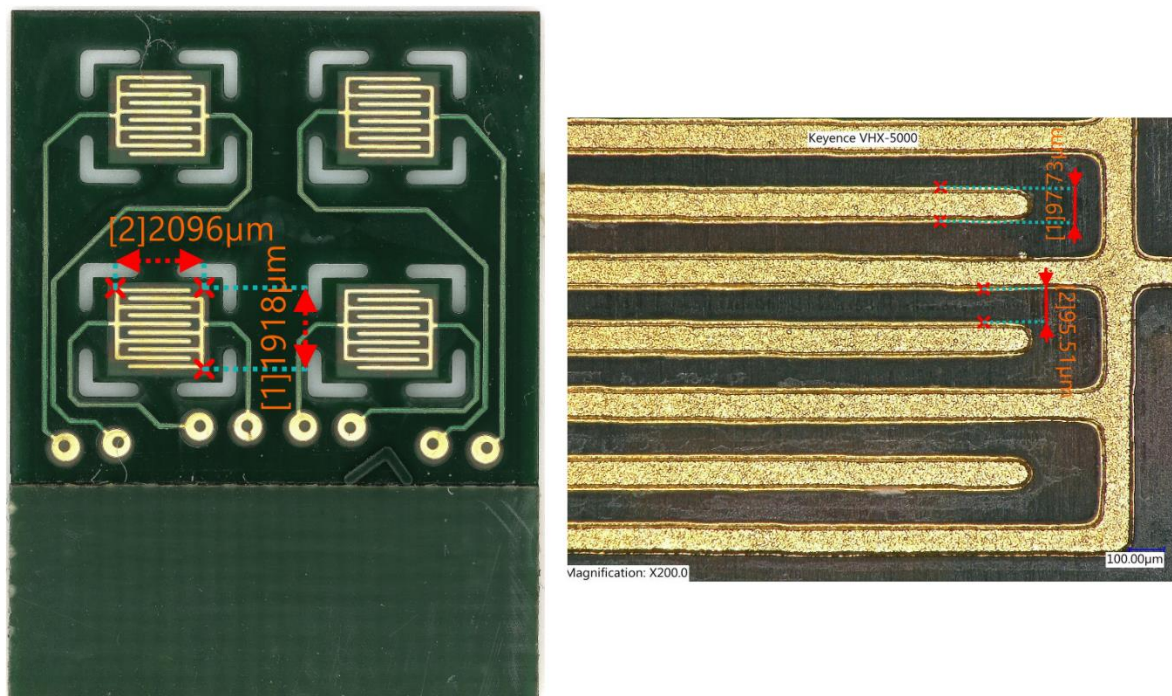


Figure 30. *Microscopic image of prefabricated platform of golden IDE on FR4 substrate with a sensitive area approx. 2x2 mm and electrodes width and spacing approx. 100 µm.*

3.2.2. Results of electrical and gas response characterisation

Before measuring the response of the sensors to target analyte, measurement of VA characteristic of each prepared sensor has been executed, to gain information about the thin film conductivity. After this measurement, it was possible to specify functionality of prepared sensors. For illustration, in the Figure 31. we can see VA characteristics of the sample array No33 sensor D.

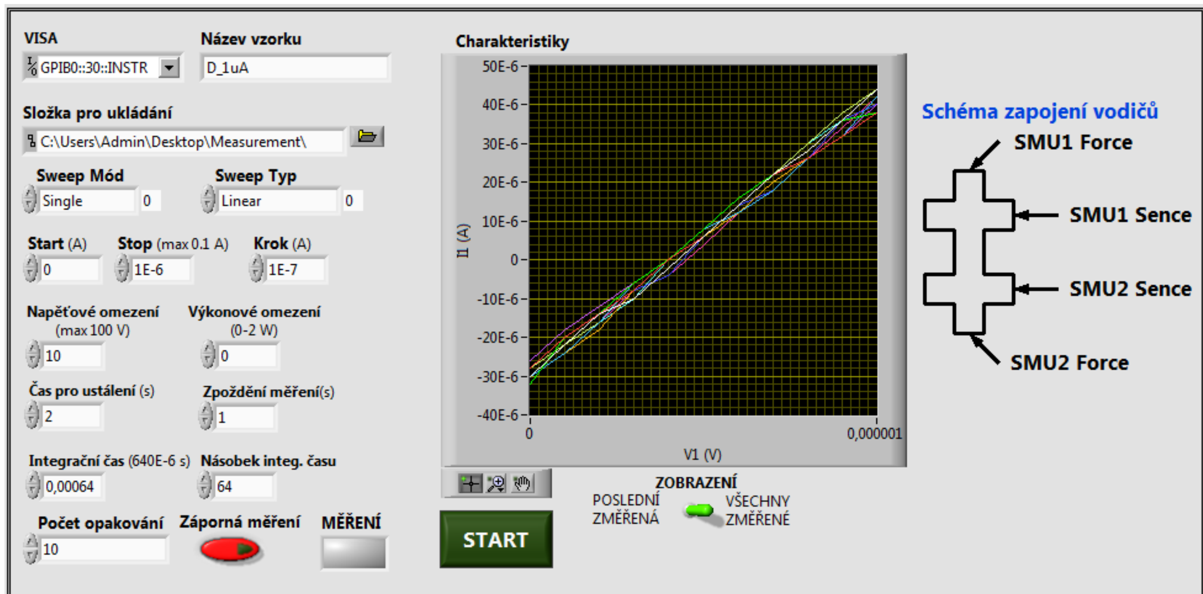


Figure 31. *Measured VA characteristic of the Sensor D on array No 33.*

Sensors on FR4 array has been exposed to different analytes under various concentrations. The basic measuring procedure was composed by three cycles of: 10 minutes purge with N_2, followed by 10 minutes of the exposure to the target analyte. Several samples of sensors on prefabricated array has been prepared, since there was limited number of platforms available.

In the Figure 32, it is possible to see the response of PEDOT:PSS based sensors to 75ppm of NH_3. The sensitive layer of those two sensors from array number 12, was prepared from 0.8% PEDOT:PSS in water solution. This thin film was deposited by drop casting method, using pipette with defined droplet volume of 5 µl. Thin film was then annealed for 20 minutes at 60°C on the hotplate. In the Figure 33, it is possible to see the response of Polyaniline based sensors to 75 ppm of NH_3. The sensitive layer of those two sensors from array number 33 was prepared from 5% dispersion of Polyaniline in Xylene solution which was sonicated for 10 minutes before the deposition. Thin film was also deposited by drop casting method with defined droplet volume of 3 µl and then annealed for 20 minutes at 60°C on the hotplate. The response of the same array to the same concentration of NH_3 was measured three times over the period of 13 days. The changes in the response of the array No33 can be seen in the Figure 34. We can see that after several days the response stabilizes and there is a minimal change in measured response between fifteenth and twenty first of May.

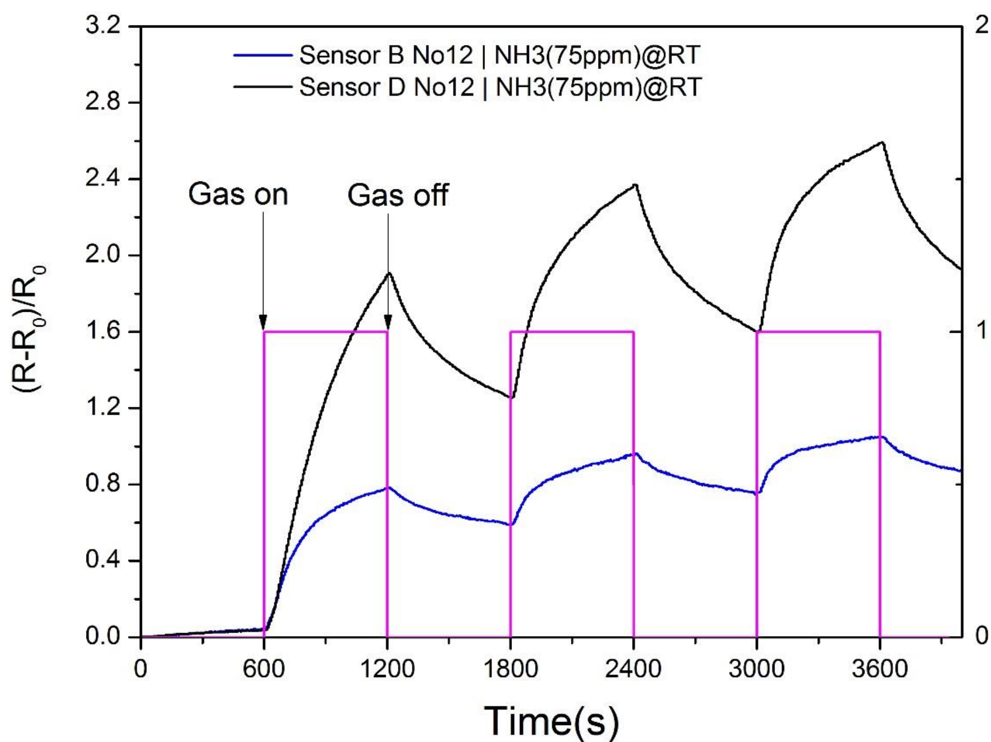
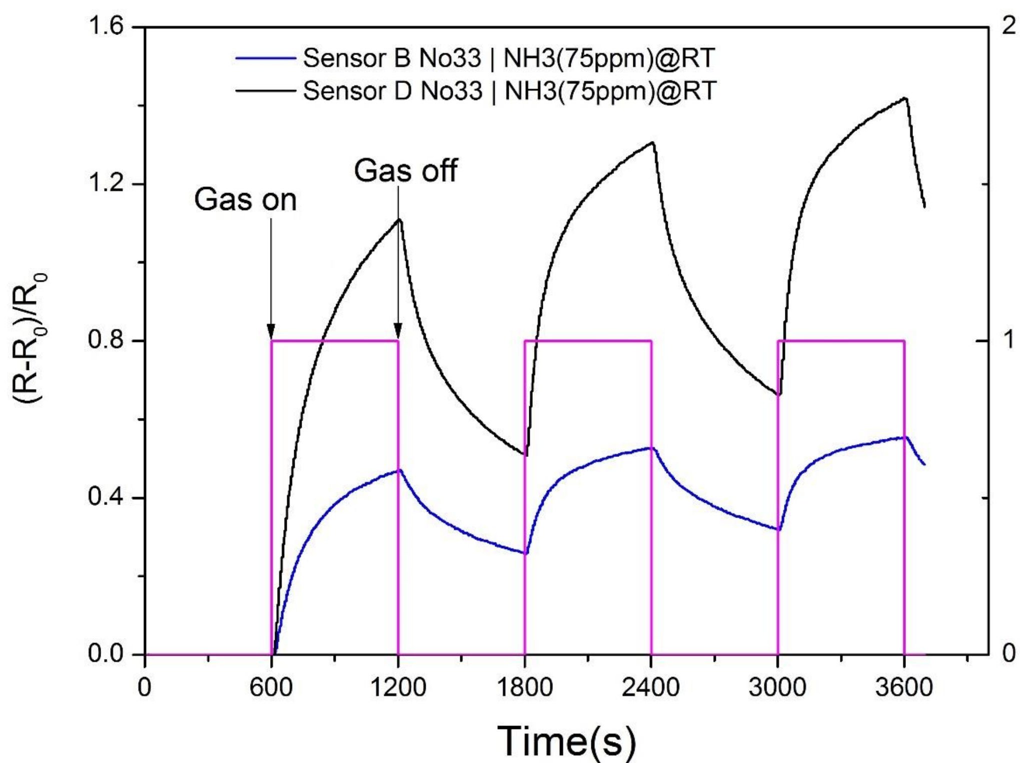
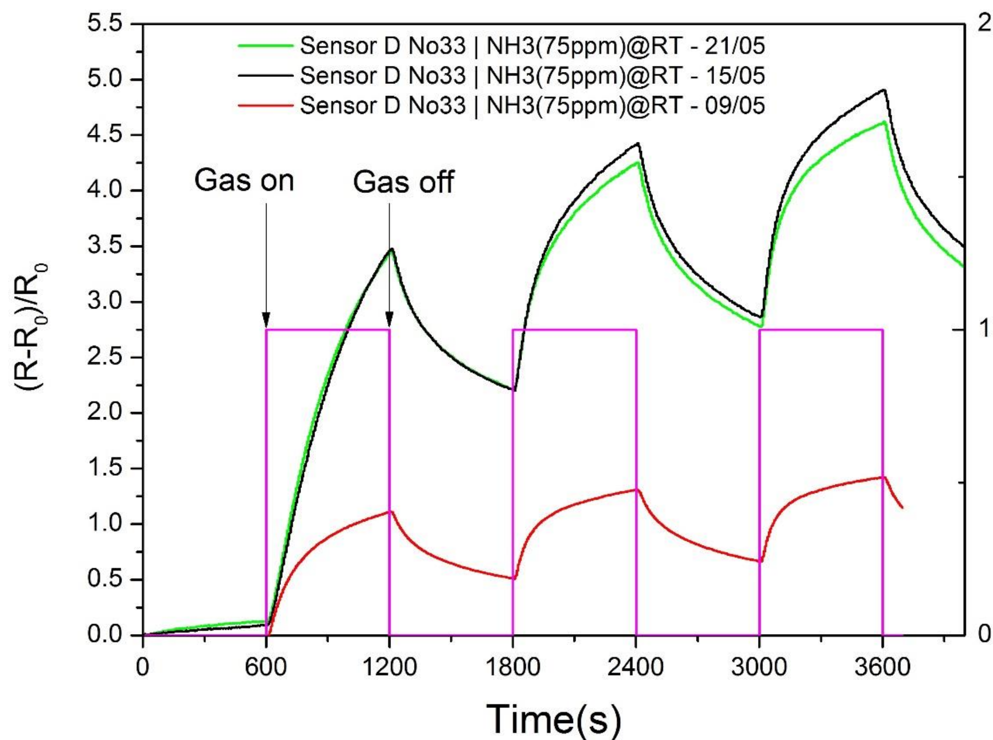


Figure 32. *Response of the sensors from array No12 to 75 ppm of NH_3*



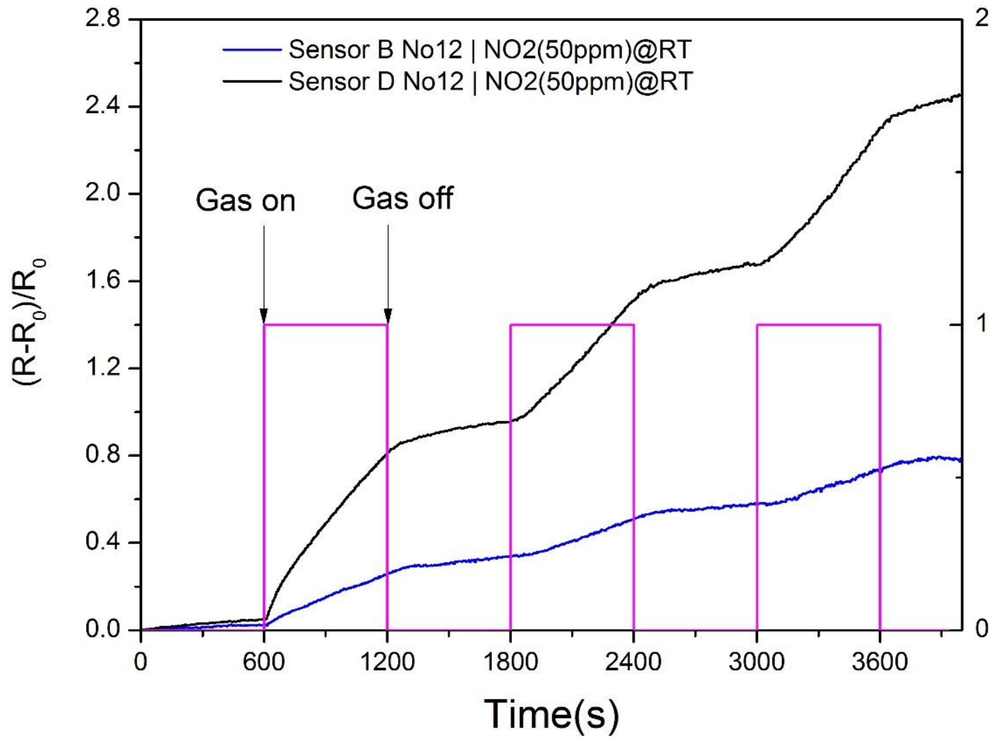
The Figure 33. *Response of the sensors from array No33 to 75 ppm of NH_3 09/05*



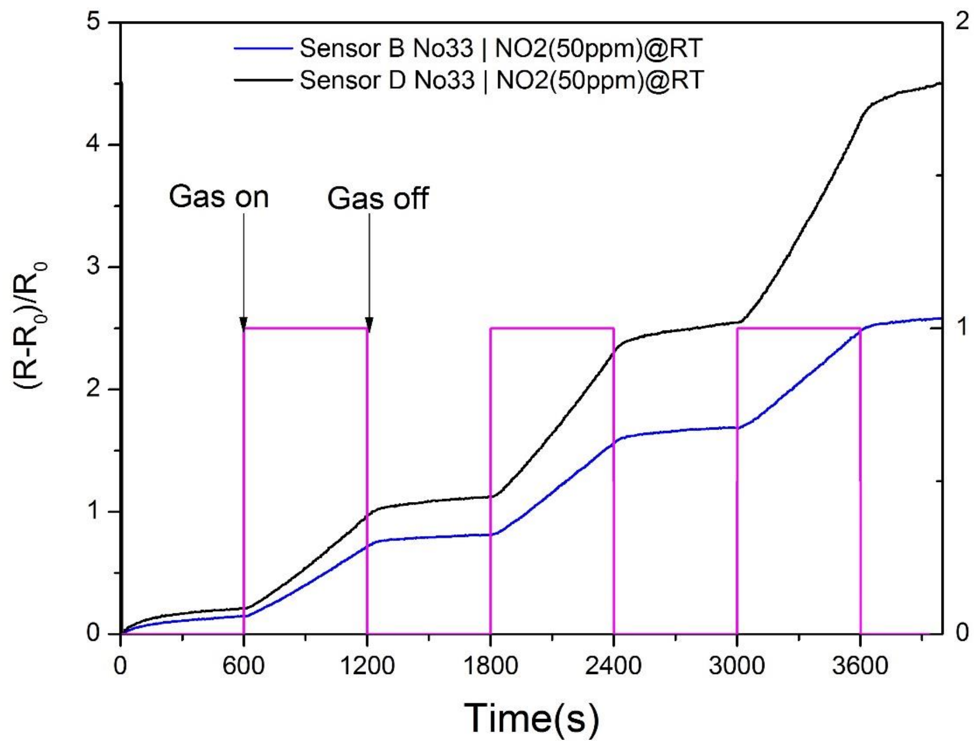
The Figure 34. *Changes in the response of the sensor from array No33 to 75 ppm NH3 over the period of 13 days.*

NO_2 response

In the Figure 35 and the Figure 36, we can see the response to the 50 ppm of NO_2 of the sensors number 12 and 33, respectively. In case of this analyte, the sensors showed additive response.



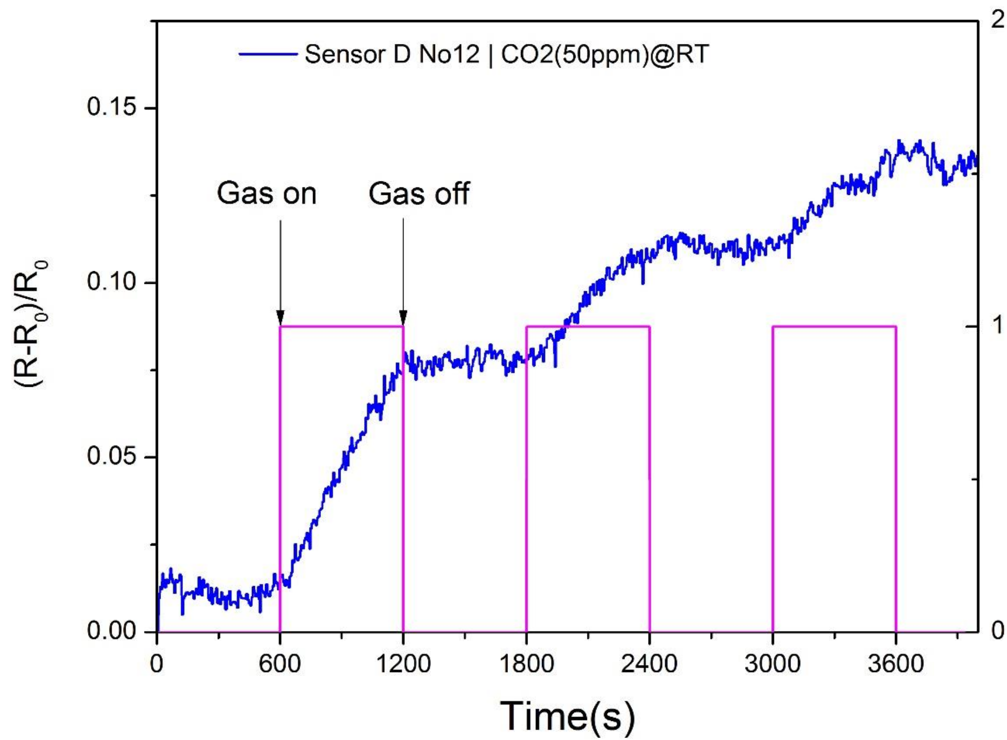
The Figure 35. *Response of the sensors from array No12 to 50 ppm of NO_2.*



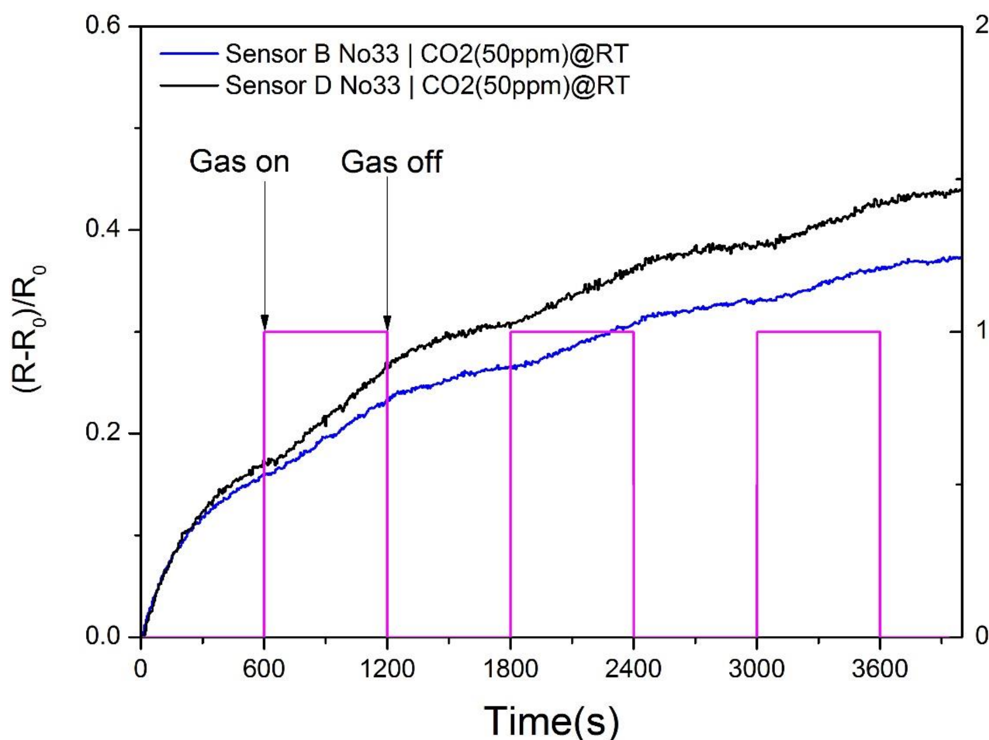
The Figure 36. *Response of the sensors from array No33 to 50 ppm of NO_2.*

CO_2 response

The response to the CO_2 can be seen in the Figure 37 and the Figure 38. As we can see from the Figure, the PEDOT:PSS based gas sensor No12 showed minimal additive response in order of percent in magnitude of to target analyte. The sensors from array No33 showed also minimal additive response, but since the resistance has been increasing also during the purge stage, the response is also the result of decreasing humidity.



The Figure 37. *Response of the sensors from array No12 to the 50ppm of CO_2.*



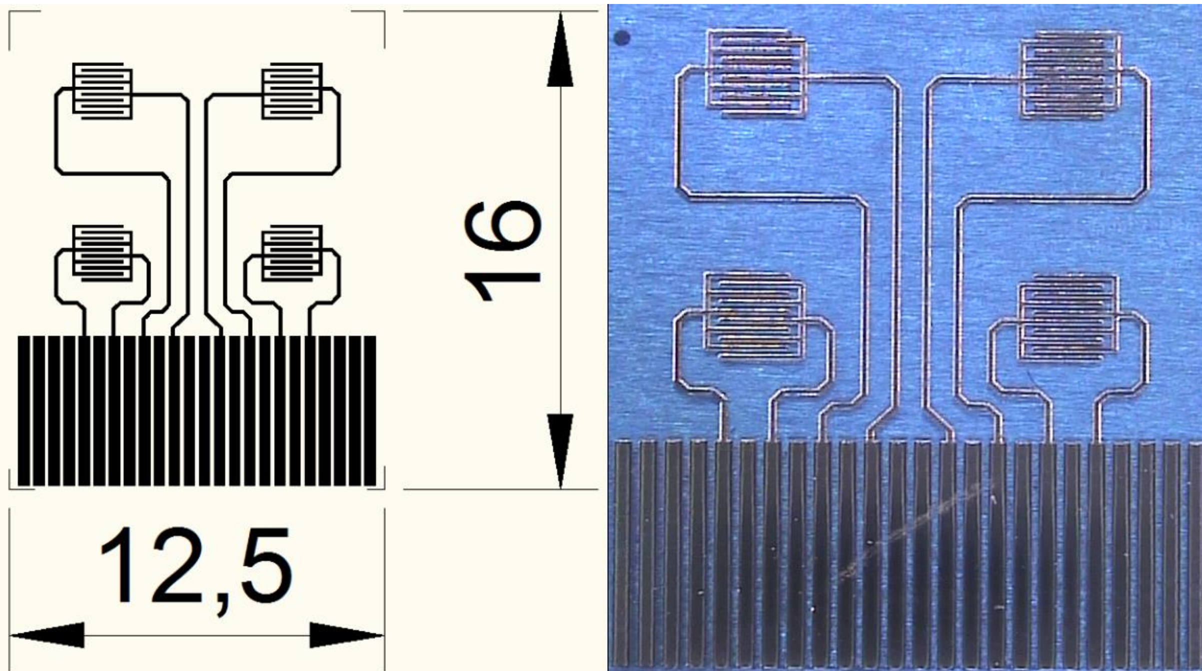
The Figure 38. *Response of the sensors from array No33 to the 50ppm of CO_2.*

3.3. Gas sensors on PET foil

This chapter describes fabrication processes of inkjet printed Ag IDE array on PET foil with an active sensitive layer with different modifications and measured responses of those sensors.

3.3.1. Preparation process

One of the goals of this thesis was to compare, inkjet printed IDE array with silver electrodes on PET foil, with a prefabricated IDE array with golden electrodes on FR4 substrate. So, there was an effort to create IDE array with the same dimensions as prefabricated Au array. The pattern for inkjet printing was designed in AutoCAD and after printing and measuring its dimensions correlated with result and modified to obtain needed spacing and size of individual electrodes. The final design can be seen in the Figure **39**. The sensor platform consisted of four IDE arrays with sensitive area approximately 2x2 mm in size. The individual electrodes have been 100 µm width with a 100 µm spacing. This platform has been printed used above mentioned DMP 2831 printer using silver nanoparticle ink Silverjet DGP-40LT-15C, from Advanced Nano Products. It is silver nanoparticle dispersion with 30-35 wt. % in triethylene glycol monomethyl ether, particle size ≤50 nm, adjustable viscosity in range of 10-17 cP and specific resistivity of 11-12 µΩ.cm

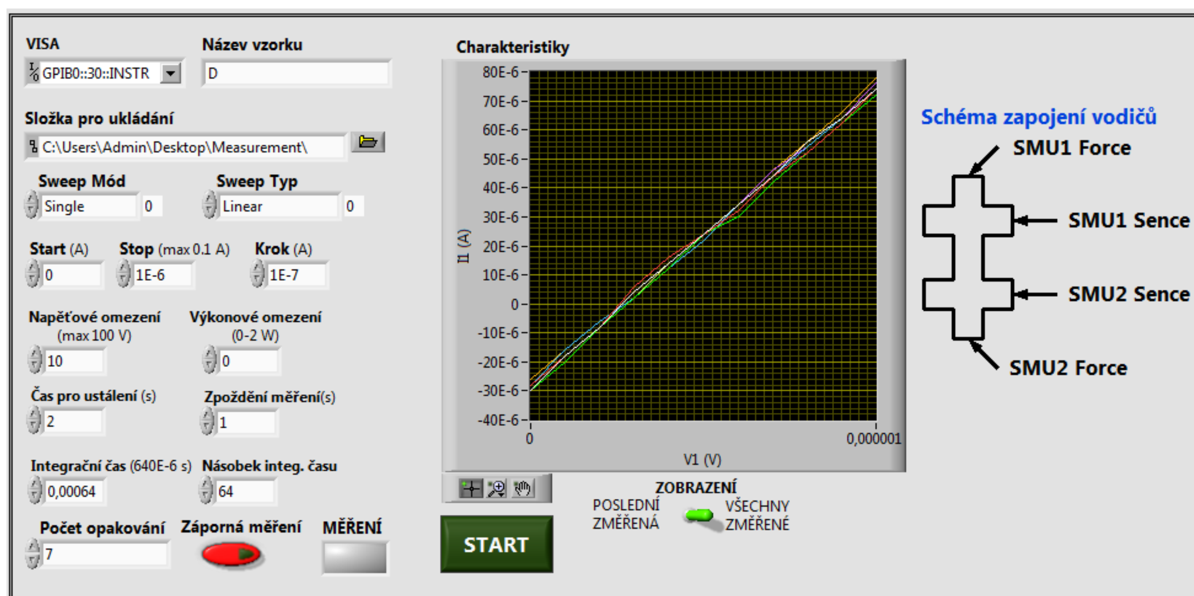


The Figure 39. *(Left) AutoCAD design used as a pattern for inkjet printing. Total dimensions 12,5 x 16 mm. (Right) Magnified image of prepared Ag silver array on PET substrate on the blue background.*

As a substrate has been used Novele^{TM} IJ-220 foil from Novacentrix. It is PET-based printed electronics substrate for low-cost and low-temperature applications. It is 140 ± 12 µm thick and weights 175 ± 10 g/m^2. The table with the setting of the cartridge can be seen in the Figure **X.** in the appendix. The speed of the ejected droplet was set to almost ideal 5.5 m.s^{-1}, the procedure of the droplet formation using single nozzle jetting can be seen in the Figure 54. in the appendix. The cartridge setting and the waveform of the membrane's driving signal can be seen in the Figures 52 and 53 in the Appendix To speed up the printing process of last samples, four nozzles has been used simultaneously, jetting using four nozzles can be seen in the Figure 54 in Appendix. After printing process, prepared arrays have been sintered inside the thermal oven for two hours at 120 ° C. The morphology of fabricated array has been investigated using AFM at FEE at CTU. The image obtained by atomic force microscopy (AFM) scan can be seen in the Figure 63. In the Appendix. Several sensitive layers have been deposited on those IDE arrays. PAni in form of emeraldine salt dispersed in water and xylene and solution of 0.8% PEDOT: PSS in water. Sensitive layers have been deposited by drop casting technique, using labopette pipettes with defined volume of the fluid drops. To deposit PEDOT:PSS sensitive layer, there has been effort to use inkjet printing technique as well, to obtain fully inkjet printable sensor. There have been difficulties with the nozzle clogging during this process. After dismantling the cartridge, unclogging of some nozzles was successful, after the cartridge head was sonicated in IPA for approx. 30 minutes. Unfortunately, the clogging repeated and after few cleaning cycles it wasn't possible to use the cartridge anymore. The images of the PEDOT:PSS layer and the difficulties with a jetting can be seen in the Figure 59 and the Figure 60 respectively.

3.3.2. Results of electrical and gas response characterisation

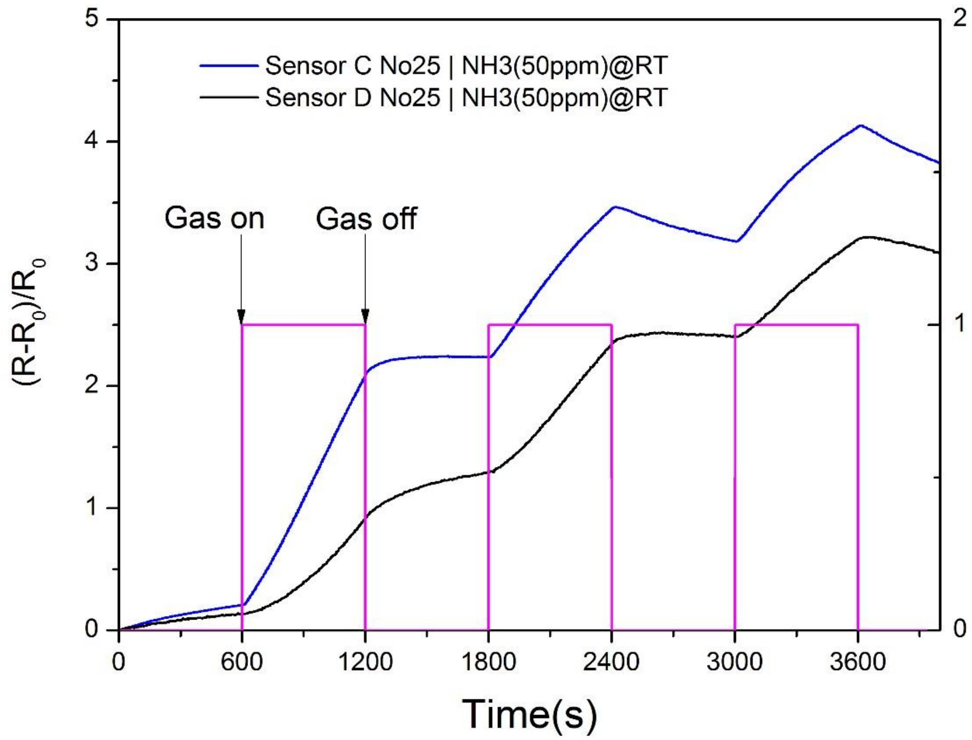
After deposition and annealing of the sensitive layer, electrical characterization has been conducted to measure VA characteristics of deposited film. This step has been conducted to prove the conductivity and linear behaviour of the sensitive layers.



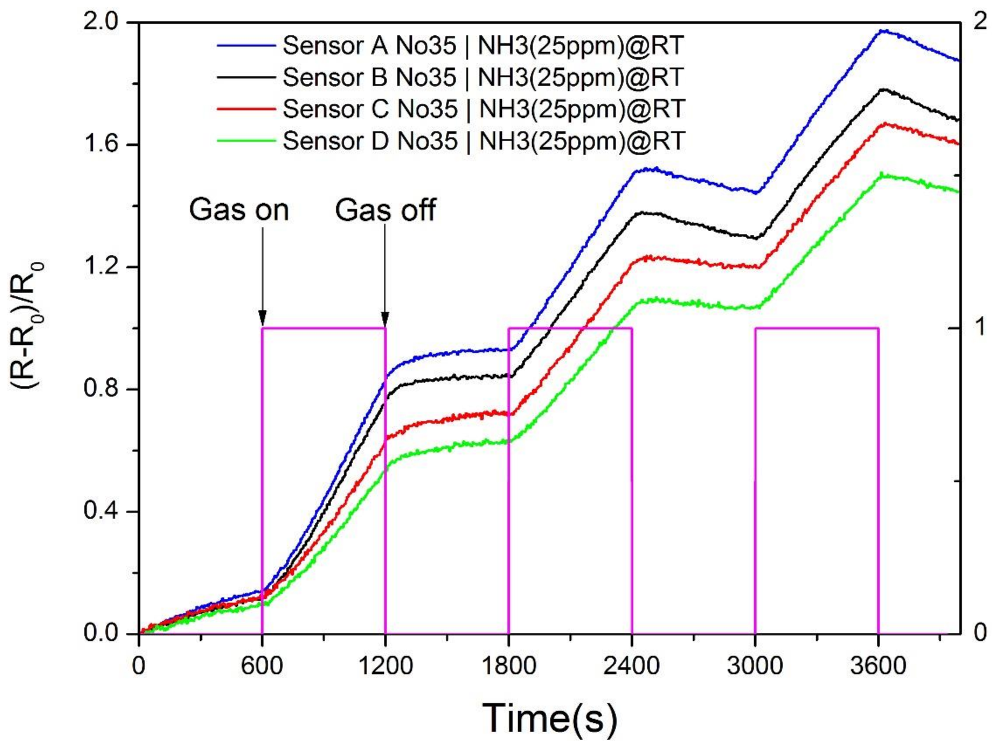
The Figure 40. VA characteristics of PAni on silver IDE array on PET substrate.

In next step, there has been measured the response of prepared device to the various concentration of the target analytes NH_3, NO_2 and CO_2. In the paragraphs bellow we can see the response of the polyaniline nanostructured layer to the NH_3. Some samples were prepared by dispersion of PAni in water, with various concentrations. Though, the results obtained from the sensors with this sensitive layer showed high response, they did not recover very well. In the Figure 41, we can see response of such a sensor No25 to 50 ppm of NH_3. Much better recovery of the sensors has been observed, when the polyaniline powder has been dispersed in xylene. Array with number 35 was prepared with PAni dispersion in Xylene and before drop casting deposition (3µl droplet) was sonicated for 10m at 30°C. The response of this sensor to 25/50/75 ppm concentration of NH_3 can be seen in the Figures 42,43 and 44 respectively.

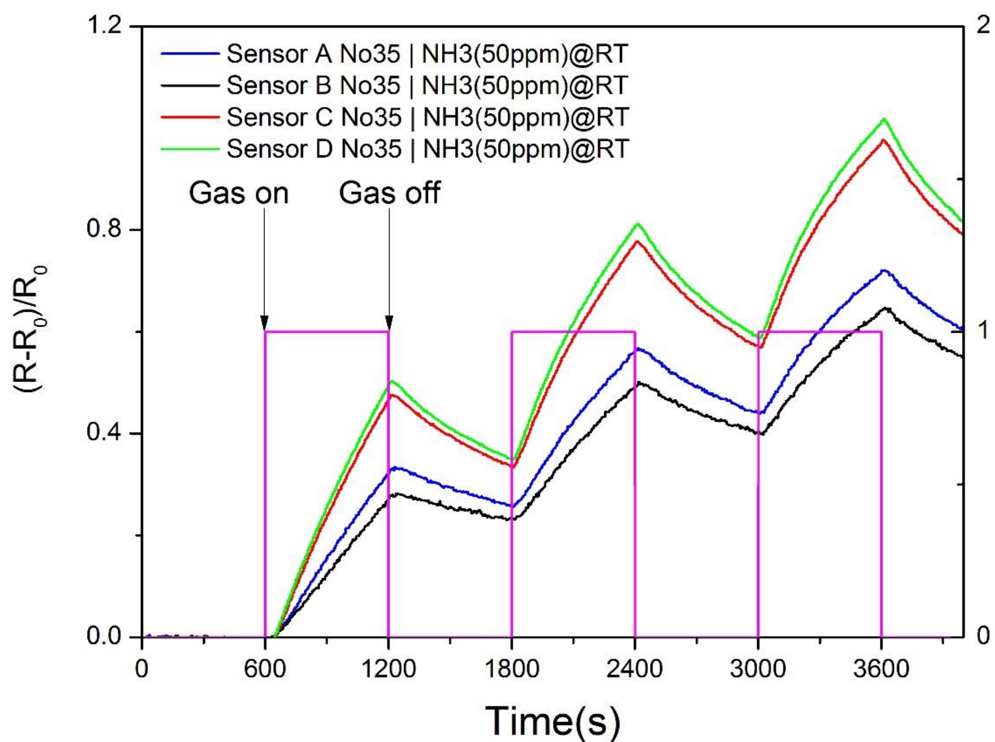
Since the PAni incline to aggregate rapidly, I had Idea to thoroughly sonicate the dispersion o PAni 5% wt in xylene to "tear" apart aggregates of PAni macromolecules. Before Drop casting, the dispersion was sonicated for 2 hours at 60°C and the drop volume was decreased to 2ul. There was no annealing, since the xylene's short evaporation time. The idea was to thoroughly disperse the PAni this fact was confirmed by the responses of the sample No37. The response of sensor array 37 to the 25/50/75 ppm can be seen in The Figures 45,46 and 47 respectively. In the Figure 48, we can see the comparison of responses of arrays No35 and 37 to the 75ppm of NH_3. The response of the sensor array No37 was also, measured with increasing gas concentration in three steps from 25ppm in the first cycle, 50ppm in second cycle, to 75 ppm of NH_3 in last cycle. In the Figure 49, we can see the response of the sensor array to those cycles.



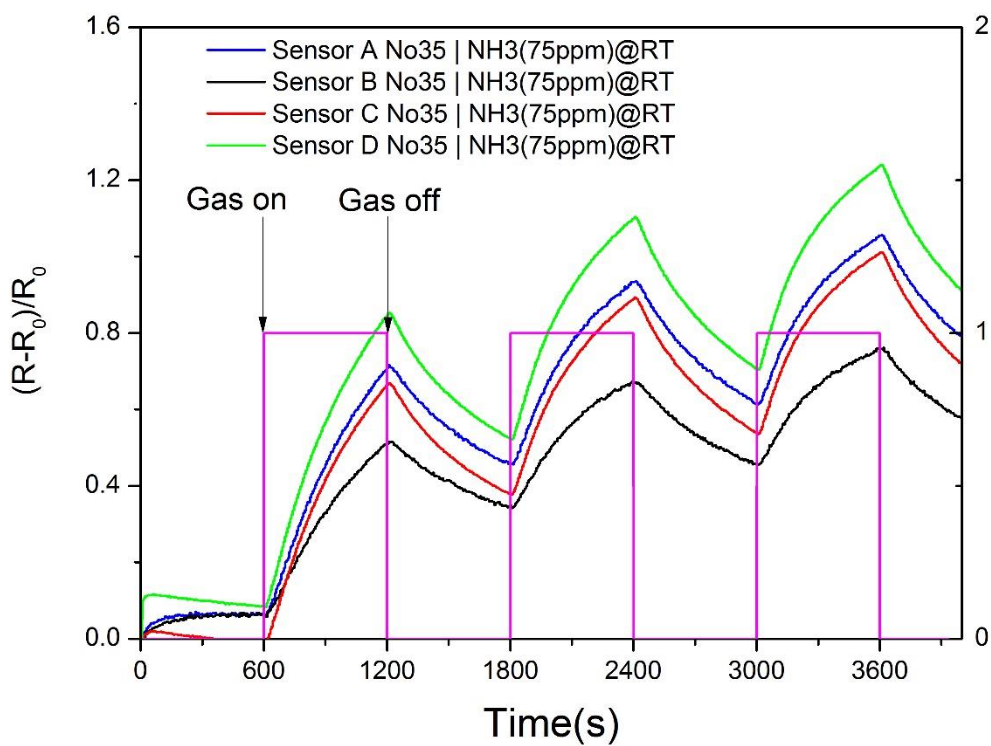
The Figure 41. *Response of the sensors from array No25 to the 50ppm NH_3.*



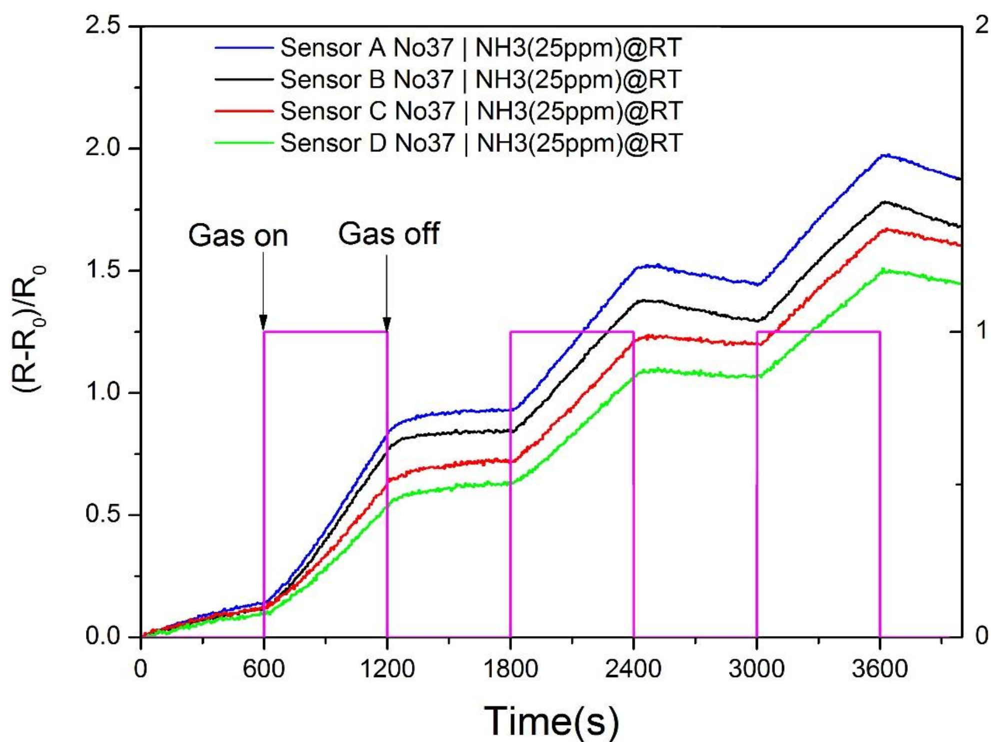
The Figure 42. *Response of the sensors from array No35 to the 25ppm NH_3..*



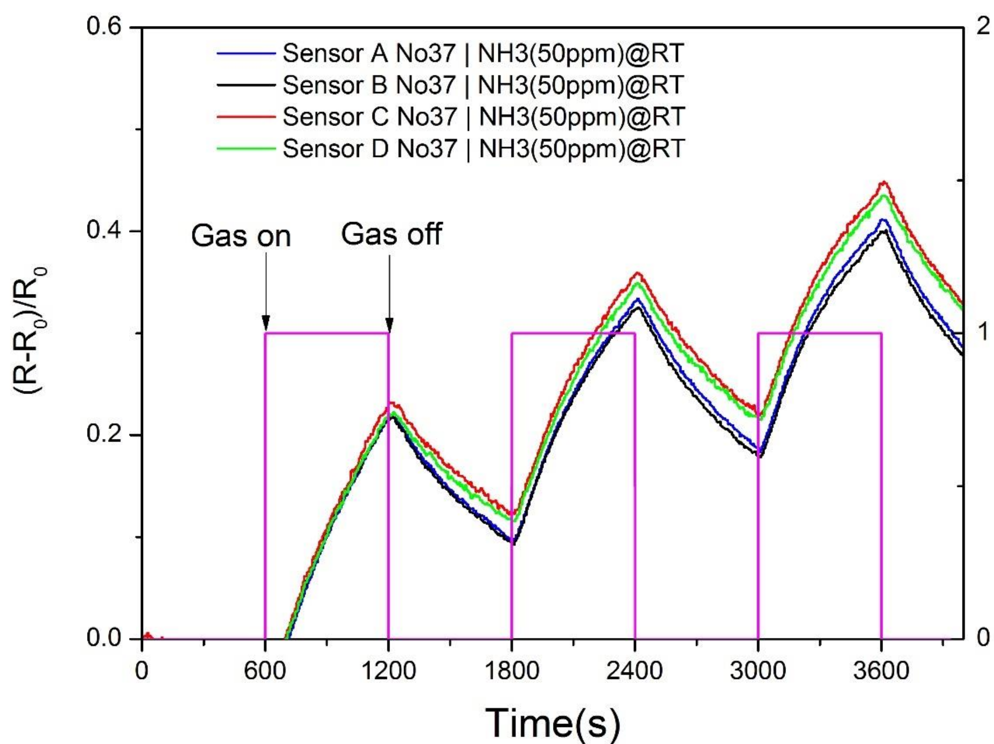
The Figure 43. *Sensor array No35, PAni response to 50ppm of NH_3.*



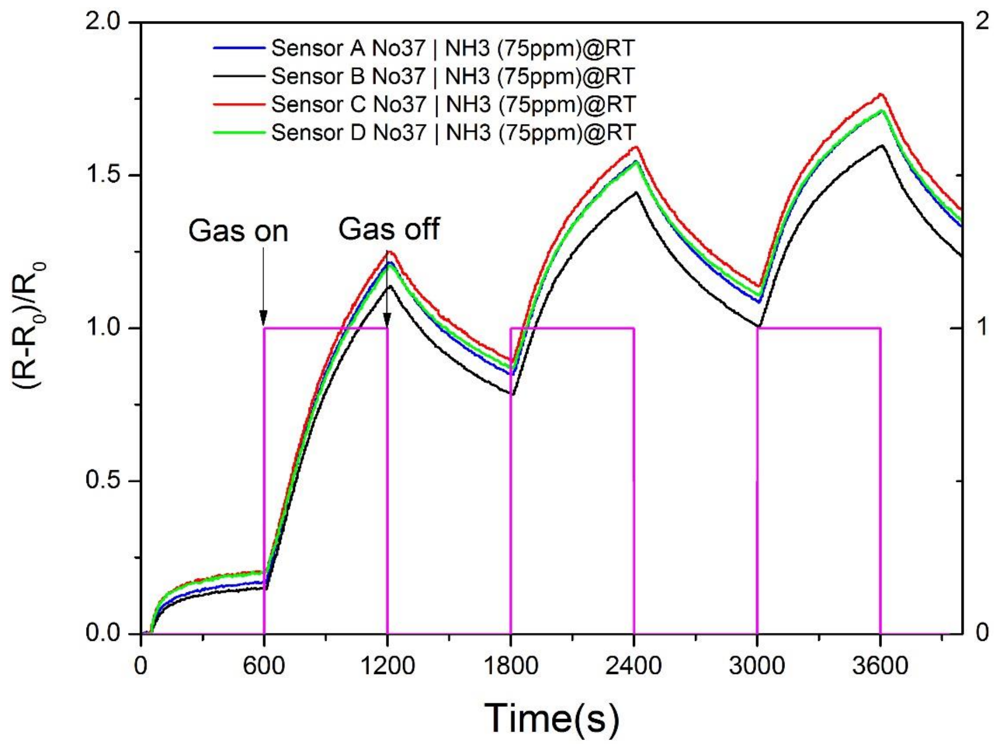
The Figure 44. *Sensor array No35, response to 75ppm of NH_3.*



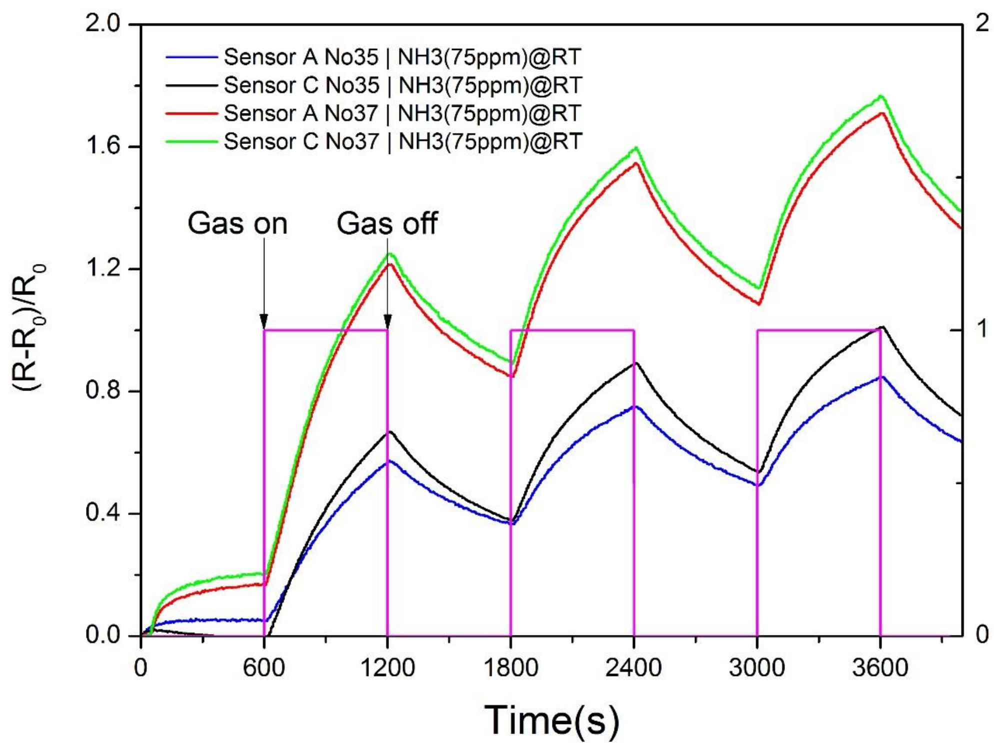
The Figure 45. *Sensor array No37, response to 25ppm of NH_3.*



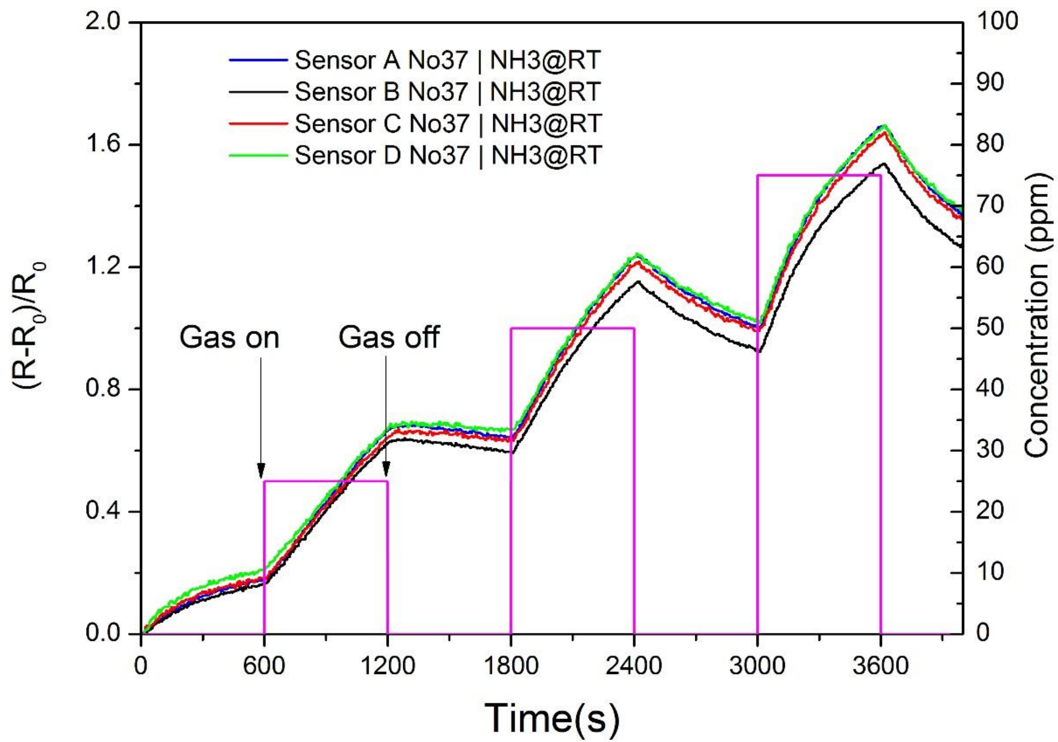
The Figure 46. *Sensor array No37, response to 50ppm of NH_3.*



The Figure 47. *Sensor array No37, response to 75ppm of* NH_3*.*



The Figure 48. *Comparison of responses of arrays No35 & No37 to the 75ppm of* NH_3*.*



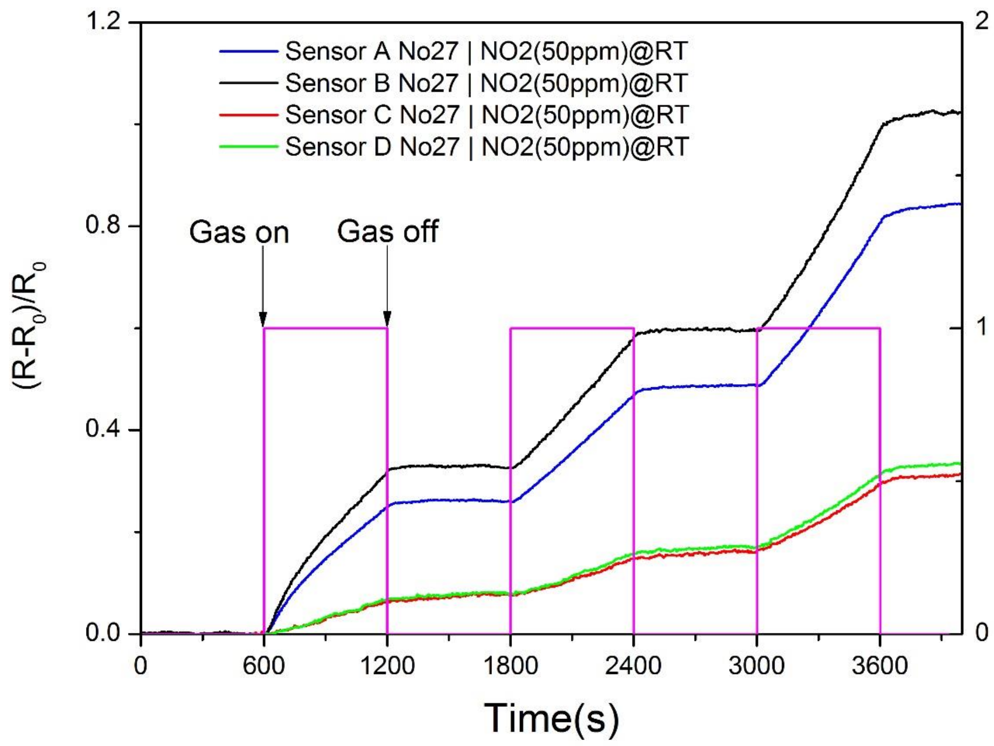
The Figure 49. *Sensor array No37, response to rising concentration of* NH_3

NO_2 response

In the Figure 50. We can see the response of the sensor array No 27 to the 50 ppm NO2. The sensor showed additive response, when the sensors resistance increased with exposure to the NO_2.

CO_2 response

Since, there was almost no response of inkjet printed sensors to CO_2 there are no responses included in this chapter.



The Figure 50. *Response of the sensor array No27 to the 50ppm of* NO_2

4. Conclusions

During practical part of this thesis, chemoresistive gas sensors have been prepared and the response to the target analytes have been measured. First group were gas sensors on prefabricated platform with golden IDE on FR4 substrate. Two types of sensitive layers have been deposited on this platform, polyaniline (emeraldine salt) and PEDOT:PSS. The response of those two sensor arrays to NH_3, NO_2 and CO_2 have been measured. Those sensors showed good sensitivity and a response time to the NH_3 analyte, although during the 10 minutes cleaning cycle (purge with N_2) they did not fully recover resulting in the drift in the response of the measured sensors. There has been also conducted measurement of response of those two sensors to NO_2 and CO_2 gases. They showed additive behaviour to those two gases, without any recovery response during purge stage of N_2.

The second group of prepared gas sensors, were inkjet printed chemoresistive gas sensors with silver IDE on a flexible PET based foil. Those sensors were designed to match the dimensions with a golden IDE and were successfully inkjet printed by Dimatix DMP 2831 printer. Different dispersions of polyaniline as a sensitive layer have been deposited on those platforms. There was an effort to inkjet print PEDOT:PSS. Unfortunately, there were problems with clogging of nozzles and even after cleaning the cartridge it was not possible to continue with this technique, since the cartridge was inevitably damaged. Because of the cost of the cartridge and unsatisfying results with PEDOT:PSS, probably due to degradation, I did not continue with this approach. Also, I conducted few experiments of deposition by spin coating, but it wasn't successful. The sensitive layers of PAni have been deposited using drop casting method and different dispersion in demineralised water and xylene were used for deposition. The sensors showed good sensitivity and response time during exposure. The recovery time was longer then response so there was a drift in the response during each cycle. Although I can say that the chemoresistive type of inkjet printed flexible gas sensor for NH_3 have been successfully manufactured as a part of this thesis. The response of the sensors improved when the PAni dispersion was properly ultrasonicated before deposition. The setbacks of those sensors are long recovery times and big differences in response of individual sensors, which was probably caused by non-uniformity of sensitive thin film deposited by drop casting technique. Example of IJP prepared gas sensor can be seen in the Figure 56 in the Appendix.

In the future, I would like to optimize the printing process for PEDOT:PSS as well as for PAni dispersion, so fully IJP sensor with a defined dimensions of sensitive layer could be manufactured. Another interesting development would be in creating hybrid materials, such as polymer with organic metals or carbon nanostructures. I would also like to develop procedure for successful inkjet printing on ceramic substrate such as corundum (97%Al2O3) and other materials with higher thermal stability. This would allow the use of dispersions containing solvents such as ethylene glycol with a high boiling point.

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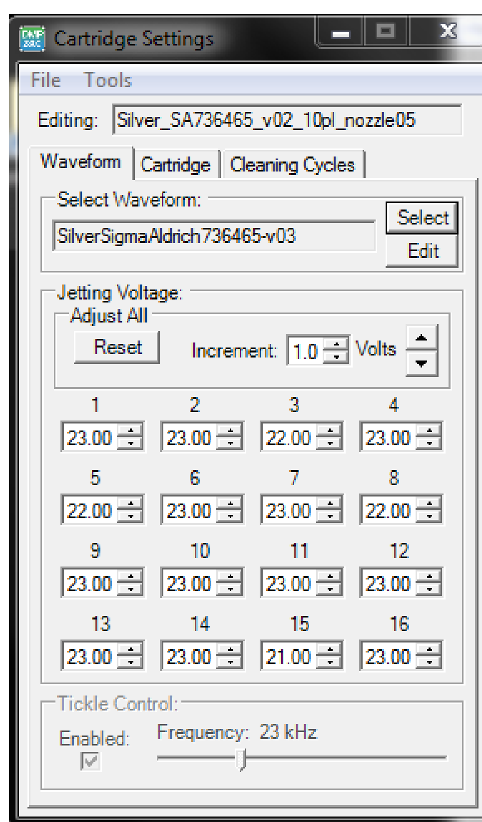
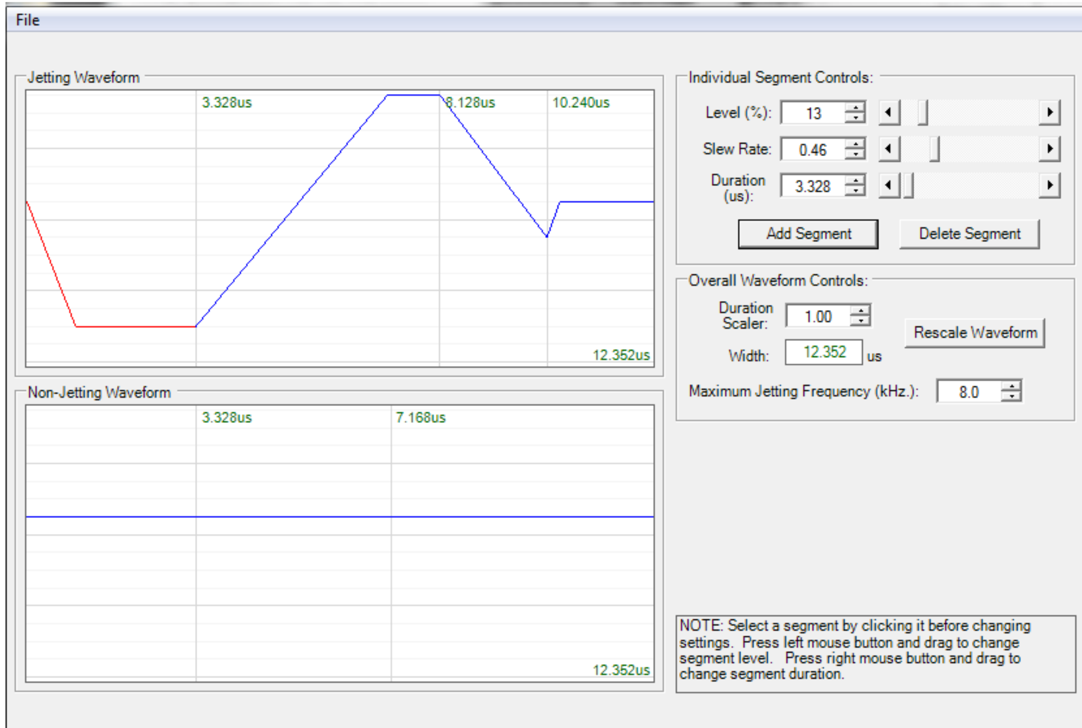
Appendix

Inkjet printing process

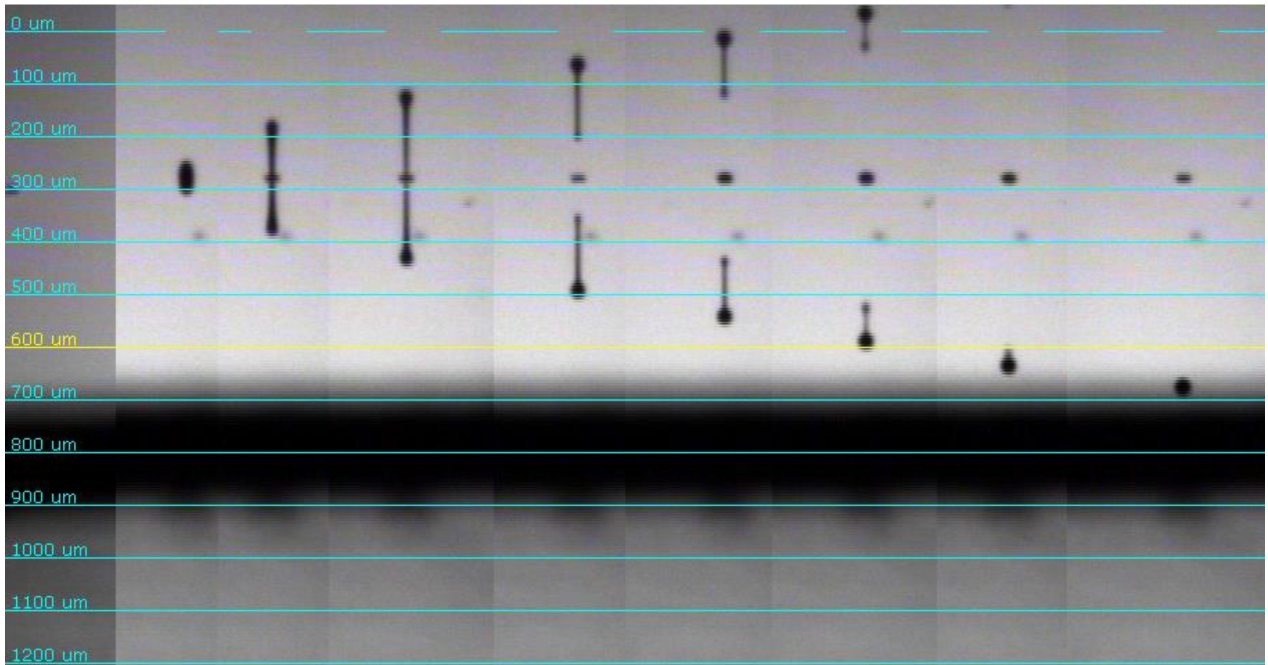
The Figure 51. *Photo of Dimatix DMP2831 inkjet printer workspace.*



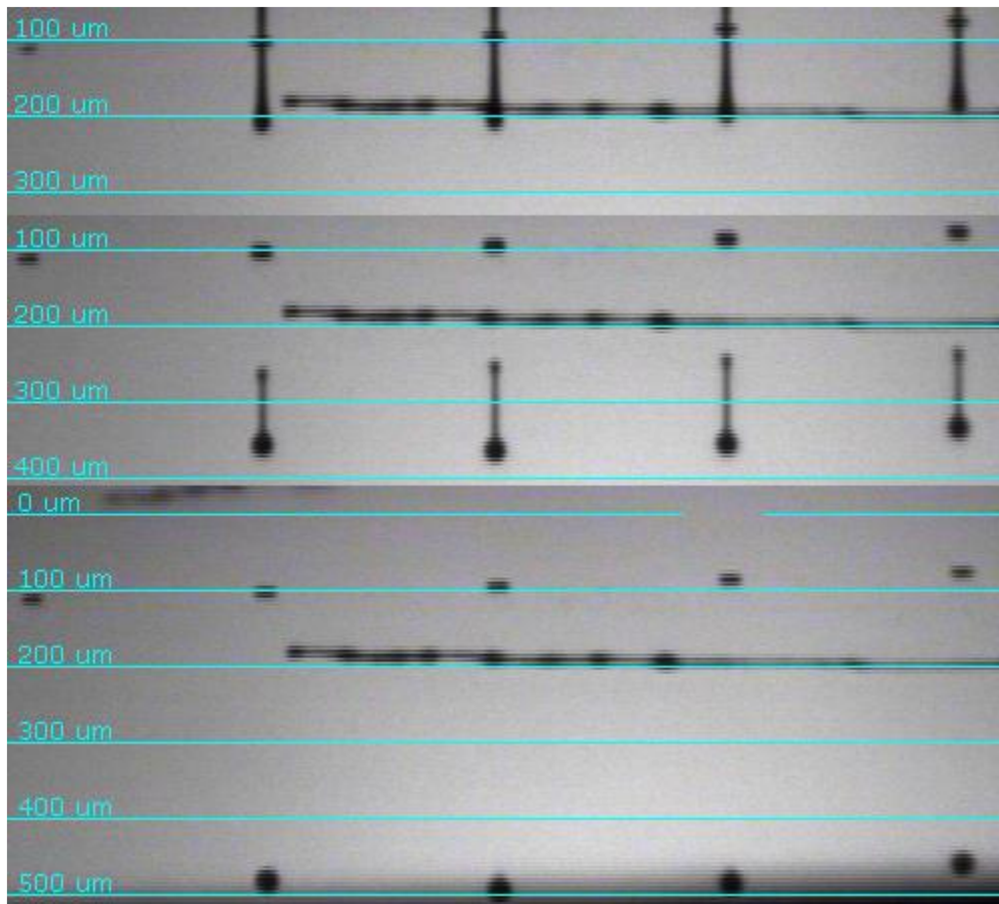
The Figure 52. *Print screen of cartridge setting for Silver Ink in DDM.*



The Figure 53. *Waveform of file for Silver Ink printing*



The Figure 54. *Jetting of silver ink droplet by Dimatix DMP 2831, using single nozzle, drop speed 5.5 m/s*



The Figure 55. *Inkjet printing using four nozzles. Jetting of silver ink by Dimatix DMP 2831.*

Silver nanoparticle ink printed IDE array on PET foil

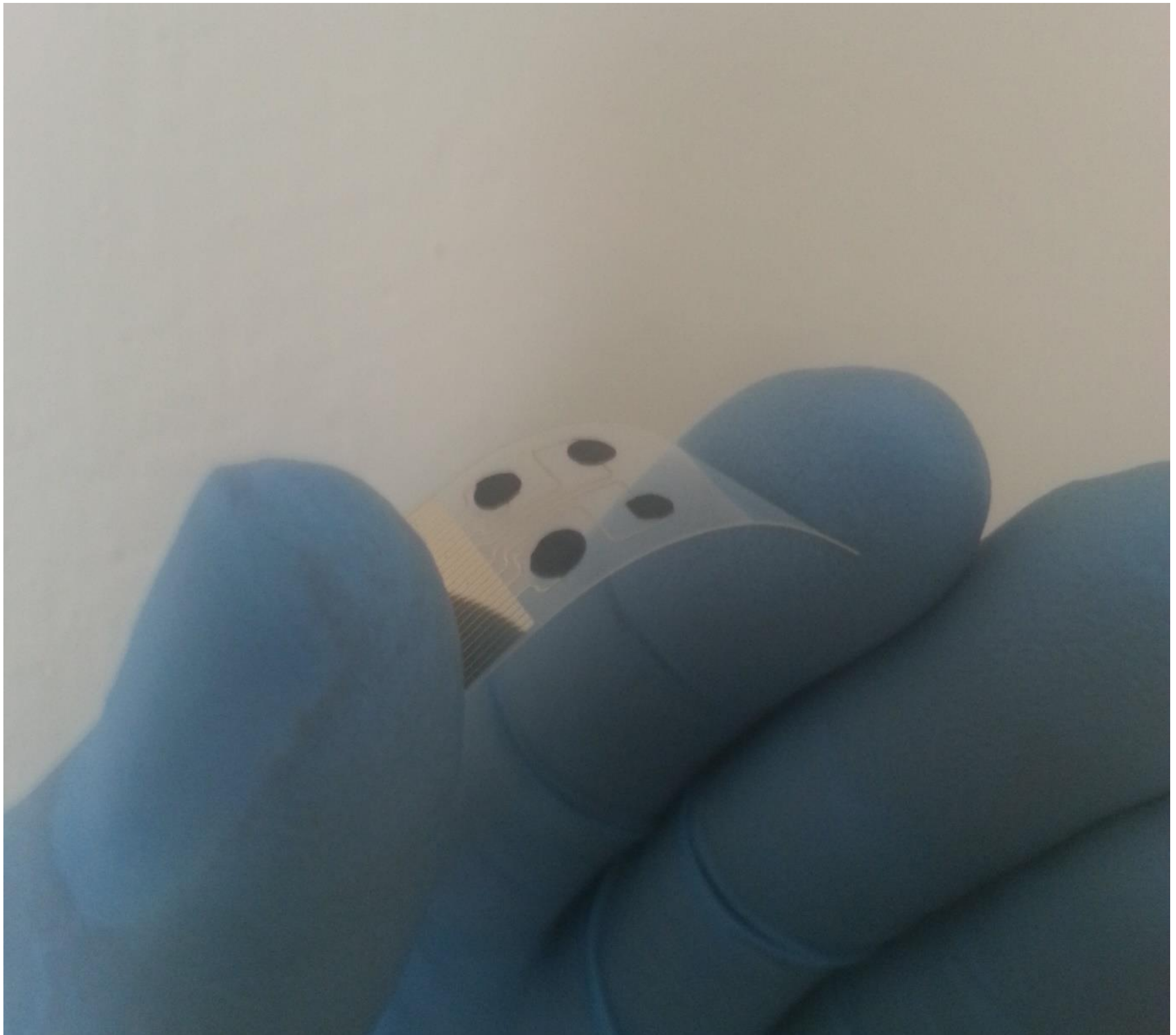
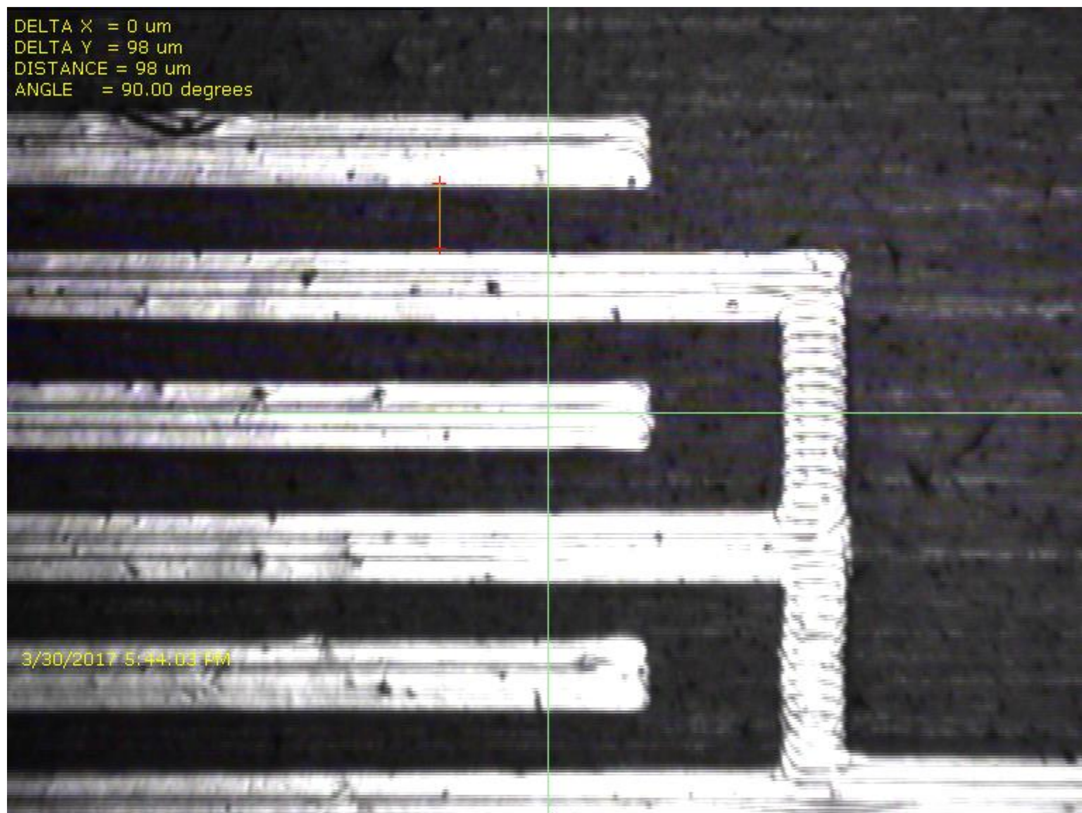


Figure 56. *Photo of IJP silver IDE on flexible PET foil*



The Figure 57. *Detail of silver IDE with marked dimensions taken by DMP 2831's fiducial camera.*

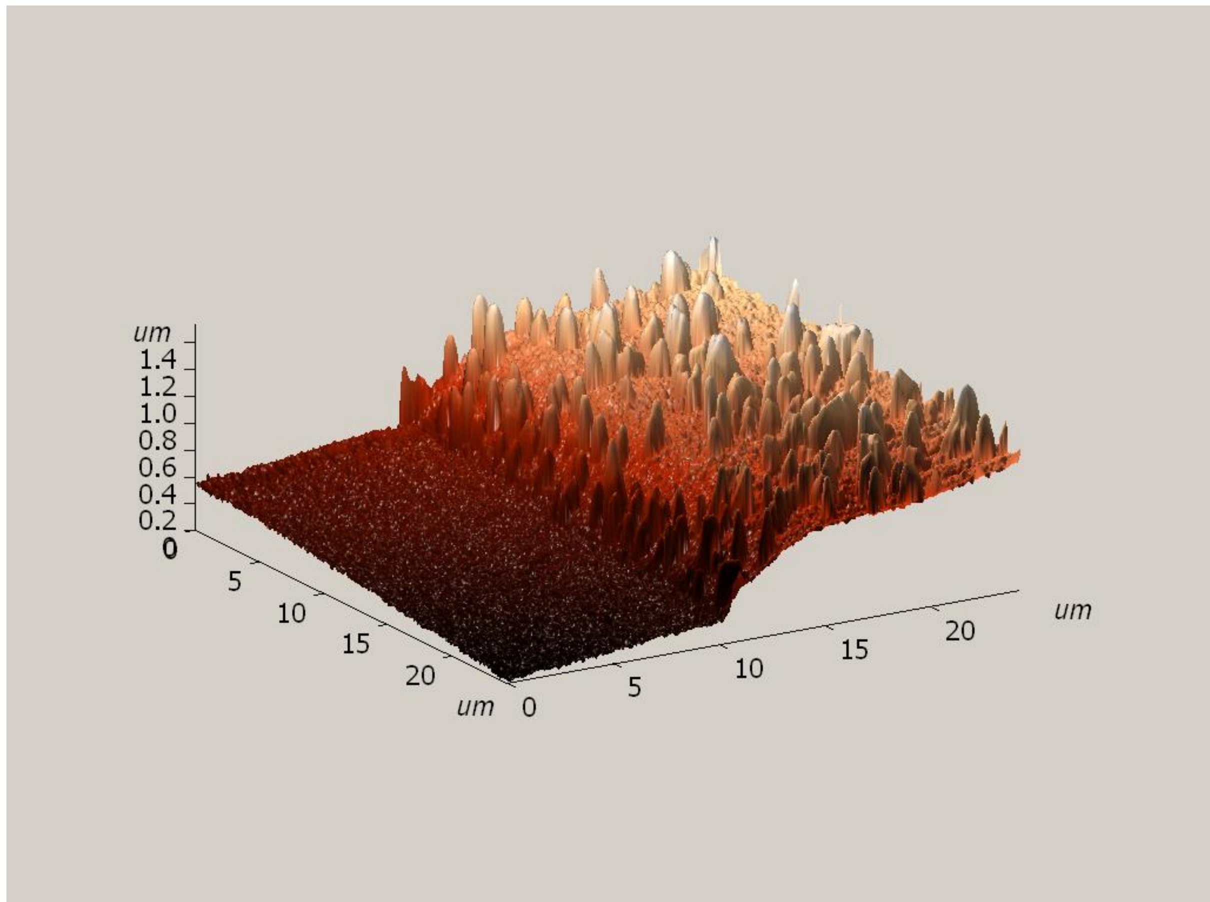
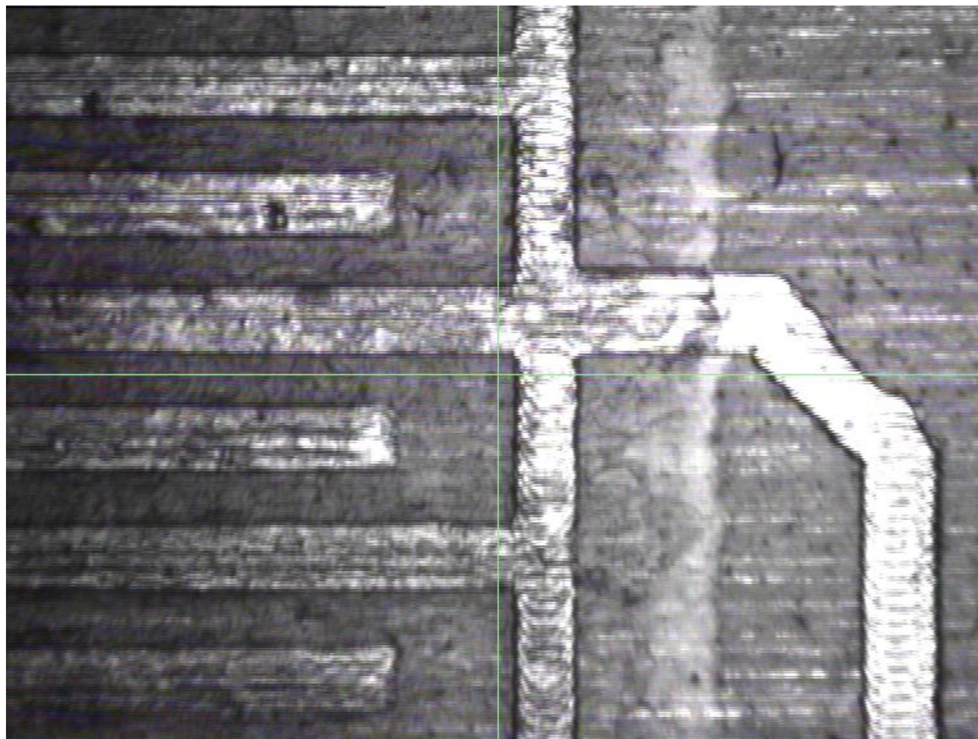
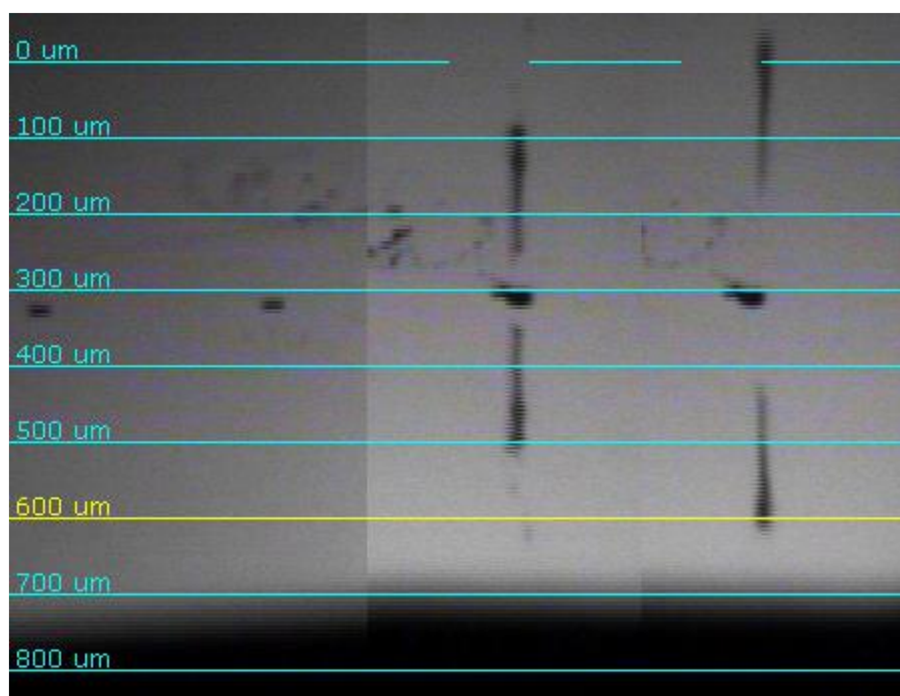


Figure 58. *The AFM image of IDE silver array on PET foil.*

PEDOT:PSS printing difficulties

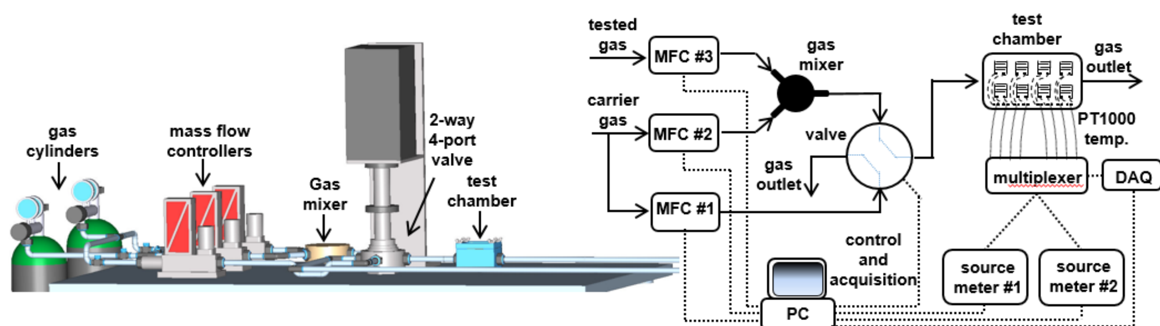


The Figure 59. *Image of inkjet printed PEDOT:PSS layer on PET substrate with Ag IDE.*

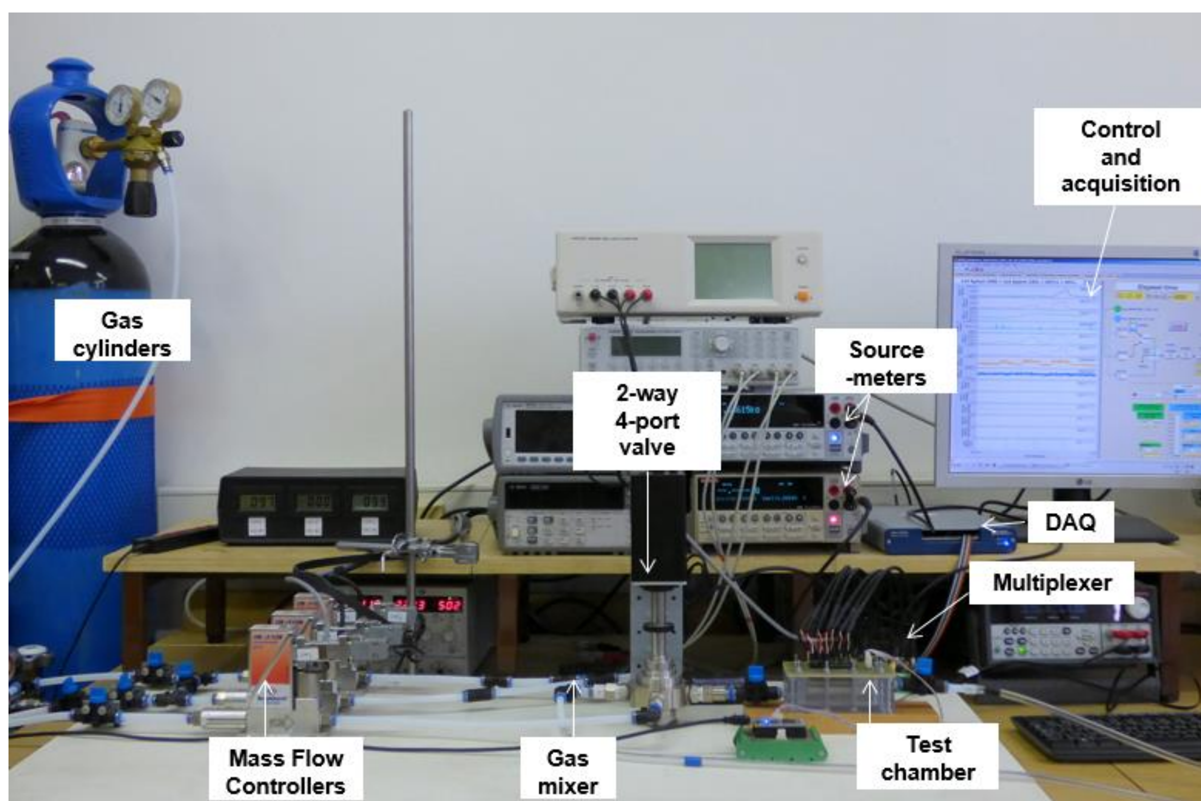


The Figure 60. *Images of faulty jetting characteristics during the PEDOT:PSS inkjet printing caught through drop watcher camera*

Gas response measuring setup

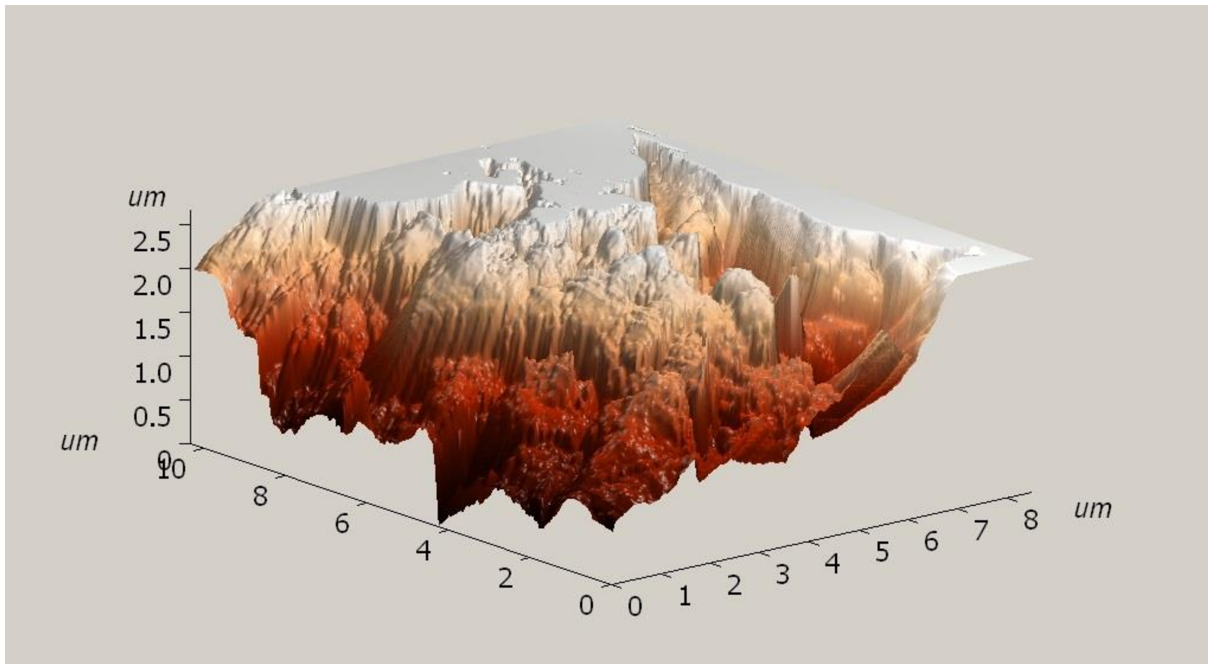


The Figure 61. *Schematic diagram of gas response measuring setup.*



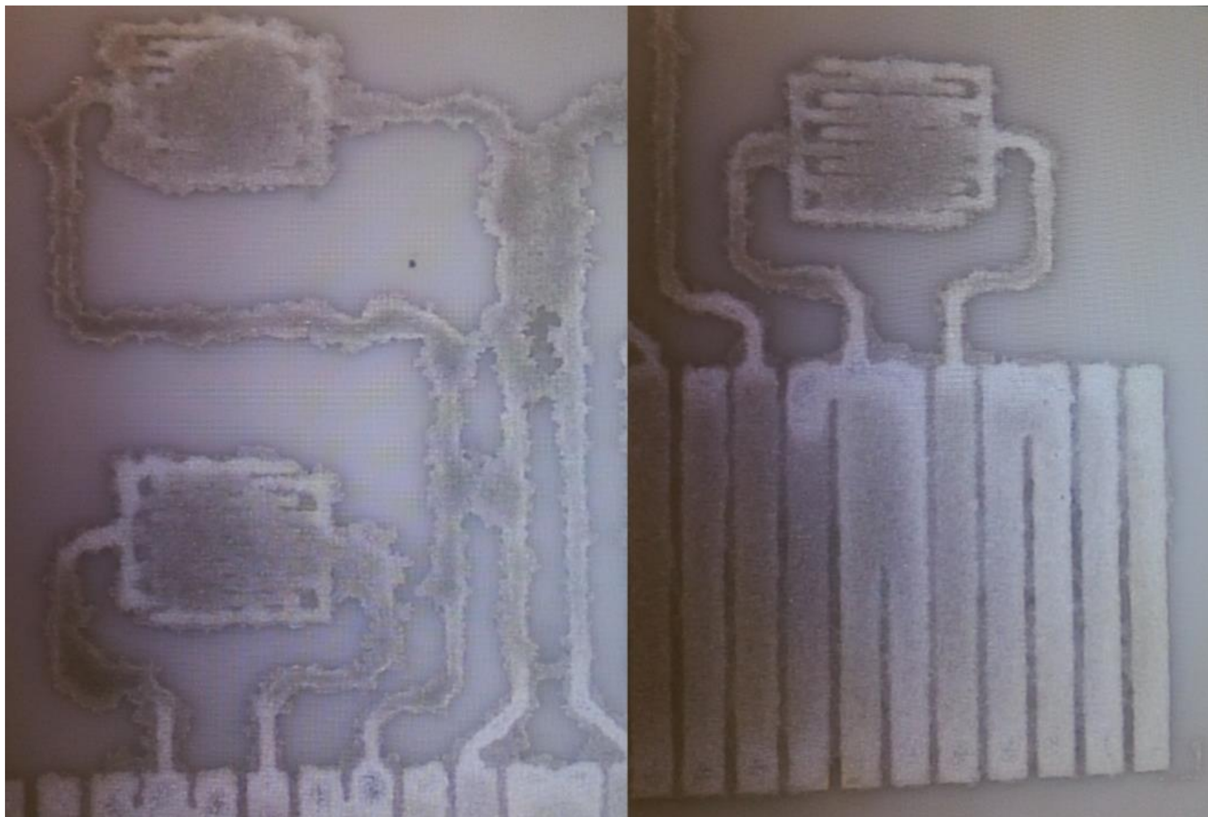
The Figure 62. *Photo of gas response measurement setup*

Polyaniline (emeraldine salt) thin film surface characterization



The Figure 63. *AFM image of PAni sensitive layer.*

Inkjet printing on ceramic substrate



The Figure 64. *Attempts of IJP on ceramic substrate (Al2O3 – corundum).*