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New Gas Sensor for Exhaust Emissions of Internal Combustion Engines

Sari Lakkis

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Université de Versailles Saint Quentin en Yvelines

Ecole Doctorale Sciences et Technologies de Versailles, N° 539

Pour l'obtention du grade de

Docteur de l'Université de Versailles Saint Quentin en Yvelines

New Gas Sensor for Exhaust Emissions of Internal Combustion Engine

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Spécialité : Electrique, Electronique, Photonique et Systèmes

Le 17 Décembre 2014

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Abstract

Gases represent one of the most important key measurands in many industrial and domestic activities. One of the most important applications of gas sensing is in the concentration measurement of exhaust emissions in internal combustion engines. The variety of gases emitted by these engines and the necessity for a precise measurement of their concentrations are the major incentives for researchers to develop gas sensors that are not only limited to a certain type of gases but to a variety of gases. The most interest gases include CO, NO, NO₂, NH₄, SO₂, CO₂, CH₄ and other hydrocarbons. These gases can be harmful to human health if present beyond a certain concentration.

The analysis of exhaust emissions of internal combustion engines has traditionally been achieved in laboratories using bulk gas analyzers and costly equipments. In order to create a system which can do the work of these analyzers, a sensor that can measure the concentration of multiple gases at the same time is needed. Instead of using a sensor for each gas which is costly and introduce another complexity to the analysis procedure due to the different technologies that are used in the detection of different types of gases. This directly translates into loss of financial and human resources that could otherwise be productively used. In an effort to remedy this situation, this dissertation proposes an alternate approach that uses one sensor to analyze multiple gases simultaneously. This has a significant potential in reducing the aforementioned complexity, size and data collection tasks, and at the same time can lower the cost of the overall system.

This dissertation presents the design, methodology, and development of a new method for gas concentration measurement using digital image processing through modeling the color mixing of light emissions in gas discharge tube. The application of the inverse model allows us to get the percentages of each gas in a mixture of up to four gases knowing already the color of emission of the whole mixture and the color of emission of each gas alone. It also discusses the miniaturization potential of some of the methods that are promising in the ability of their miniaturization but suffer from different problems. A comparison is also done among the miniaturized sensors in terms of different parameters like sensitivity, selectivity, cost and other terms.

In achieving the research objectives, major technical challenges such as color mixing modeling, imaging sensor calibration, and measurements' error handling have been successfully identified and addressed.

Résumé

Dans plusieurs applications industrielles et domestiques, les gaz sont des éléments de mesure importants. L'une entre elles est la mesure de la concentration des gaz d'échappement des moteurs à combustion interne. La variété des gaz émis par ces moteurs et la nécessité d'une mesure précise de leurs concentrations sont les principales motivations des chercheurs quant au développement de capteurs à gaz. Ces derniers peuvent détecter un ou plusieurs types de gaz tels que CO, NO, NO₂, NH₄, SO₂, CO₂, CH₄ et d'autres hydrocarbures, car ils sont nocifs pour la santé humaine au-delà d'une certaine concentration.

L'analyse des gaz d'échappement des moteurs à combustion interne a été traditionnellement réalisée en laboratoires en utilisant des analyseurs de gaz en vrac avec des équipements coûteux. Afin de créer un système capable de réaliser le travail de ces analyseurs, un capteur pouvant détecter plusieurs gaz simultanément est indispensable pour en mesurer la concentration. En effet, utiliser un capteur pour chaque gaz est coûteux et peut amener à des procédures complexes d'analyse en raison des différentes technologies utilisées. De plus, l'utilisation de multiples capteurs donne lieu à une perte de ressources financières et humaines. Pour pallier ce problème, une approche alternative proposée dans cette thèse consiste à utiliser un seul capteur pour l'analyse simultanée des différents gaz. Cette approche contribue à réduire la complexité des analyses, la taille et la collecte de données des mesures de gaz mentionnés précédemment. Elle permet également la baisse du coût de l'ensemble du système des mesures.

Cette thèse présente la conception, la méthodologie et le développement d'une nouvelle approche pour la mesure de la concentration de gaz utilisant le traitement d'images numériques à travers la modélisation du mélange des couleurs d'émission de lumière dans le tube de décharge de gaz. L'application du modèle inverse permet d'obtenir le pourcentage de chaque gaz dans un mélange contenant jusqu'à quatre gaz connaissant la couleur d'émission du mélange et la couleur d'émission de chaque gaz. Nous discutons aussi le potentiel de certaines méthodes quant à leurs propriétés de miniaturisation et leurs limites. Une comparaison entre les différents capteurs miniaturisés est réalisée en termes suivant la sensibilité, la sélectivité, le coût et d'autres conditions. Pour atteindre les objectifs de recherche, les problèmes techniques rencontrés tels que la modélisation de mélange des couleurs, l'étalonnage de capteurs pour l'acquisition d'images, et le traitement des erreurs de mesures ont été identifiés et des solutions ont été proposées.

To My Family

And

To The Memory of Alaa Kharsa

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Abstract

Gases represent one of the most important key measurands in many industrial and domestic activities. The need to detect single gas or a group of gases at the same time varies from one application to another. One of the most important applications of gas sensing is in the concentration measurement of exhaust emissions in internal combustion engines. The variety of gases emitted by these engines and the necessity for a precise measurement of their concentrations are the major incentives for researchers to develop gas sensors that are not only limited to a certain type of gases but to a variety of gases. The most interest gases include CO, NO, NO₂, NH₄, SO₂, CO₂, CH₄ and other hydrocarbons. These gases can be harmful to human health if present beyond a certain concentration.

The analysis of exhaust emissions of internal combustion engines has traditionally been achieved in laboratories using bulk gas analyzers and costly equipments. In order to create a system which can do the work of these analyzers, a sensor that can measure the concentration of multiple gases at the same time is needed. Instead of using a sensor for each gas which is costly and introduce another complexity to the analysis procedure due to the different technologies that are used in the detection of different types of gases. This directly translates into loss of financial and human resources that could otherwise be productively used. In an effort to remedy this situation, this dissertation proposes an alternate approach that uses one sensor to analyze multiple gases simultaneously. This has a significant potential in reducing the aforementioned complexity, size and data collection tasks, and at the same time can lower the cost of the overall system.

This dissertation presents the design, methodology, and development of a new method for gas concentration measurement using digital image processing through modeling the color mixing of light emissions in gas discharge tube. The application of the inverse model allows us to get the percentages of each gas in a mixture of up to four gases knowing already the color of emission of the whole mixture and the color of emission of each gas alone. It also discusses the miniaturization potential of some of the methods that are promising in the ability of their

miniaturization but suffer from different problems. A comparison is also done among the miniaturized sensors in terms of different parameters like sensitivity, selectivity, cost and other terms. In achieving the research objectives, major technical challenges such as color mixing modeling, imaging sensor calibration, and measurements' error handling have been successfully identified and addressed.

**New Gas Sensor for Exhaust Emissions of Internal
Combustion Engines**

1. Introduction

This research objective was to find a new gas sensor used especially in measurement of the concentrations of exhaust emissions of internal combustion engines. The variety of gases emitted by these engines and the necessity for a precise measurement of their concentrations are the major incentives for researchers to develop gas sensors that are not only limited to a certain type of gases but to a variety of gases. The most interest gases include CO, NO, NO₂, NH₄, SO₂, CO₂, CH₄ and other hydrocarbons. These gases can be harmful to human health if present beyond a certain concentration [1].

Gas sensors have gained a lot of attention in the last decades due to their wide role ranging from industrial applications to atmospheric monitoring. Gas sensing methods are numerous due to the variety of physical parameters that can be measured and can reflect the gas concentration. However, each technology has its strengths and weaknesses and there is no one perfect solution for all applications.

The principle function of a gas sensor is to obtain quantitative or qualitative information about specific gases in a selected ambient; *quantitative information* like concentrations and partial pressures of specific components or classes of chemical compounds with similar properties such as their flammability in air and *qualitative information* like the presence or absence of certain odors, detection of organic volatiles exceeding a certain threshold-limited value (TLV), or the lower explosive limits (LEL) of combustible gases.

Depending on the application, the gas sensor has to be carefully designed taking into consideration many factors that affect its performance. The improvement of the sensor sensitivity, selectivity, response time, cost, power consumption and size are the basic goals for research in the field of gas sensing.

In order for a gas sensor to be used effectively in real life applications, the initial and operation costs must be taken into consideration. The miniaturization of the gas sensor can decrease both the cost and power consumption of the sensor, this opened the door toward using gas sensors in new applications and on-site measurements that were only possible in laboratories. Such sensors

are intensively searched and many miniaturized sensors have been made [2]. Most of the sensing technologies can lead to a miniaturized sensor with each method has its own pros and cons, however no single technology is the best candidate for miniaturization and it depends on the factors that are mostly important for the application.

1.1 Importance of the Research Activity

Gas sensing is a critical component of constructing and operating of a wide range of applications. A good sensor that can provide fast and accurate measurements of different kind of gases is a key to significant saving in time and costs, and at the same time results in providing important information for decision making and control systems. The ability of measuring concentrations of several gases at the same time with minimum amount of time spent on measurement process, that in many applications are not directly related to the scope of the project, is an important factor in realizing many real-life projects like pollution monitoring or real time industrial control systems. This ability to use one sensor for measuring several gases concentrations at the same time reduces the cost and complexity of the whole operation. This is a major incentive for using such sensor in applications like measuring emissions' concentrations in internal combustion engines in order to identify and measure gases produced during engine examination and testing or during the course of the real operation. This can identify potential engine related issues and problems that may cause unexpected failure or fuel consumption inefficiency, and plan ahead of time to avoid during actual operation.

For a relatively small number of distinct gases to be measured in a certain application the operation, interpreting, verifying, and validating of the results of measurements can be done manually using a sensor for each gas and numerical tools. However, as the size of the measured gases increases and with the limitation caused by size, cost, power consumption and the need for automating the whole process of measurement, all of these make the presence of one low cost sensor that can measure several gases simultaneously turns into a crucial need.

Amongst several approaches of gas sensing methods, Optical Emission Spectroscopy (OES) has gained significant credibility since it can detect and analyze almost any kind of gas and it results in an accurate measurement of concentration. OES provide both quantitative (gas concentration) and qualitative (gas identification) results. One of the effective methods of interpreting the

results of an OES system is to use digital spectrometers. However the cost of using such system is relatively high and their sizes limit the overall miniaturization potential of the sensor. The introducing of the digital image processing for the spectrum of the gases can be an effective mean to achieve this objective and reduce the need of complex bulk spectrometers to analyze the optical emission of gases under measurement.

The application of image processing in plasma imaging has been investigated by several researchers [3]. In contrast, there have been very few studies conducted in gas sensing primarily due to the fact that the successful implementation of a digital imaging system requires addressing several critical challenges and problems in order to produce an acceptable degree of reliability and credibility in the measured results.

Gas sensing technology can offer high potential for significant improvement in many scientific and engineering domains such as industrial, medicine and manufacturing. For example, using gas sensors in space missions can allow the monitoring of oxygen levels and detect toxic gases in space shuttles. It can also be applied to detect pollution levels within the atmosphere and in living areas like big cities where exceeding a certain limit of some gases can be considered as a life threatening issue. Gas sensing can also help car manufacturers in providing required percentage of pollutants and design different components to enhance fuel efficiency.

1.2 Applications of Gas Sensors

Gas sensors are widely used in many fields ranging from industrial to domestic applications. The application where the sensor is used is the key factor behind choosing the type of the gas sensor as not all types fit all applications. Some of the applications are:

- Air pollutant measurement.
- Human breath analysis and disease detection.
- Life support in manned space applications.
- Car ventilation control.
- Gasoline vapor detection.
- Alcohol breath tests.
- Safety (Fire detection, Leak detection).
- Toxic/flammable/explosive gas detectors.

- Indoor air quality.
- Air purifiers.
- Ventilation control.
- Environmental control (Weather stations & Pollution monitoring).
- Food quality and Process control.
- Industrial production like in fermentation control.
- Medical Breath analysis.
- Prevent of industrial gases emissions especially near large towns, plants.

1.3 Prior State of Knowledge

Gas sensing related research has been conducted in a growing number of scientific and engineering disciplines. Integration of a gas sensor in many products helps manufacturing companies (e.g. automotive, airlines, etc.) to monitor gas emissions concentrations and pollution. The gas sensing technologies are wide and diverse due to the several physical and chemical effects that can be measured and reflect the gas characteristics [4]. Commercial and conventional methods in gas sensing like infrared spectroscopy, gas chromatography or mass spectrometry (GC/MS) are considered to be good methods, they have good detection limits and fast response times but they are relatively bulky and expensive [5]. Thus new methods for gas sensing were needed to take place the conventional ones, however most of the new emerged sensing techniques still depend on the same principles of the old ones.

The conducting polymer gas sensors have been in continuous research for liquid petroleum gas sensing [6] and humidity sensors [7] and showed a good selectivity and sensitivity. Piezoelectric gas sensors measures variations in the propagation of acoustic waves, or the changes of physical properties of interfacial thin films caused after exposition to an analyte, they are divided into two parts: bulk acoustic wave (BAW) or quartz crystal microbalance (QCM) and surface acoustic wave (SAW) detectors [8]. The ultrasound based sensor [17] can detect the changes in the gas concentrations by measuring the attenuation of the ultrasound waves caused by the gas under measurement. Carbon nanotubes CNT-based gas sensors can be classified into chemical and physical types. Chemical CNTs gas sensors depend on the changes of their conductivity and permittivity due to the gas adsorption. Several sensors of this type have been reported [9]. They have extremely small size, high sensitivity, and low cost of manufacturing and a good electrical

response even at room temperature [10]. Physical CNTs gas sensors utilize the gas ionization technique invoked by applying high voltage [11]. CNTs suffer from a problem that they could be oxidized and degraded easily in the presence of oxygen. Semiconductor gas sensors are typically based on metal oxides (like SnO₂, TiO₂, etc.) they have many advantages like low cost, high sensitivity, simplicity and its easy integration with other elements [2] but with poor reproducibility and long-time instability due to aging, nonlinearity, and lack of selectivity of certain gas measurement when different reactive gases exist in the same atmosphere that cause interference.

Optical methods in gases detection are numerous like ellipsometry, spectroscopy, interferometry and surface plasmon resonance (SPR) [12]. Optical emission spectroscopy (OES) techniques are often used in chemical laboratories as analyzers, also they have been used in instruments for air pollutant measurements [13] also a small sized OES based sensor for exhaust emission has been reported [14]. Optical spectroscopy gas detection techniques are rapid and often provide highly selective means of measuring gas concentration with good sensitivity they also have a good precision, their disadvantages are in being expensive and the measured gas must have a significant and distinct absorption, emission or scattering in a convenient region of the optical spectrum in order to be detectable [15]. Optical fiber based gas sensors have small size and light weight, remotely operated, they have an electromagnetic immunity which enable them to work in high noise environment, and they are also passive devices and require no electric power in the sensing zone which makes them reliable in environments with flammable gases [16].

Each of the above mentioned sensors, however, was focused on developing a domain specific gas sensor that was intended for a very specific purpose, thereby limiting its widespread applicability. For example, some methods were developed for the detection of a single gas and others required specific conditions to work. In addition, prior research in gas sensing:

- Does not consider using same sensor for measuring multiple gases simultaneously in a real time scenario.
- Does not afford unrestricted mobility to the gas sensor to be used on-site in applications that require dynamic way of measurements like in moving vehicles.

- Does not consider the cost and operation costs of using multiple sensors to measure multiple gases in the same application.
- Does not consider problems associated with using gas sensors in unprepared environments.

1.4 Research Objectives

In order to address the limitations in the existing state of knowledge, the overall objective of this research was to develop a relatively low cost gas sensor, with the ability to measure multiple gases concentrations at the same time, which can be used for measuring the concentration of gases emitted by internal combustion engine. Also this research investigates the miniaturization potential of several gas sensing technologies for recommending the best candidate among the studied sensors for miniaturization.

The specific objectives of this research were identified as follows:

- Study both existed and novel methods used in gas sensing technologies and sensor design methods determining the required parameters (i.e. sensitivity, selectivity, power consumption, and size) that can evaluate the sensor efficiency.
- Study the methods used in various sensors to obtain and retrieve the sensor's data to determine the complexity, response time and cost in processing data gathered by the sensor. As in the optical emission spectroscopy where the using of a spectrometer implies a high cost and increase in the size of the overall system.
- Review and discuss the miniaturization potential of the most existed and novel gas sensors and search for best candidate among them based on several criteria.
- Investigate feasible methods to apply to obtain a sensor that can measure multiple gases at the same time, with a relatively low cost, in order to apply on the internal combustion engines' emissions measurement. For our goal we found that the optical methods and especially the ones that depend on gas emissions under electric fields is a good candidate due to its high selectivity and sensitivity.
- Develop an expressive yet simple method to analyze the gas emissions to replace the spectroscopes and spectrographs. The developed method depends on digital image processing to register and process the color emitted by gas under experiment.

- Identify and effectively address issues such as errors in measurements that significantly affect the precision and credibility of the sensor. Such issues arise from the imaging sensor and the impurities in the gas mixtures.

This dissertation presents the developed methodology and the design of an optical based gas sensor with the detailed study the state of the art gas sensing technology. It explains the operation mechanism, data processing algorithms, and sensor calibration together with their practical implementation inside an experiment. The designed sensor provides a convenient method to automatically measure a mixture of up to four gases simultaneously using a low cost technique. The results of the research have been tested and validated by the experiment and the measurement error has been determined by making several controlled measurements using different gas mixtures.

1.5 Research Methodology

In order to effectively achieve the objectives of this research, the identified problems and challenges were clustered into several groups for investigation. The following is an abridged list of the major steps followed in this research to fulfill the requirements of a functional, reliable, and practical gas sensor capable of measuring the concentration of several gases simultaneously that can be conveniently used in internal combustion engines gas emissions and in many other applications:

- Studied the details of involved parameters in gas sensing without dependence on any type of sensors or applications that might possibly limit the criteria of parameter selection.
- Reviewed the existed and novel gas sensing technologies and discussed their miniaturization potential making a comparison between the most important categories for the aim of miniaturization.
- Created a model for light color mixing in gas discharge emissions to understand the phenomena and applied the reverse model to determine the gas concentration in the discharge from the color emitted.
- Build an experiment to validate the proposed model of light mixing in gas discharge tube and for the testing and validation of the proposed gas sensing method that rely on the image processing of the color emitted by the gas under the discharge tube.

1.6 Dissertation Outline

During the course of this research, the author produced several scientific manuscripts in the form of journal papers as each identified challenge or research problem was successfully addressed. Each chapter serves as a stand-alone document that describes the details of individual scientific questions successfully addressed, major challenges involved, and algorithms and methods studied, adopted, developed, and implemented in achieving a particular research objective. Each Chapter concludes with an extensive list of references (books, papers, and internet URLs) that direct the reader to further resources related to the main topic of the chapter. In Chapter 2, the review of recent trends in gas sensing technology and their miniaturization potential is introduced and described. The pros and cons of each studied technology and the comparison between these methods for the aim of sensor miniaturization are presented. Chapter 3 describes the theory of plasma emission and gas discharge tube, optical emission spectroscopy. In Chapter 4, we introduced the color mixing model, and the theoretical model of the proposed sensor in this research and its integration into a real experiment, the experiments were done to test and validate the results from several validation experiments that has been conducted to evaluate the functionality and reliability of the developed sensor.

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2. Review of Recent Trends in Gas Sensing Technologies and their Miniaturization Potential

2.1 Introduction

Gases represent one of the most important key measurands in many industrial and domestic activities. The most interest gases include CO, NO, NO₂, NH₄, SO₂, CO₂, CH₄ and other hydrocarbons. These gases can be harmful to human health if present beyond a certain concentration [1]. The applications of the sensors vary from the need to detect single gas or a group of gases at the same time; this is expressed by the term *selectivity* which is the ability of the sensor to detect what is interest over what is not interest [2].

The diversity in gas sensing methods are due to the several physical and chemical effects that can be measured and reflect the gas characteristics. However, each technology has its strengths and weaknesses and there is no one perfect solution for all applications.

A great deal of research is directed toward the miniaturization of gas sensors, this can lead to reduced weight, lower power consumption, and lower cost gas sensors. Recently, new sensing technologies appeared where they offer good promises for the design of robust miniature sensors.

In this review we will discuss the conventional and the novel techniques used in gas sensors. We will also discuss the research done in the miniaturization of these sensors and compare between them to find the best candidate for miniaturization.

2.2 State of the Art

Many reviews of gas sensors had been published but most of them are specific to a certain type of sensors, due to the diversity of technologies used, or specific to a certain application. Metal Oxide Semi Conductor (MOS) gas sensors were reviewed by many [1,7,11,12,92,94]. In [1] Sharma and Madou reviewed the evolution in both the gas-sensitive materials used and the heater structures of MOS, they discussed the miniaturization from macro to nanosize of both the sensor and its heating element. In [7] the 1-D nanostructured Metal-Oxides based sensors were

reviewed evaluating their performance. In [92] MOS gas sensors specific to Environmental Monitoring were reviewed. Bai and Shi in [18] reviewed gas sensors based on conducting polymers, they discussed the sensing mechanism, configurations and the factors that affect the performance, listing some of the disadvantages. Gas sensors based on gravimetric detection was reviewed by L. Duraffourg et al in [10], Xu et al. reviewed the Zeolite-based materials for gas sensors in [66] highlighting the potential of these materials in gas sensing especially in terms of sensor selectivity. Kauffman and Star in [37] reviewed the carbon nanotube gas and vapor sensors considering it a promising new technology in terms of sensitivity and selectivity. Ceramic gas sensors that operate at high temperatures were reviewed by Akbar et al in [3]. Gas sensors based on electrospun nanofibers was reviewed by Ding et al. in [93] featuring them in terms of sensitivity and response time over sensors based on flat films. A review of gas sensors employed in electronic nose applications was done by Arshak et al. in [5].

In this chapter, we will review most of the methods used in gas sensing and discuss their miniaturization potential delimiting our research to a certain type of technology or application.

2.3 Conducting Polymer Gas Sensors

The first type of gas sensors to be discussed is the conducting polymer gas sensors. They have been in continuous research for Liquid Petroleum Gas sensing [16, 17] and humidity sensors [19, 22] and showed a good selectivity and sensitivity.

2.3.1 Conducting Polymer Chemiresistor Gas Sensors

Chemiresistor polymer gas sensors [18] consist of a layer of conducting polymer connected to one or several pairs of electrodes, as illustrated in Figure 2.1.

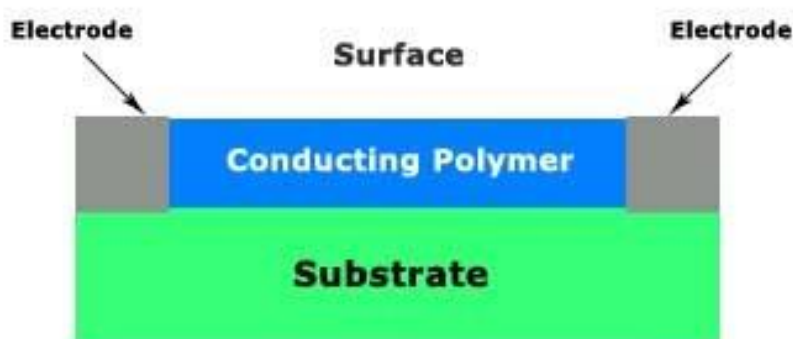


Figure 2.1 - The General Structure of a Chemresistor.

The electrical resistance change of the sensing material, due to gas interaction, is measured as the output. A constant current or potential can be applied on the sensor, and the measuring output signal is their changes, respectively. Also alternating current (AC) can be used [20, 26], in this case the capacitance C and inductor L should be included since they are both affected by the gas interaction with the sensing film. Another value can be taken into account; the value of dissipation factor (resistance/absolute value of reactance) that changes with frequency, where the peak position in the dissipation versus frequency curve is shifted when exposed to different gases. This shift is unique for each gas [23] and can be used to detect the type of the gas.

2.3.2 Conducting Polymer Transistor and Diode Gas Sensors

Transistors and diodes have more parameters for measurements than the chemiresistor polymer and have better detection limit and sensitivity because of the signal amplification of transistor devices and diode conducting polymers are simpler than transistors. Based on semiconductor properties, the polymer transistor gas sensors works by applying a source-drain voltage and measuring a source-drain current modulated by a gate potential as an output. The output current is changed when the polymer sensing film interacts with an analyte (Figure 2.2). Conducting polymer transistors are classified according whether the current passes through the conducting polymer or not [18].

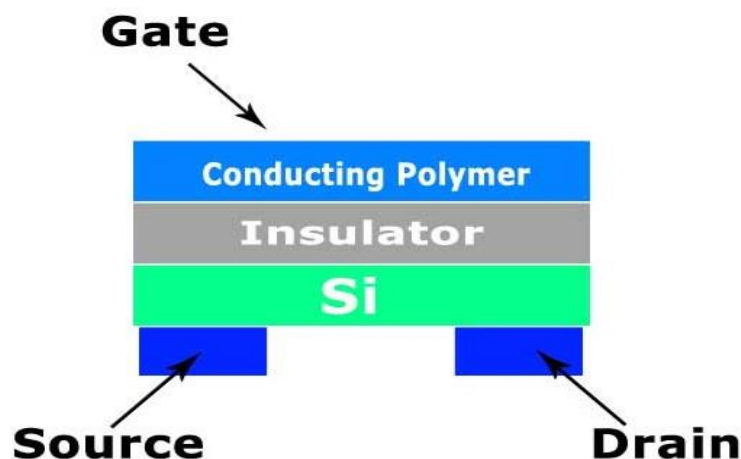


Figure 2.2 - Thin film transistor (TFT) with a conducting polymer active layer.

There are other types of polymer based gas sensors like the optical polymer gas sensors [24, 25] where gas can be analyzed when it is in contact with the conducting polymer film by measuring transmittance or absorbance changes. Conducting Polymers can also be used in piezoelectric crystal sensors. Recently research is focusing on enhancing certain parameters like sensitivity [21] by incorporating different materials.

2.4 Piezoelectric Crystal Gas Sensors

Piezoelectricity was observed by Pierre and Jacques Curie in 1880, when a quartz crystal is compressed, an electric potential is produced. On contrary, if an alternating electric potential is applied on a piezoelectric material, an acoustic waves in solids is generated, see Figure 2.3.

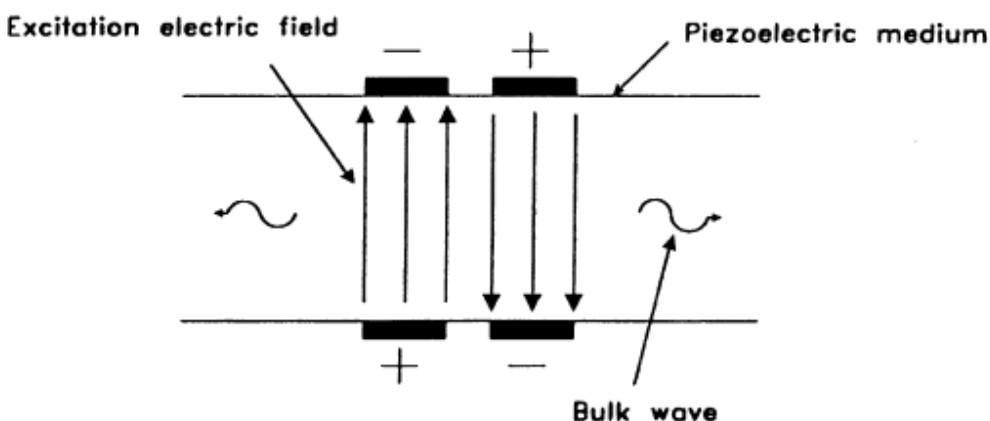


Figure 2.3 - The principle of piezoelectric device.

Piezoelectric crystal gas sensors are divided into two parts; bulk acoustic wave (BAW) or quartz crystal microbalance (QCM), and surface acoustic wave (SAW) detectors (Figure 2.4). For a detailed review of SAW and BAW gas sensors refer to [10].

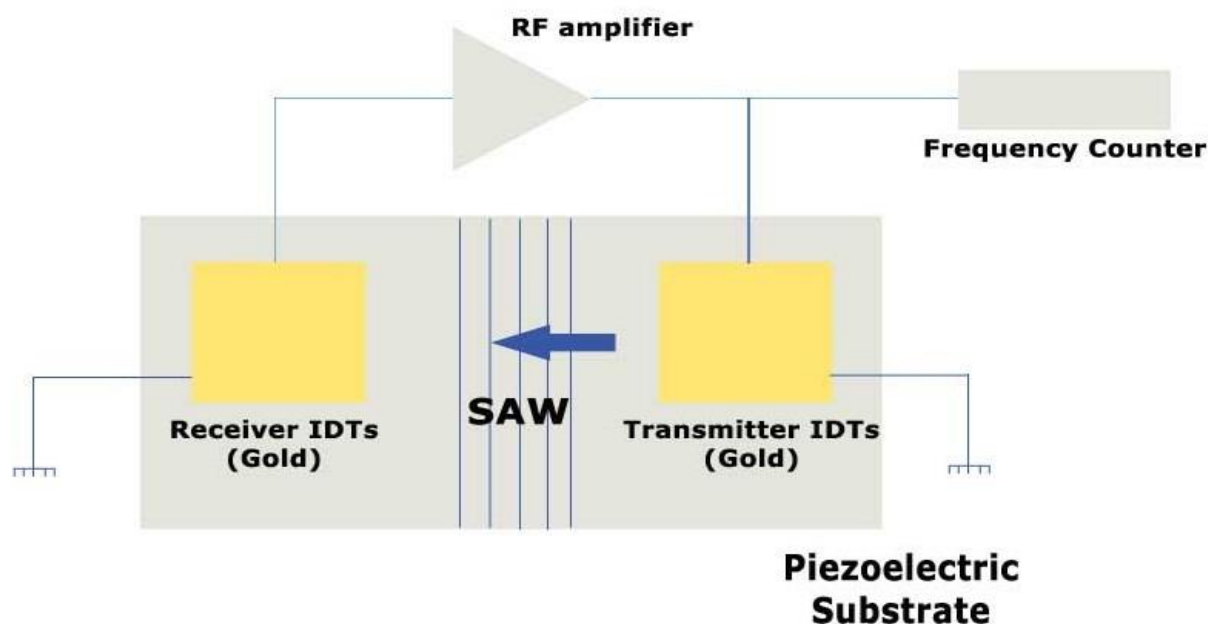


Figure 2.4 - Schematic diagram of a SAW sensor.

In both types, the sensor is made of a piezoelectric substrate coated with a suitable sorbent coating where the gases are detected by their effect on the propagation of the acoustic wave causing changes in the resonant frequency and the wave velocity as the adsorption of gas onto the coating surface cause a shift in the oscillation frequency corresponding to the mass of the adsorbed compound. [6].

Sensing in piezoelectric gas sensors is done by measuring variations in the propagation of acoustic waves, or the changes of physical properties of interfacial thin films caused after exposition to an analyte. Sensors based on ultrasound technique [81] can detect the changes in the gas concentrations by measuring the attenuation of the ultrasound waves caused by the gas under measurement.

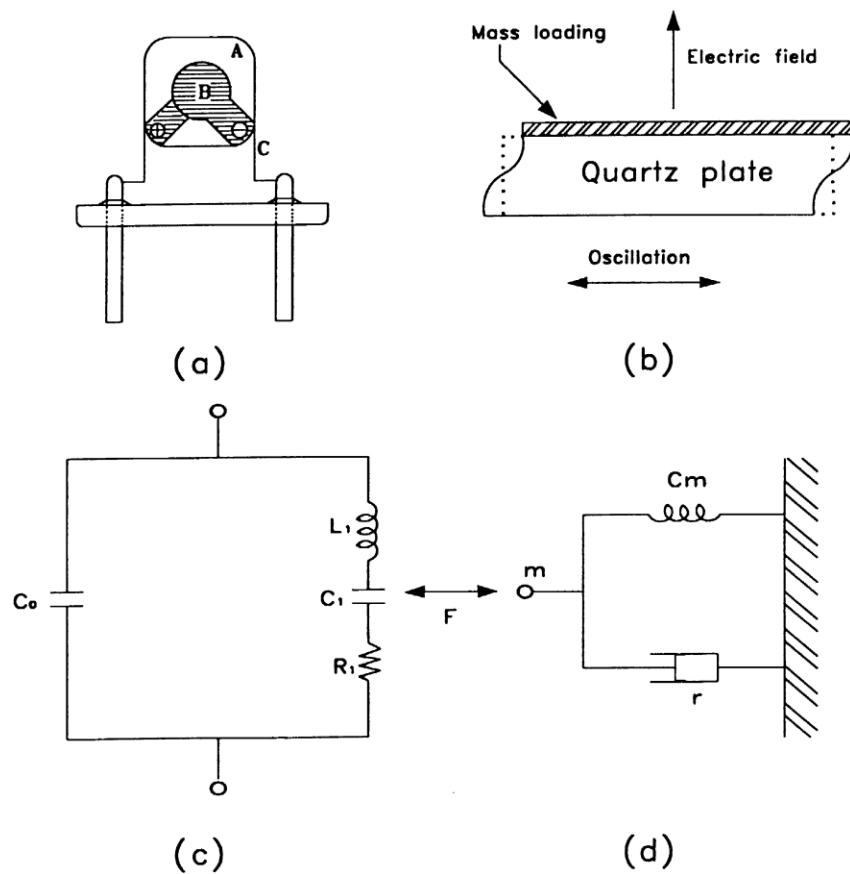


Figure 2.5 - Schematic diagram of AT-cut quartz crystal. (a) The structure of AT-cut quartz crystal, A: Quartz crystal, B: Electrode, C: Lead wire. (b) The principle of piezoelectric quartz crystal and oscillation model. (c) Electrical equivalent circuit. (d) Mechanical model.

The QCM (Figure 2.5) detection principle is based on the fact that the change in resonance frequency of a thin quartz crystal covered with a gas sensitive layer is proportional to the additional mass of the adsorbed gas atoms. The detection limits of the QCMs are in the parts-per-million (ppm) range [10].

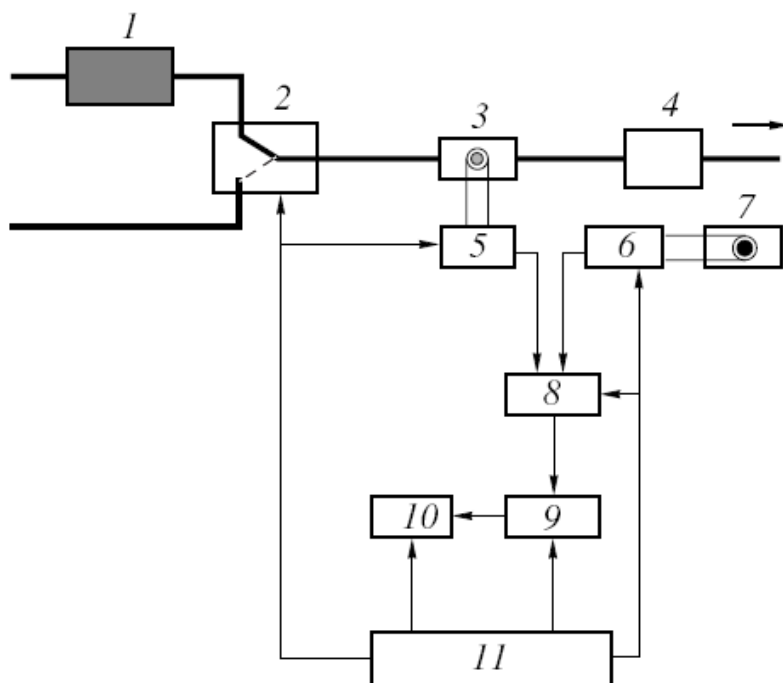


Figure 2.6 - Schematic diagram of a portable piezoelectric-resonance gas analyzer: (1) permeable filter with a selective adsorbent; (2) switching valve; (3) CPRMS; (4) micropump; (5, 6) high-frequency oscillators; (7) reference resonator (or SWA sensor); (8) frequency transformer; (9) control and data processing unit; (10) indicator; (11) power supply unit.

In SAW, the sensor consists of two separated electrode pairs on a substrate playing a role of a transmitter and receiver of acoustic waves. The separation region is coated with gas sensitive substances that allow adsorption of gas atoms that change the phase and/or amplitude of the SAW. SAW devices operate at much higher frequencies than BAW systems (about 10 times). The lower detection limit for these SAW sensors lies in the range of a few ppb [10].

The sensitivity in SAW is directly proportional to the square root of resonant frequency, and inversely proportional to the surface area which is very small. SAW devices have a relatively low fabrication cost and they can be miniaturized with precise and reproducible characteristics using photo-lithographic techniques [9]. However AT-cut quartz is more stable than SAW device.

Chemical piezoelectric-resonance mass sensors (CPRMSs) for gas sensing application had also been intensively developed [29-31]. These sensors (Figure 2.6) usually have a fast response and long lifetime.

The advantages of piezoelectric gas sensors are in being sensitive, relatively cheap and have a fast response time. Their disadvantage is their limited selectivity which depends on the availability of coating layers. Other special issues related to SAW detectors are noise and higher costs for materials due to the higher operating frequency.

2.5 Carbon Nanotubes (CNTs) Based Gas Sensors.

CNTs are hexagonal networks of carbon atoms; they are about 1 nm in diameter and from 1 to 100 microns in length. There are two types of nanotubes: single-walled nanotubes (SWNTs) and multi-walled nanotubes (MWNTs); SWNTs have only one layer of graphene cylinders (Figure 2.7); while MWNTs have about 50 layers.

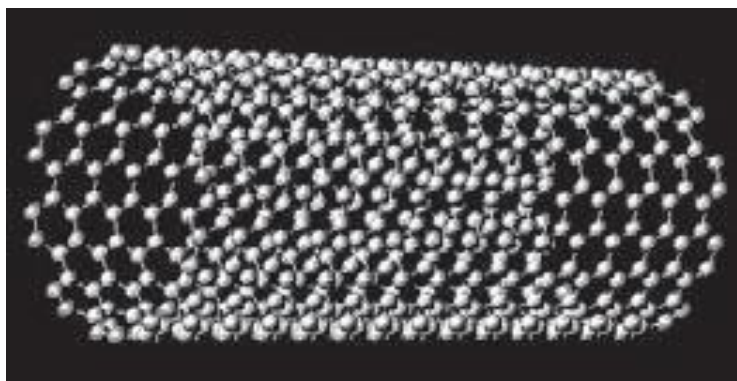


Figure 2.7 - A single-walled nanotube structure.

Carbon nanotube (CNT)-based gas sensors can be classified into chemical and physical types. Chemical CNTs gas sensors depend on the changes of their conductivity and permittivity due to the gas adsorption. Several sensors of this type have been reported [33 - 36].

They have extremely small size, high sensitivity, and low cost of manufacturing [37] and a good electrical response even at room temperature [38].

Physical gas sensors utilize the gas ionization technique invoked by applying high voltage [39, 40]. They have stable structure under high electric fields and considered one of the best field emitters among conventional field emitting metals.

Kong et al [33] showed that the electrical resistance of semiconducting SWNTs changes when exposed to gaseous molecules, having a response time of at least an order of magnitude faster than those based on solid state sensors. They have small size and operate at room temperature with a high sensitivity.

In another study by Modi et al. [41] proposed sensors that have good selectivity and sensitivity, and were unaffected by various environmental conditions (moisture, temperature, and gas-flow), featuring the electrical breakdown of gases mixtures at the tips of CNTs, the cathode of the sensor was made of aluminum and the anode was vertically aligned MWNT film. The proposed method was for solving what they called certain limitations of sensors based on electrical conductance changes (poor diffusion kinetics, inability to identify gases with low adsorption energies and high sensitivity to changes in moisture, temperature and gas-flow velocity).

Surface acoustic waves (SAWs) sensors coated by CNTs with high sensitivity were also reported [42]. The sensor was used for the detection of volatile organic compounds.

Sensors based on single-stranded DNA (ss-DNA) and SWNT field effect transistors (FETs) have been proposed [43], the sensor (Figure 2.8) can detect variety of gases with rapid response time and have a fast recovery time.

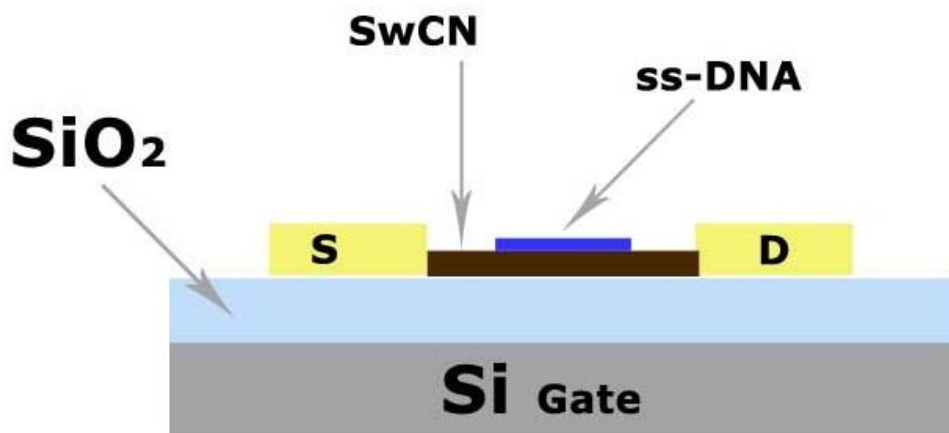


Figure 2.8 - Sensors based on (ss-DNA) and SWNT (FETs).

2.6 Optical Gas Sensors

Optical methods in gas sensing are diverse; some are widely used like spectroscopy and surface plasmon resonance (SPR) while others are less known like ellipsometry [53].

2.6.1 Optical Spectroscopy

Optical spectroscopy gives quantitative and qualitative information of gases [12]. The emitted or absorbed electromagnetic radiation spectrum tells us about the concentration or the quantitative information, while the qualitative information is related to the wavelengths of the spectrum. Mainly three different techniques are used: atomic absorption spectrometry (AAS), optical emission spectrometry (OES) and atomic fluorescence spectrometry (AFS). These techniques are often used in chemical laboratories as analyzers, also they have been used in instruments for air pollutant measurements [13].

The first optical gas sensors were based on the absorption spectrum difference measurement like the infrared IR gas detectors which have been in use for long time ago, they have long life time with greater stability over time. Their disadvantages are that they can only detect gases that are strongly absorbent in the infrared spectrum like hydrocarbons, they require a relatively large volume of gas for response testing and their ambient temperature is limited to 70°C [7].

Inductively Coupled Plasma-Atomic Emission Spectroscopy (ICP-AES) (Figure 2.9) is one of several techniques available in analytical atomic spectroscopy. ICP-AES utilizes plasma as the atomization and excitation source. Plasma is an electrically neutral, highly ionized gas that consists of ions, electrons, and atoms. The ICP is a radiofrequency-(RF, 27.12 MHz, 40 MHz) induced plasma that uses an induction coil to produce a magnetic field (H). The ICP operates between 1 and 5 kilowatts. The induction coil is wrapped two or three times around the ICP torch and has water flowing through it for cooling purposes. All ICPs have a capacitor bank that is continuously tuned to match the plasma's inductance. In order for the RF to travel along the surface of the hollow coil with minimum resistance, the coil is either gold or silver plated since neither gold nor silver forms metal oxides upon contact with air. Although the RF power supply maintains the plasma, a tesla coil is used to ignite the plasma through the generation electrons and ions that couple with the magnetic field.

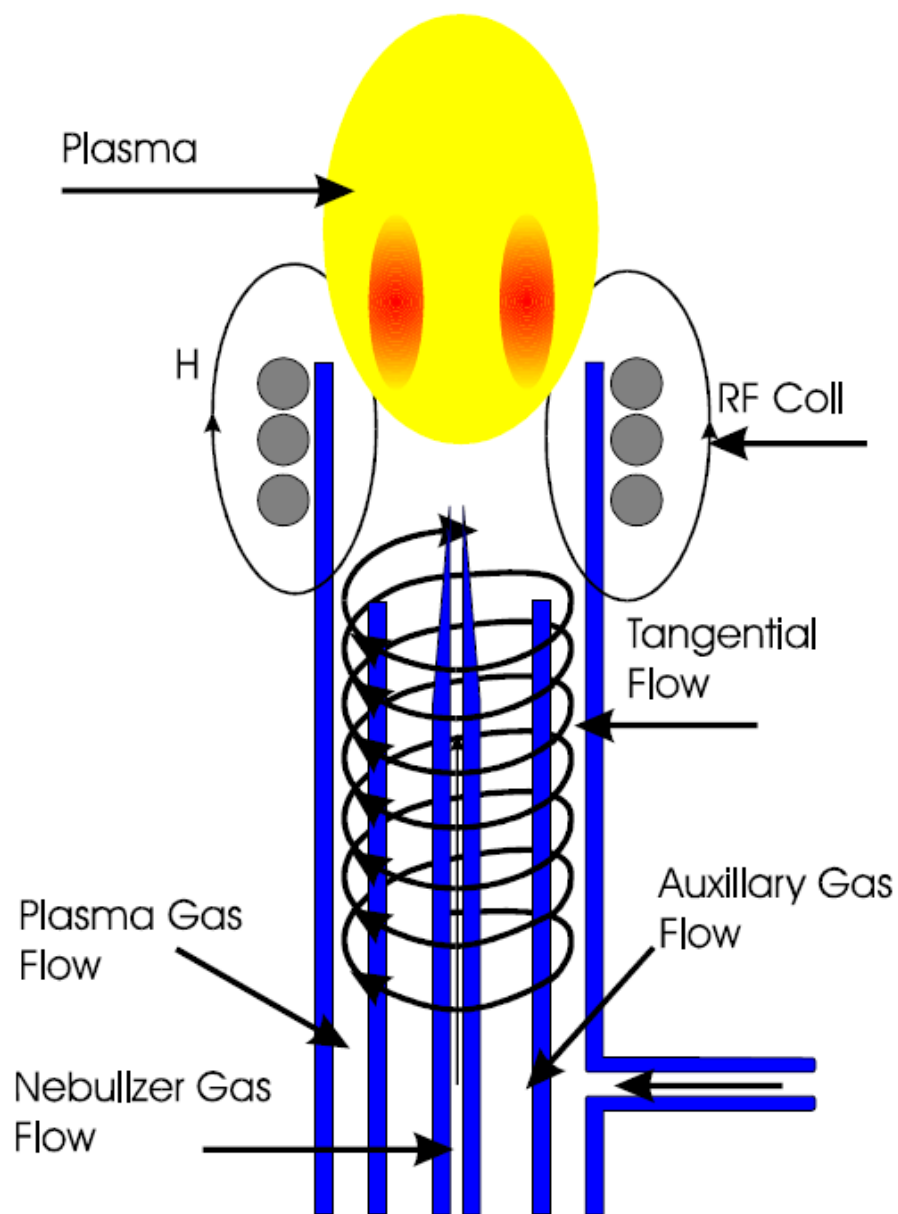


Figure 2.9 - SCHEMATIC OF AN ICP TORCH.

Small sized OES based sensor for exhaust emission has been reported [44] and another handheld micro-system to analyze chemicals both in vapor and liquid phases using discharge spectroscopy was presented in [46]. Furthermore, the design and fabrication of micro-machined silicon plasma igniters, that can operate at atmospheric pressure and under a relatively low voltage (400V), for using in gas sensing was reported in [45].

Optical spectroscopy gas detection techniques are rapid and often provide highly selective means of measuring gas concentration with good sensitivity they also have a good precision, their disadvantages are in being expensive and the measured gas must have a significant and distinct absorption, emission or scattering in a convenient region of the optical spectrum in order to be detectable [14].

2.6.2 Ellipsometric Gas Sensor

An optical gas sensor, with sensitivity in the ppm range for vapors of alcohols, based on polarizer compensator sample analyzer (PCSA) ellipsometric readout system working in the off-null mode (Figure 2.10) was reported in [53]. The principle of this sensor is based on the detection of the intensity change of polarized light that is reflected by a sensing layer exposed to gas in oblique incidence; this intensity change holds the information about gas concentrations.

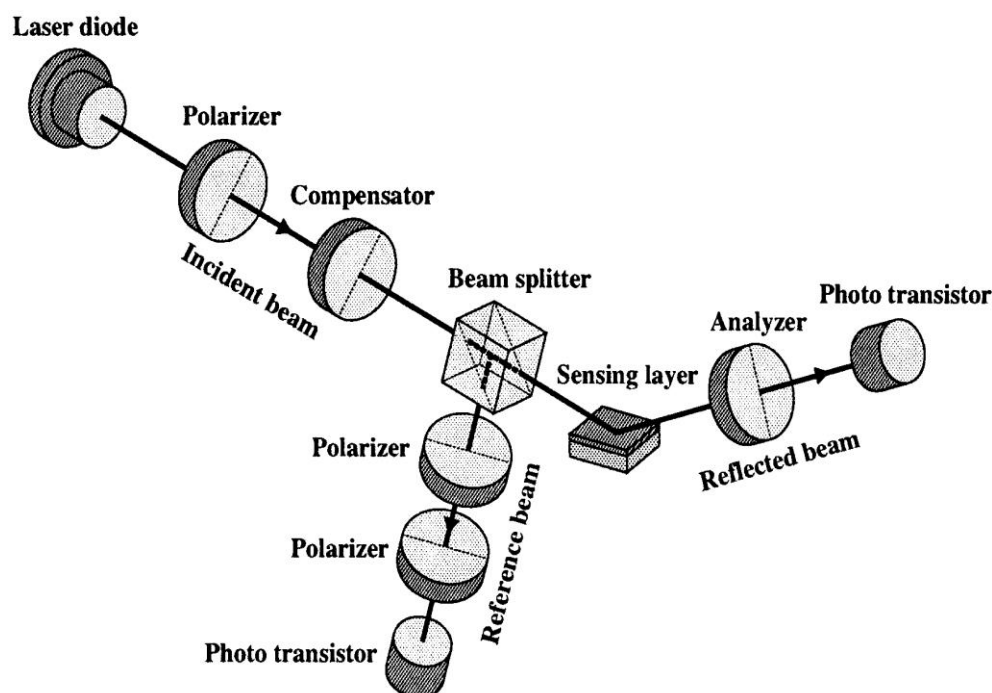


Figure 2.10 - Optical setup of the ellipsometric gas sensor system.

The sensing layers suitable for this system are thin layers (0.01–10 nm) thickness deposited on silicon or metal substrates where their refractive index and/or thickness can change reversibly due to the gas exposure.

2.6.3 Non Dispersive Infrared (NDIR) Gas Sensor

Gas molecules selectively absorb radiation according to their quantized vibrating energy; the absorption degree is proportional to the concentration of the gas [47]. The principle of this sensor is based on the absorption of infrared (IR) light by the gas to be measured [48], where a source of light with a radiated energy I is emitted and directed through a path of length l containing the gas sample, with concentration and absorptivity C and α , then the radiated energy I_0 after absorption is detected by the IR detector according to Beer-Lamberts law (eq.1).

$$I(t)=I_0(t)\exp^{-\alpha(\lambda)LC} \text{ (eq.1)}$$

Where $I(t)$ is the output light intensity, $I_0(t)$ is the input light intensity, α is the absorption coefficient, L is the optical path length, C is the concentration of gas sample. Using a monochromatic beam with a large absorptivity enables the detection of the concentration of the target gas without interfering with the other gases [47].

A similar technology is used in photoacoustic gas sensor [54, 48] where the ratio I/I_0 is detected using a pressure sensor as a varying over time pressure signal.

NDIR sensor is selective and several commercial sensors detection exists with detection limit down to 30 ppm for CO₂ [49] and 200 ppm for hydrocarbons [50] with size in order of centimeters.

2.6.4 Photoacoustic Gas Sensor

The principle of this sensor is similar to the (NDIR) technique where the ratio I/I_0 is detected using a pressure sensor as a varying over time pressure signal.

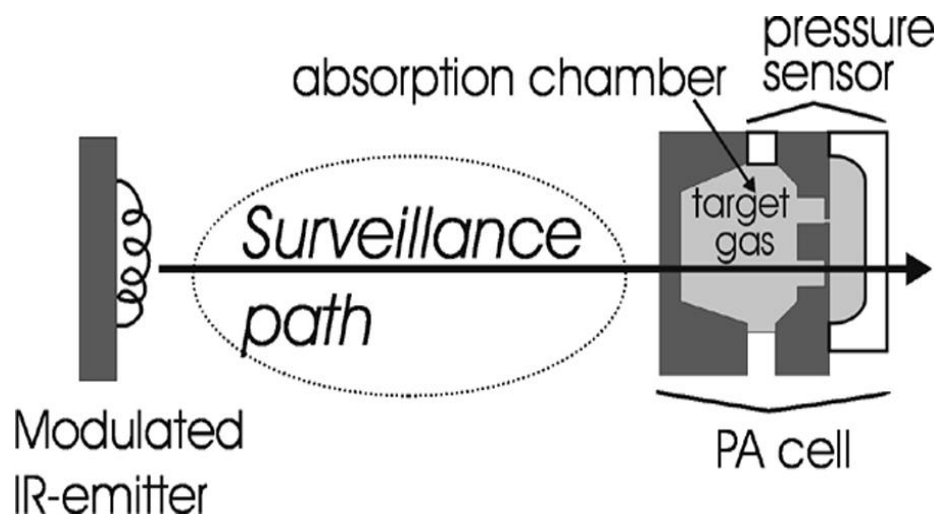


Figure 2.11 - Principle of a photoacoustic gas sensor with IR-emitter, surveillance.

As illustrated in (Figure 2.11) the absorption of the IR radiation by the target gas, enclosed in the absorption chamber of the PA cell, heats up the gas which increase the pressure in the absorption chamber. The incident light is modulated at a given frequency which gives a periodic pressure variation in the absorption chamber

The target gas which is presented in the surveillance path, will cause absorption of the IR radiation by the tested gas outside the PA cell and therefore reduce the radiation intensity that is entering the absorption chamber. This will cause a less heating of the enclosed gas in the PA cell, and invoke a reduction in the amplitude of the periodic pressure signal. This reduction in pressure amplitude is logarithmic and it is proportional to the concentration of the target gas in the surveillance path.

2.6.5 Active Laser Gas Sensor

Active Laser gas sensors have a major application in the remote measurement of gas concentrations like the in situ measurements of impurity gases of the atmosphere [51]. The principle of these sensors depends on the reflection of the laser beam, emitted by the sensor, from various obstacles like earth surfaces, buildings, roads, etc.), the measurement of the reflected light is done at specified wavelengths corresponding to the absorption ones of gases to be measured and this allows the determination of their concentrations.

When employing a high power pulsed solid state laser [52] particle concentrations can be determined at distances up to 1–2 km with an accuracy of about 0.1 ppm which is high enough for the monitoring of SO₂, NO and NO₂ gases in the atmosphere.

2.6.6 Surface Plasmon Resonance (SPR) Gas Sensors

SPR sensors are based on Kretschmann-Raether geometry [55]; they consist of thin metal film deposited on the surface of a glass substrate (Figure 2.12).

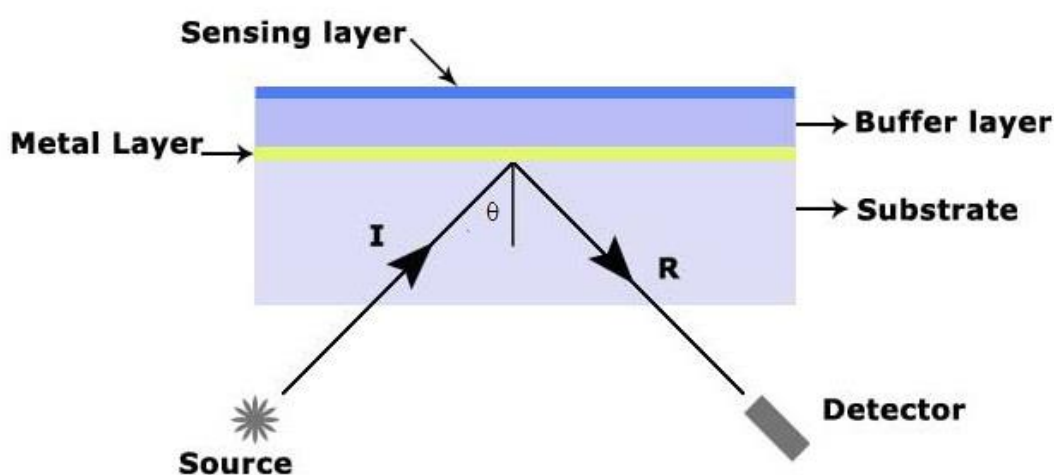


Figure 2.12 - SPR-based sensor schematic diagram.

In their functioning principle the source light is a p-polarized incident light excites an electron density surface plasmon wave (SPW) along the metal. In SPR based sensor, the angle of incidence of the light beam is varied at fixed wavelength and the intensity of reflected signal is measured, the change in the refractive index of the sensing medium shifts the resonance to a different value [56]. Measuring the light reflected from the sensor interface can be done by several methods. These include analysis of angle modulation, wavelength modulation, intensity modulation and phase modulation. Many gases like toxic gases such as ammonia, toluene, xylene, ethylacetate, 4-methyl-2-pentanone and propionic acid can be detected by measuring the SPR using angle modulation [6].

2.6.7 Optical Fiber Gas Sensors

Optical Fiber Gas Sensors appeared lately in the past two decades. For their application in gas sensing, the optical changes in the optic fiber are used as the response mechanism for the detection of gases or odors. The sides or tips of the optic fibers are coated with a fluorescent dye encapsulated in a polymer matrix, when interacted with gases the dye's optical properties such as intensity, spectrum, lifetime or wavelength shift in fluorescence are changed [5].

Absorption spectrum optical sensors are considered kind of practicality sensors [57-59] since they are more sensitive than other optical sensors, can conduct higher respond speeds, less affected by temperature or humidity and have a simpler structure and higher credibility.

A method based on harmonic detection was developed by [59], according to the Beer-Lambert Law, in this sensor the light intensity is attenuated when it passes through the gas sample due to the absorption effect. In this sensor the wavelength of light source is modulated and the wavelength scan is made through the entire absorption peak periodically according to sine function. The harmonic is produced due to the interaction between light and gas absorption peak and from this harmonic analysis the concentration of gas sample is calculated where the fundamental wave component is obtained from the difference between referenced light intensity and metrical light intensity and the gas concentration is then obtained from detecting the 2nd harmonic of the difference signal. The sensor was able to detect concentration of acetylene greater than 20ppm and has a linear output proportion to gas concentration, if the gas concentration is greater than 40ppm.

Another sensor that is based on thermal lens (TL) spectroscopy was also reported in [60] as an all-fiber TL gas sensor system with a fiber ring laser, which was a new approach for TL techniques, featuring an optical absorption path with a shorter length than other optical spectroscopic techniques. The proposed sensor effectively enhanced sensitivity and increased the limit of detection by twice.

Optical fiber based gas sensors offers some important advantages; they have small size and light weight, remotely operated, they have an electromagnetic immunity which enable them to work in high noise environment, they are also passive devices and require no electric power in the sensing zone which makes them reliable in environments with flammable gases [61].

2.7 Semiconductor Gas Sensors

Semiconductors are chemoresistive or Conductometric gas sensors, they are typically based on metal oxides (like SnO₂, TiO₂, etc.). Metal oxides are deposited as thin films through vacuum deposition onto a silica or aluminum oxide substrate in a similar process to that used for fabricating semiconductors. Semiconductor gas sensors are used for the detection of combustible gases at low concentration levels and in toxic gas detection. They are robust but also very sensitive to humidity and have low selectivity.

2.7.1 Metal-Oxide Semiconductor (MOS) Gas Sensors

Semiconductor gas sensors are typically based on metal oxides (like SnO₂, TiO₂, etc.) their interaction with the gas results in a reversible and significant change in electrical resistance due to phenomena occurring at the surface like: reduction/oxidation processes, adsorption of the gases and surface chemical reactions between the different adsorbed chemical species. The sensor detects gases from the change in the electrical resistance of a porous sensing body [4]. The sensitivity depends on the sensor's film thickness and the operation temperature, where thinner films are more sensitive [5]. A heating element is used to elevate the sensor's temperature in order to reduce response and recovery times. The heating element can be a platinum or platinum alloy wire, a resistive metal oxide, or a thin layer of deposited platinum (Figure 2.13).

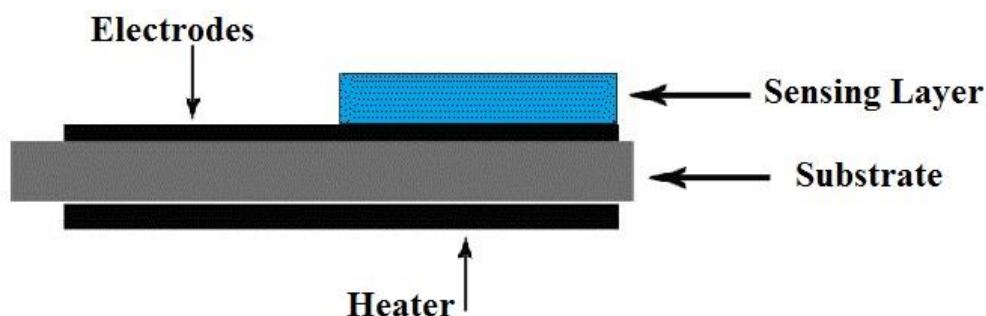


Figure 2.13 - Structure of a conductivity sensor.

The selectivity of the sensor can be changed to detect different gases or compounds by changing the operating temperature of the sensor or by modifying the sensing films [6].

Semiconductor metal oxide-based gas sensors can be divided into two principal types according to changes in the surface conductance or changes in the bulk conductance during the gas/solid interactions [11]. The working temperature varies depending on the target gas and on the sensor material.

Ralf Moos et al. in their review [62] discussed the novel trends in semiconductor gas sensors differentiating between the n-type, p-type and zeolites. The n-type (zinc oxide, tin dioxide, titanium dioxide or iron (III) oxide) responds to reducing gases where the redox process occurs at surface and p-type (nickel oxide, cobalt oxide) responds to oxidising gases [63, 5] where the reduction process affects the entire bulk [64].

2.7.2 Zeolite-Based Semiconductor Gas Sensors

Zeolites have a particular interest in the field of gas sensing, they were mainly used in gas sensing indirectly [65- 67] for example as a filter for the interfering or as gas-sensitive agent encapsulation, however, recent researches were done on using the zeolite itself as the sensitive element in the gas sensor.

Zeolites are class of aluminosilicates that consist of Si or Al denoted by T that form a framework of tetrahedral building units of TO_4 (Figure 2.14).

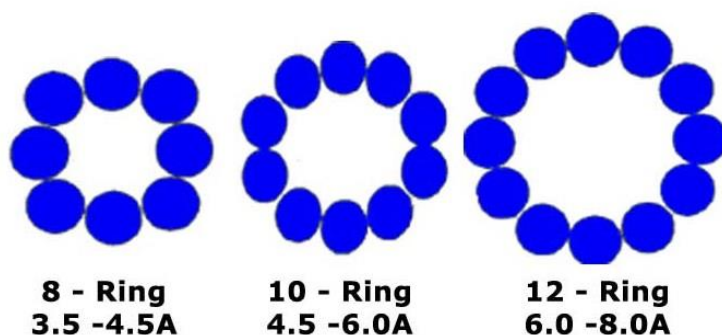


Figure 2.14 - Structure of different typical Zeolite windows with 8, 10 and 12-ring of TO_4 units.

The molecular sieve effect is caused by the different cages with different window sizes that allow some molecules to pass through or not. The ion-exchange with different cations causes the

modification of the pore size, the ion conductivity, the adsorption and catalytic selectivity (Figure 2.15).

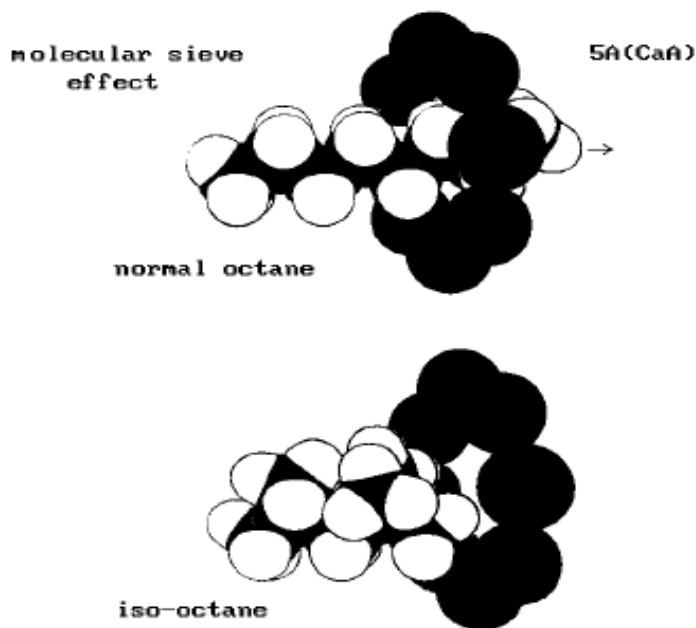


Figure 2.15 - Molecular Sieve Effect.

Zeolite-based gas sensors were reported in several publications, a robust impedimetric zeolite sensor [68] was used for automotive exhaust gas applications; it didn't show any significant cross-interference of hydrocarbons, CO₂, CO, and O₂ when operated at 420 °C. Other sensors were also reported for O₂, CO₂, CO, NH₃ and amine [69], humidity, combustible gases, NO, SO₂, Hydrocarbon and organic molecules.

The semiconductor gas sensors have many advantages like low cost, high sensitivity, simplicity and its easy integration with other elements that simplifies the design of a sensor, a detection limit up to 100 ppm of CO could be achieved, which is higher than the highest values, so far achieved with various devices, by two orders of magnitude. Also they have many disadvantages like poor reproducibility and long-time instability due to aging, non-linearity, cross sensitivity effect when measuring a certain gas concentration, where the sensor response is affected by other gases; this is fixed by using more than one sensor or more than one operation modes of the same

sensor, sensitivity to water vapor and lack of selectivity of certain gas measurement when different reactive gases exist in the same atmosphere where interference occurs. Many ways exist to improve the selectivity and eliminate the interference effects like using of filters [70] or catalysts or more specific surface additives [71,72] and the fine selection of the sensing layer material.

2.7.3 Metal Dielectric Material Semiconductor (MDS) Sensor

MDS-sensors are based on film structures of metal–dielectric material–semiconductor. They have a very high sensitivity and they are sensitive to a number of gases including NO₂ [73]. A portable gas analyzer for small NO₂ concentrations has been reported in [74-75]. The sensor consists of a silicon plate and two layers, a layer of dielectric material and a layer of palladium.

The semiconductor gas sensors have many advantages like low cost, high sensitivity, simplicity and its easy integration with other elements that simplifies the design of a sensor, a good detection limit up to 100 ppm of CO [4]. Also they have many disadvantages like poor reproducibility and long-time instability due to aging, non-linearity, cross sensitivity effect when measuring a certain gas concentration, where the sensor response is affected by other gases, sensitivity to water vapor and lack of selectivity of certain gas measurement when different reactive gases exist in the same atmosphere that cause interference. However many ways exist to improve the selectivity and eliminate the interference effects like using of filters [70] or catalysts or more specific surface additives [71,72] and the fine selection of the sensing layer material.

2.8 Electrochemical Gas Sensors

One of the most widely used types of gas sensors in the market today [76]. Electrochemical gas sensors are classified into potentiometric and amperometric, according to whether the output is an electromotive force or an electrical current.

These type sensors are mainly used in application for oxygen detection in automotive applications like the oxygen sensor based on zirconium-oxide doped with Yttrium, the so called *lambda-probe* [4]. The Lambda probe works with a solid electrolyte rather than an electrolyte solution and it is the most successful and most widespread chemical sensor. It is used in modern

motor vehicles for the control of the oxygen content in combustion gas to minimize the output of poisonous carbon monoxide [8].

The advantages of this type of sensors are in their fast response, high accuracy, wide range of detection and low power consumption. Their disadvantages are in their malfunction in low temperature ($< -40^{\circ}\text{C}$) and in having a working pressure range of 10% within atmospheric pressure.

2.8.1 Potentiometric Sensors

Potentiometric gas sensors are characterized by high selectivity for certain components in a mixture of other gases, long-term stability and maintenance-free over years and fast response (ms-timescale) which makes them very interesting tool in control loops. Equilibrium or Nernstian electrochemical cells based on solid electrolytes was reported and used for gas sensing in a very selective and accurate way. Potentiometric Zirconia sensors (Nernst cell) are used in oxygen sensors based on cell that operates at high temperature above 300°C , where an electromotive potential U is obtained due to the O^{2-} ions drifts from high oxygen partial pressure regions to low ones (Figure 2.16).

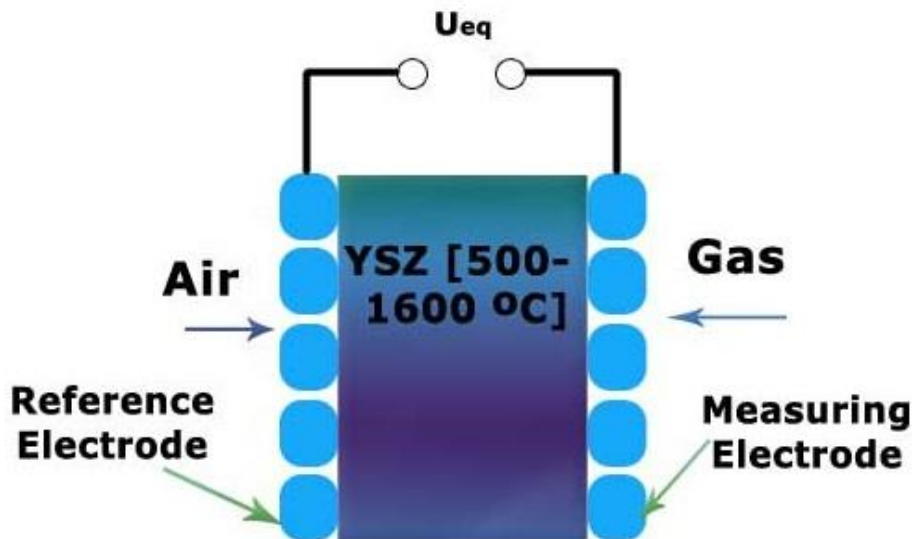


Figure 2.16 - Potentiometric Nernst Sensor.

A novel potentiometric principle: the direct thermoelectric principle where the Seebeck coefficient ε of the material is directly measured instead of the resistance has been studied recently [62] for the oxygen sensing and detection of combustibles. The principle has been tested, using doped SnO_2 , successfully for the detection of reducing gases like hydrocarbons [77, 62].

2.8.2 Amperometric Sensors

In amperometric gas sensors, a current is generated at an electrode due to the reaction with an analyte. The current generated is linearly correlated to the concentration of the analyte. Biological components like the enzymes or antigene/antibody pairs were used in [78] to decrease the cross-interference of other analytes. These biocomponents only interact with particular analytes following the “lock and key” model, their output is an electrical current and can be linked to the analyte concentration.

2.8.3 Field Effect Sensors

In this type of sensor the gate surface is exposed to a chemically variable environment in which the gases to be measured exist. This FET with a solid electrolyte as gate material (ChemFET) (Figure 2.17) is only possible as a thin-film microdevice [76].

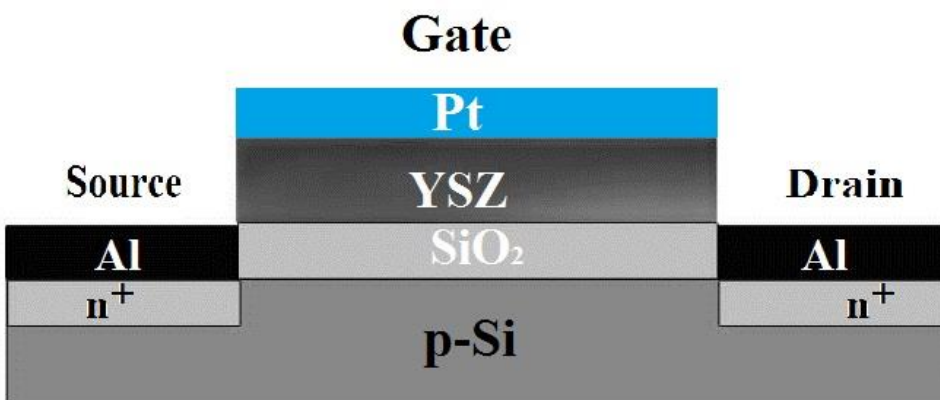


Figure 2.17 - Structure of FET-type solid electrolyte oxygen gas sensor.

The MOSFET gas sensor (Figure 2.18) is a metal-insulator-semiconductor (MIS) device, where its threshold voltage changes, due to corresponding changes in the work functions of the metal and the oxide layers when the gate material interacts with certain gases, such as hydrogen [5].

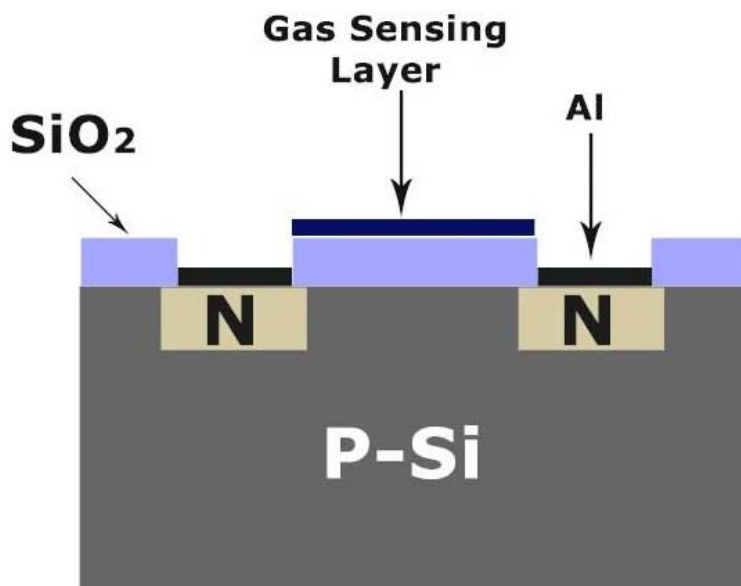


Figure 2.18 - Schematic diagram of a MOSFET gas sensor.

The threshold voltage change in the MOSFET gas sensor is proportional to the concentration of the analyte. Also the drain-source current and the gate voltage for the MOSFET gas sensors are affected by the changes in the work function and they can be used as the sensor output response [79].

This FET gas sensor can operate at room temperature due to its very high input impedance and thus doesn't require a heating element, it can be used in tiny sensing arrays on one single chip and its sensing materials do not need to be a semiconductor, other materials like metallic conductors can be also used [62].

2.9 Ionization Gas Sensors

Ionization sensors are considered as physical type of gas sensors, which work by fingerprinting the ionization characteristics of distinct gases [15], they rely on the fact, that any gas will be ionized at a certain voltage, temperature and pressure. This breakdown voltage is considered as the *ionization fingerprint* of the gas and thus a gas can be identified according to this voltage. The concentration of the gas corresponds to the discharge current that is created.

These sensors are mainly used to measure single gas concentration after the gas mixture is separated in gas analyzers like mass spectrograph or chromatograph. The disadvantages of this type of gas sensors are their bulky size, high power consumption and high operating voltages.

A novel ionization gas sensor was reported by [80] where they used CNTs and incorporate them into a short-gap electrode system through MEMS processes which decrease the onset voltage. And recently a gas sensor using CNTs arrays has been reported in [39], depending on the ionization of gas molecules under low voltage. The sensor was able to detect gases like NH₃, CO₂, N₂, O₂, He and air. However CNTs suffer from a problem that they could be oxidized and degraded easily in the presence of oxygen. Another sensor was reported in [15] that uses ZnO nanowires for stable field emission sources instead of carbon nanotubes, the sensor was experimented successfully to detect inert gases including air, it showed good sensitivity and selectivity, and being unaffected by extraneous factors such as temperature, humidity and gas flow.

2.10 Other Types of Gas Sensors

2.10.1 Ultrasound Gas Sensor

A sensor was reported in [81] based on ultrasound technique, this sensor (Figure 2.19) can detect the changes in the gas concentrations by measuring the attenuation of the ultrasound waves caused by the gas under measurement.

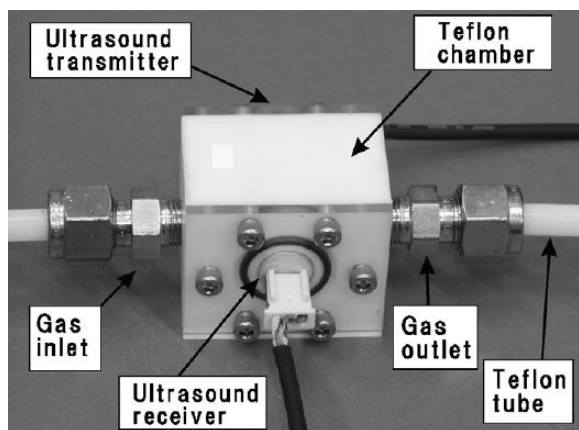


Figure 2.19 - Ultrasound transmitter and receiver units embedded in the chamber.

The Figure shows the structure of the reported sensor; the ultrasound transmitter and receiver are arranged face to face while the gas stream is perpendicular to the propagation direction of the ultrasound.

The transmitter generates a 400 kHz continuous ultrasound which passed through the gas flow and reached the receiver where the amplitude of the received ultrasound is affected by the concentration of the gas where the sensor can detect changes in the gas concentrations from the ultrasound attenuation caused by the gas flow.

2.10.2 Silicon Micromachined Gas Chromatography System

Gas chromatography (GC) is an analytical chemistry tool mainly used in the laboratory to analyze gas mixtures. The GC system separates the components of a gas mixture, identify them, and quantify their concentrations. The GC systems are very precise however they have some limitations where they tend to be bulky in size, fragile, slow and expensive. Many microfabricated GC (micro-GC) column designs have been reported [90, 91]. A miniature gas analyzer based on chromatography (Figure 2.10), using silicon micromachining and integrated circuit (IC) processing techniques, was reported in [82], the silicon micromachined gas chromatography system (SMGCS) was capable of separating NH_3 and NO_2 at parts-per-million concentration but with analysis time relatively large (30 minutes).

MEMS-enabled miniaturized GC in combination with high sensitivity MOX detectors was reported in [91]. The system was used as a stand-alone sub-ppb level monitoring system for aromatic volatile organic compounds (VOC).

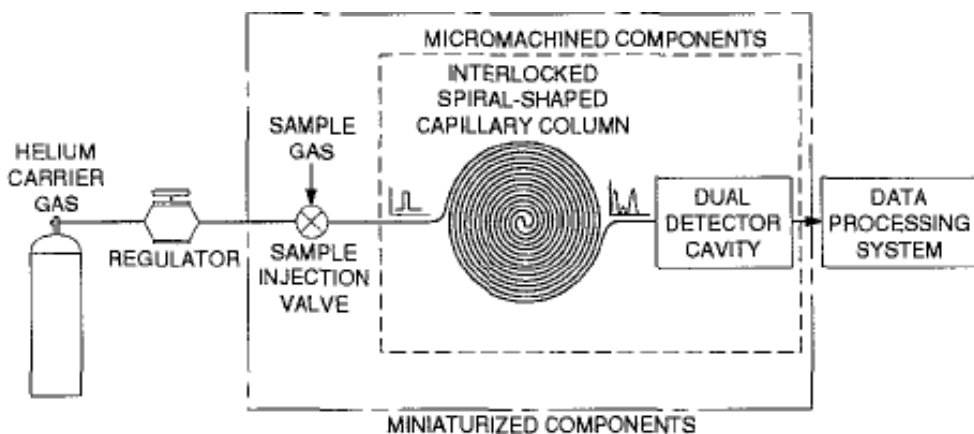


Figure 2.20 - Functional block diagram of the micromachined gas chromatography (GC) system.

2.11 Electronic Nose (e-nose) and Machine Olfaction

The electronic nose is an electronic device that mimics the human olfactory system. The idea of an electronic nose depends on the cross-sensitivity of some gas sensors where sensors with broad and partially overlapping selectivity can be used to detect a wide range of gases, odors or volatile compound by pattern-recognition means [83,84] for application mainly in environmental control and in food industry as an artificial substitute of the human olfactory system.

Research in the field of gas sensing is directed toward the developing of currently used gas sensor techniques by improving their sensitivity, selectivity and stability for the detection of gases on one hand and on the other hand toward the development of electronic nose for detection of odors and chemical compounds [11]. The electronic nose is an electronic device that mimics the human olfactory system. The Biological olfaction depends on olfactory neuron cell receptors that when volatilized molecules bind to it, produce a change in its conformation that induce signal transduction along the olfactory neurons and results identification of the smell [6].

The term 'Electronic Nose' (EN) was used for the first time 1988. The idea of an electronic nose depends on the cross-sensitivity of some gas sensors where sensors with broad and partially overlapping selectivity can be used to detect a wide range of gases, odors or volatile compound by pattern-recognition means [83] for application mainly in environmental control and in food industry as an artificial substitute of the human olfactory system.

The e-noses are built in an array configuration of many sensors, this configuration gives, as a response, a vector of values instead of one value then this response is used and analyzed using data processing approaches and pattern analysis. The transformation of a non-recognizable signal to a recognizable symbol is called pattern recognition [9]. Pattern recognition is used in e-nose applications in order to perform a qualitative and/or quantitative analysis of the response data from the ambient under examination. The current trend in research in the field of machine olfaction is to build arrays of sensors with larger size of data sets and number of sensors in the array.

One of the early used e-nose systems was used in 1984 by US Coast Guard for the detection of hazardous chemicals in waterways and on land; the system [89] used an array of four electrochemical cells, with different specificity due to the different electrocatalyst and electrochemical potential used, along with two filaments that are operated as crackers before the gas reaches the array where they work in four operation modes, the response of the system is a vector with 16 signal channels where these 16-channel signals are considered as fingerprints of the different gases concentrations.

Piezoelectric SAW devices were also implemented in e-nose applications using neural network pattern recognition [27, 28].

Pattern recognition process in e-nose application was discussed in [83]. The process can be divided into four steps: signal preprocessing, dimensionality reduction, prediction, and validation. All of these steps are done after the data from the sensors array is acquired. Signal preprocessing is done for compensating the sensor drift, extracting and preparing the feature vector for further processing then through the dimensionality reduction stage this feature vector is decreased in dimension to be used in to solve a given prediction problem like classification: to identify an unknown sample as one from a set of previously learned odorants, regression: to predict a set of properties like concentration and quality, and clustering to learn the structural relationships among different odorants. And finally the validation step where the estimation of the true error rates for a trained system is done. The most important step is the prediction step. A detailed review on modern pattern recognition methods can be found at [84].

E-nose systems suffer from a serious limitation which is the drift of the gas sensors used in the array configuration; this sensor drift phenomenon afflicts almost all kinds of sensors [85] and causes serious problems where, under identical conditions, the sensors response to the same gas becomes slow and shows a non-deterministic (random) temporal variation.

The drift affects both sensor baseline and sensitivity that results in the inability of the system to identify known odors. Therefore in order to have reliable measurements from a sensor array, the sensor drift must be detected and compensated. The study of sensor drift is still a challenging task. Currently there are many algorithms to diminish the negative effect of gas sensor drift; this is called drift compensation. Solutions for the drift can be grouped into four main categories: periodic calibration, attuning methods, filtering of drift components and adaptive models, for a detailed information and comparison between all these algorithms, one can refer to [85].

Electronic noses are not meant to be appropriate sensor systems for every application, due to the selectivity and sensitivity limitations sensor arrays deployed in the e-nose, where most of the gas sensors have certain limitations in terms of many parameters. That's why up to now no universal electronic nose capable of identifying any gas sample has been built yet [86]. Adding to that other factors, like the lack of stability overtime and the high cost of recalibration, limit the widespread of these systems in the industrial applications [87].

2.12 Discussion of the Miniaturization Potential of Gas Sensors

The comparison between the different types of gas sensors for the purpose of miniaturization is somehow limited to partial comparisons that can be done regarding the existed miniature sensor that have been published. There is no single sensor technology that is ideal by itself for purpose of miniaturization and a tradeoff seems to be mandatory.

The first type to be discussed is the metal–oxide semiconductor gas sensors, they are considered one of the best candidates for miniaturization [2] since they are easy to fabricate, have a low cost, simple to integrate with other elements, have the ability to detect broad types of gases and are the most stable among other chemiresistive materials such as polymers and organic films. The recent researches have revealed an optimization in characteristics of these types in terms of selectivity, sensitivity, stability and their integration in microsystems. The major drawbacks in

their miniaturization are their high power consumption demands due to necessity of operation at high temperature, drift, aging, and sensitivity to environmental parameters.

On the same side the polymer chemiresistor that rely on the bulk resistance change rather than the surface resistance change like in semiconductor types have the same miniaturization advantages. However, they are much subjected to noise in their d.c. mode operation, here the a.c. mode seems to be promising in signal to noise ratio enhancement but also require additional electronic circuit integration for signal processing.

To solve the high power consumption issue of the metal-oxide gas sensors and for noise enhancement considerations the electrochemical FET-based architecture, called CHEMFET gas sensors, come to be an alternative choice since they can operate at room temperature and doesn't require a heating element also their sensing area minimization does not affect the quality of the response signal of the sensor, unlike chemiresistors semiconductors and polymer based sensors, also they don't show many of the fluctuations and instability of the chemiresistor [2]. These sensors are considered to be low cost/low power gas sensors and they can be used in tiny sensing arrays on one single chip [62]. However, the disadvantages in their miniaturization are in being larger in size than the chemiresistor and require more complex signal processing.

CNTs sensors can be considered the most promising for portable miniaturized gas sensor in the chemical gas sensors since they are nano-scale sized, operate at room temperature, have a high sensitivity, low cost fabrication and can be easily incorporated into microscale electronic devices [37]. They might be considered better than other chemiresistive sensors like the metal-oxide and polymer sensors and unlike the CHEMFET types, they are much smaller than the other types of chemoresistive sensors. Although many CNTs sensors have been reported in the literature, CNTs is only a recent development and there still fundamental challenges that need to be addressed before they can be commercialized sensors.

In the field ionization gas sensors CNTs as a field emitter have better potential for miniaturization than the chemical CNTs sensor since they have stable structure under high electric fields and considered one of the best field emitters among conventional field emitting metals and have better consistent nanometer-scale surface topology than conventional planar electrodes or micro-machined electron emitters[38]. These CNTs based types of sensors solve

the problems that the chemical CNT and other sensors have like: poor diffusion kinetics, inability to identify gases with low adsorption energies and high sensitivity to changes in moisture, temperature and gas-flow velocity). However they can be crashed by large electrical current which cause a drop in the ability of field ionization and could be oxidized and degraded easily in the presence of oxygen. An Alternative field emitter is the ZnO nanowires which offer more stability than that of CNTs, high melting point and rigidity, but they have a higher breakdown voltage than that of CNTs. therefore in term of stability the ZnO nanowires are better candidate for a field ionization gas sensor than CNTs [15].

For piezoelectric gas sensors, the SAW devices are of a good potential for miniaturization and they are used in e-nose systems [27, 28], since they have a relatively low fabrication cost and they can be miniaturized with precise and reproducible characteristics using photo-lithographic techniques [9], but the most important disadvantage is their limited selectivity.

Conventional gas analyzers like gas chromatographs were miniaturized [82, 90, 91] using silicon micromachining and integrated circuit (IC) processing techniques but its miniaturization cost and response time is relatively high.

For optical gas sensors the miniaturization process involves high complexity and requires the implementation of integrated optics in their design; hence micro-optical gas sensors should be considered miniature instruments [8]. In optical emission spectroscopy sensors the silicon micromachining allows the miniaturization of plasma sources [45], but the realization of a micro-optical gas sensor require the integration of these micro-plasma sources with different optical instruments like spectrometers, refractometers etc. this can be done by the processes of integrated optics that allow the fabrication of extremely cost efficient complete miniaturized optical instruments [8]. The relatively new optical surface plasmon resonance (SPR) spectroscopy method promises good sensitivity for a miniaturized sensor with a low power consumption, due to advancements in the Si-based micro-fabrication and micro-fluidic system, the sensor can be miniaturized and integrated on a single Si-based chip [56]. However their lack of selectivity could be a problem.

Finally, we can classify sensors according to their miniaturization potential into four classes (see Table1); the first class containing the CNT and ZnO nanowires could be considered the most

promising one but as it is still in the R&D phase more research must be addressed regarding their sensitivity and selectivity. In the second class comes the semiconductor based sensors with a drawback in their relatively high power consumption and high noise. The third class contains the Piezoelectric and SPR based sensors suffer from the limited selectivity disregarding their cost. Finally the fourth class which contains conventional Chromatography and optical spectroscopy that suffer from their high manufacturing costs and relatively large size. However, no single technology is the perfect candidate for the miniaturization due to the trade-off that must be made concerning each one and the decision in choice must be according to the type of application.

Sensor Parameter	Class 1		Class 2			Class 3		Class 4	
	CNT	ZnO Nanowires	MOS	Polymer Chemiresistor	ChemFET	Piezoelectric (SAW)	SPR	Chromato graph	Emission Spectroscopy
Selectivity	+	+	+	+	+	-	--	++	++
Sensitivity	+	+	+	+	+	+	+	+	+
Power saving	+	+	-	-	+	+	++	+	+
Low cost	+	+	+	+	+	+	--	--	--
Noise efficiency	+	+	-	--	+	+	+	+	+
Size Miniaturization	+++	+++	++	++	+	+	+	-	-
High response time	++	++	+	+	+	+	+	--	+

Table 2.1- The trade-off between the discussed types of sensors concerning the different parameters; the negative sign indicate a disadvantage and the positive one indicate an advantage for the sensor at the corresponding parameter.

2.13 Conclusion

In this chapter, we have reviewed the major types of gas sensing technologies mentioning some of the developments in their field of research. The recent trends are focusing on investigating

novel technologies and approaches in addition to improving of the conventional state of-the-art sensor technologies. The increase in demands for improving the sensors' capability and reliability have pushed the research in this field toward the production of a new high performance and low cost, miniature gas sensors. We discussed and compared the miniaturization potential of most types of gas sensorsclassifying them, according to their miniaturization potential, into four classes. We have found that many technologies are promising and can fit the requirements but there is no single technology that can be considered the perfect candidate. Major problems are still facing the achievement of the ultimate sensitive and selective miniature sensor.

2.14 References

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3. Chapter Three: Gas Discharge Plasmas

3.1 Introduction

In the previous chapter we discussed the recent trends in gas sensing technologies and their miniaturization potential, one of the technologies that we have reviewed is the optical emission spectroscopy (OES) [1,2]. This technology is used to detect the spectrum of atoms and molecules; it's also used in gas sensing. We found this technology to be very promising for the aim of our research which is to analyze multiple gases simultaneously using one sensor. The optical emissions of a gas depends on the gas discharge plasma; a well known phenomenon that is used in many fields. In our proposed sensor we looked for a parameter that can be measured and uniquely reflects the identity of a certain gas. The idea came from the plasma discharge where we can obtain a light emission from the mixture of the gases that we want to analyze since the spectrum of this emission is considered as a finger print to a certain gas.

There are varieties of ways to produce a light emission from gases by transforming them into plasma and they are familiar to most spectrochemists. The classical configuration, a d.c. glow discharge operating either at reduced or atmospheric pressure, is widely known and used. However, new excitation modes, such as powering with an rf generator (either in the capacitive or inductive configuration), applying a magnetic field or microwave power, etc, have been developed to increase the plasma density and the efficiency of power absorption.

Plasma discharge is widely used in other (mainly technological) application fields due to the large chemical freedom offered by the non-equilibrium aspects of the plasma. This wide variety of chemical non-equilibrium conditions is possible, since (external control) parameters can easily be modified, such as the working gas, the pressure (ranging from approx. 0.1 Pa to atmospheric pressure), the electromagnetic field structure, the discharge configuration (e.g. with or without electrodes), and the temporal behavior (e.g. pulsing the plasma). In what follows we will discuss the gas discharge plasma, types, applications and the physical theory behind it.

3.2 State of the art

In 1960s and 1970s Glow Discharge (GD) became a major focus of research in many analytical chemistry laboratories. The research work has been directed towards glow discharge source development and the fundamental study of the physical characteristics of the analytical glow discharge, and towards the development and application of glow discharge spectroscopic techniques. The Miniaturized discharge devices are the major field of research in plasma discharge since in a miniaturized discharge glow discharges can be generated at atmospheric (or even higher) pressure [3]. Capacitively coupled rf discharges at atmospheric pressure have been used [4] for analytical applications. In [5, 6] the use of an atmospheric pressure helium d.c. glow discharge on a microchip, as a molecular optical emission detector for gas chromatography, was reported. Another atmospheric pressure micro-discharge in hollow-cathode geometry was developed [7, 8, and 9]. The hollow cathode diameter was typically 100–200 mm. In Czerfalvi et al. [10] and Mezei et al. [11], a small atmospheric pressure discharge for analysis of water and waste water solutions was operated in open air with an electrolyte solution as the cathode.

3.3 Atomic Transitions and Light Emission

The physical background behind light emission in gas discharge tube relies on the quantum theory of emission and absorption. In emission the energy of a photon is released by an atom whose electrons make a transition between two electronic energy levels. Electrons are excited to a high energy states when they absorb excess energy. The excess energy can be provided by heat, light, or electrical discharge. As the electrons return to lower energy states, they release their excess energy generally in the form of a single photon of light for each electron energy transition they make.

There are two kinds of atomic transitions: excitational where the atom gains energy and de-excitational in which it loses energy. Excitation can be Collisional or Radiative; In a Collisional excitation the atom interacts, mostly, via electromagnetic interaction with another atom, an ion, or any other charged object and gains energy. In Radiative excitation the atom absorbs one or more photons. In a de-excitation the inverse is applied where the atom goes from a higher energy level to a lower one and release energy either by Collisional de-excitation or Radiative de-excitation by emitting a photon, this is also called Radiative emission (Figure 3.1).

Radiative Transitions

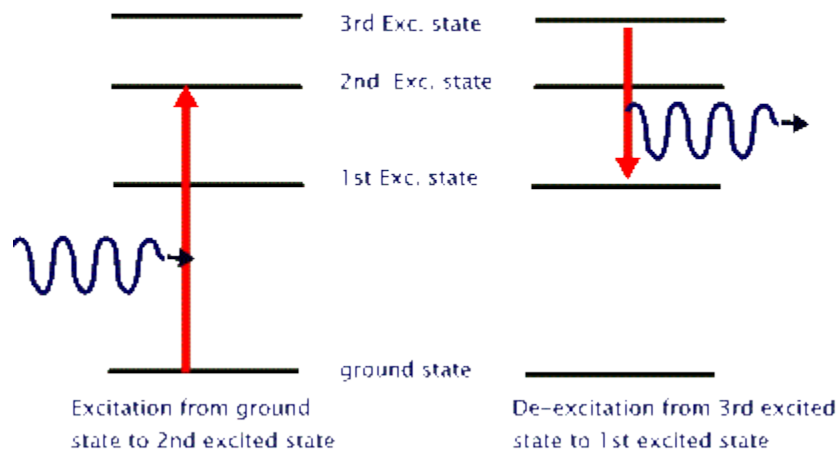


Figure 3.1 - Two kinds of atomic transitions excitation and de-excitation

3.4 The Emission Spectrum

When an atom or a group of atoms undergoes a radiative de-excitation from the different states an emission spectrum of emitted photons is produced. Different atoms will have different sets of possible emitted photon energies that are characteristic of that element. This spectrum is considered as a finger print of that atom (Figure 3.2).

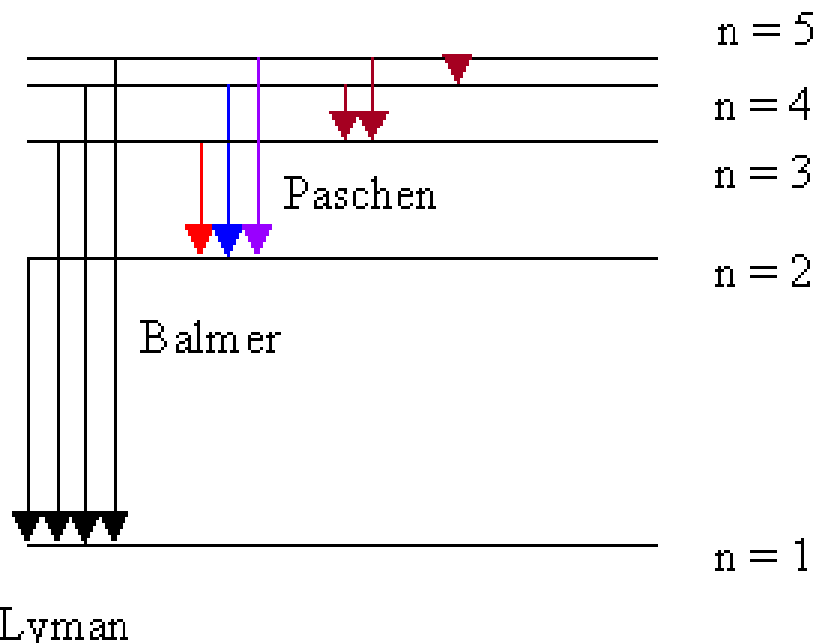


Figure 3.2- De-excitation transitions of hydrogen atom

The atomic emission spectrum is composed of discrete spectral lines. An emission line is formed when emitting a photon of a particular energy and wavelength (Table). A spectrum of many such photons will show an emission spike at the wavelength associated with these photons.

Color	wavelength (nm)	nm	eV
Red	625 - 740	700 nm	1.77
Orange	590 - 625	620 nm	2.00
Yellow	565 - 590	580 nm	2.14
Green	520 - 565	530 nm	2.34
Blue	435 - 500	470 nm	2.64
Violet	380 - 435	420 nm	2.95

Table 3.1 - Emission lines and their correspondig photon wavelength.

3.5 Case of Molecules

Molecules have additional internal degrees of freedom than atoms, and their states are not only determined by the electron cloud like in the case of atomic transition but also by the geometrical arrangement of the nuclei and their movements.

First, molecules possess more electronic states than atoms. Second, the nuclei in the molecule can vibrate around their equilibrium positions. Finally, the molecule as a whole may rotate around axes through its center of mass. Therefore, for each electronic molecular state there exist a large number of vibrational and rotational energy levels.

3.6 Gas Discharge Plasmas

Much of the visible matter in the universe is in the plasma state, it is the fourth state of matter, and it is a gas in which an important fraction of the atoms is ionized. Hence, they consist of positive (and negative) ions and electrons, as well as neutral species. The ionization degree can vary from 100% (fully ionized gases) to very low values (e.g. $10^{-4} - 10^{-6}$; partially ionized gases). There are two main groups of plasmas: the high-temperature or fusion plasmas, and the low-temperature plasmas or gas discharges. Plasma can be also divided into according to their temperature distinguishing between either with local thermal equilibrium' (LTE) where temperature of all species (electrons, ions, neutral species) is the same or not. The thermal equilibrium requires high temperature to attain [12]. The gas discharge plasmas can also be classified into LTE and non-LTE plasmas. This subdivision is typically related to the product of both the pressure and the length between the anode and the cathode (typically denoted as pD). There are many types of Gas Discharge Plasmas like:

3.6.1 Direct current (d.c.) glow discharges

Direct current (d.c.) glow discharge occurs when a constant potential difference is applied between the cathode and anode causing a continuous current to flow through the discharge. It should be mentioned that in a d.c. glow discharge the electrodes play an essential role for sustaining the plasma by secondary electron emission. The potential difference applied between the two electrodes is generally not equally distributed between cathode and anode (Figure 3.3).

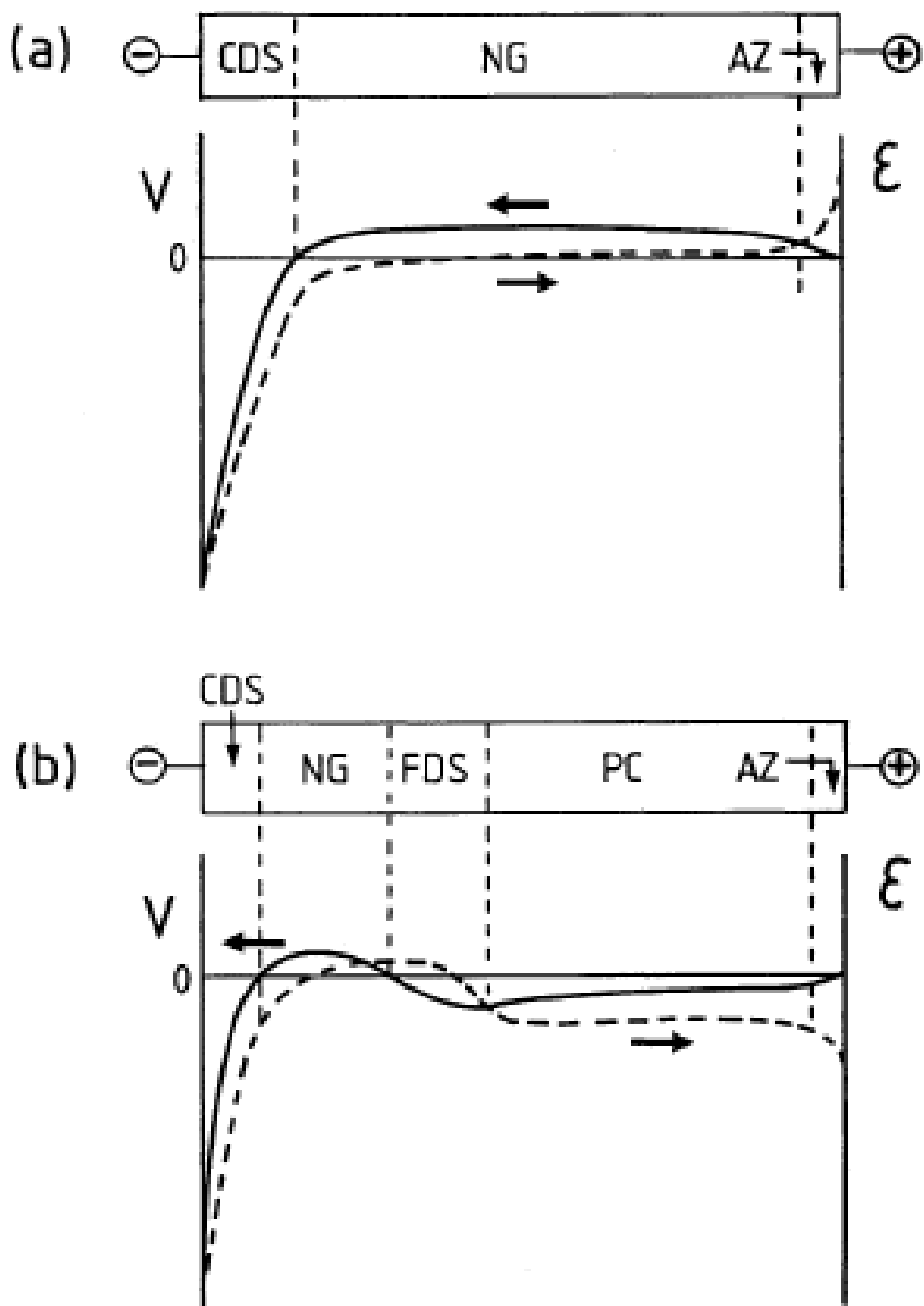


Figure 3.3 - Schematic diagram of the spatial regions present in d.c. glow discharges, (a) at short cathode-anode distance and/or low pressure; (b) at longer interelectrode distance and/or higher pressure (CDS=cathode dark space; NG=negative glow; FDS=Faraday dark

The region adjacent to the cathode is called the ‘cathode dark space’ (CDS) or ‘sheath’; the voltage drops almost completely. In the largest part of the discharge is the ‘negative glow’ (NG), the potential is nearly constant and slightly positive also called the ‘plasma potential’. A short anode zone (AZ) is present beside CDS and NG when the distance between cathode and anode is generally short, where the slightly positive plasma potential returns back to zero at the anode.

When the distance between cathode and anode is relatively long, two more regions can be present, i.e. the ‘Faraday dark space’ (FDS) and the ‘positive column’ (PC) (see Figure 3.3. 2b). They are characterized by a slightly negative electric field. These two regions are often present in glow discharges used as lasers and as fluorescence lamps.

In a d.c. glow discharge, the pressure varies from below 1 Pa to atmospheric pressure, the voltage is generally in the range between 300 and 1500 V and the current in the mA range. The discharge can operate in a rare gas like Argon or Helium and in a reactive gas (N₂, O₂, H₂, CH₄, SiH₄, SiF₄, etc.) and as well as in a mixture of these gases.

This makes this technique a strong candidate for our proposed sensor since it will have a great selectivity.

3.6.2 Capacitively coupled (cc)

In ‘capacitively coupled’ the way of coupling the input power into the discharge is by using of two electrodes and their sheaths forming a kind of capacitor. When one or both of the electrodes in the gas discharge are non-conductive, the electrodes will be charged up due to the accumulation of positive or negative charges. The glow discharge will not be sustainable if a d.c. voltage is applied between the two electrodes but by applying an alternating voltage, each electrode will act alternately as the cathode and anode. In this case the charge accumulated during one half-cycle is neutralized totally or partially by during the next half-cycle. The frequencies generally used for these alternating voltages are typically in the radiofrequency (rf) range (1 kHz–103 MHz). In practice, many rf GD processes operate at 13.56 MHz, because this is a frequency allotted by international communications authorities at which one can radiate a certain amount of energy without interfering with communications.

This glow discharge is used for the spectrochemical analysis of non-conducting materials or for the deposition of dielectric films, where the electrodes become gradually covered with insulating material.

3.6.3 Pulsed glow discharges

A pulsed glow discharge is very similar to a d.c. glow discharge, i.e. it can be considered as a short d.c. glow discharge, followed by a generally longer after glow. In Pulsed glow discharges the voltage applied to the glow discharge is in the form of discrete pulses, typically with lengths in the order of milli- to microseconds. Pulsed discharge can operate at much higher peak voltages and peak currents for the same average power as in a d.c. glow discharge that results a higher instantaneous sputtering, ionization and excitation. Recent works in pulsed glow discharge has focused mainly on microsecond discharges, where higher peak voltages and currents, and hence better sensitivities, can be obtained [13].

3.6.4 Atmospheric pressure glow discharges (APGDs)

The gas discharge depends on the product of two parameters: the pressure of the gas (p) and the distance between the electrodes (D). So theoretically it is possible to increase the gas pressure from the typical pressure range (100 Pa) if the linear dimension of the device is decreased [14]. The Operation of a discharge at high (even atmospheric) pressure leads to gas and cathode heating and arcing. The key for generating glow discharges at atmospheric (or even higher) pressure is by miniaturization of the discharge devices. The applications of the APGD include the surface modification of materials like enhancing the wettability of polymers used for paints and glues [15] and the sterilization of surfaces (Figure 3.4).

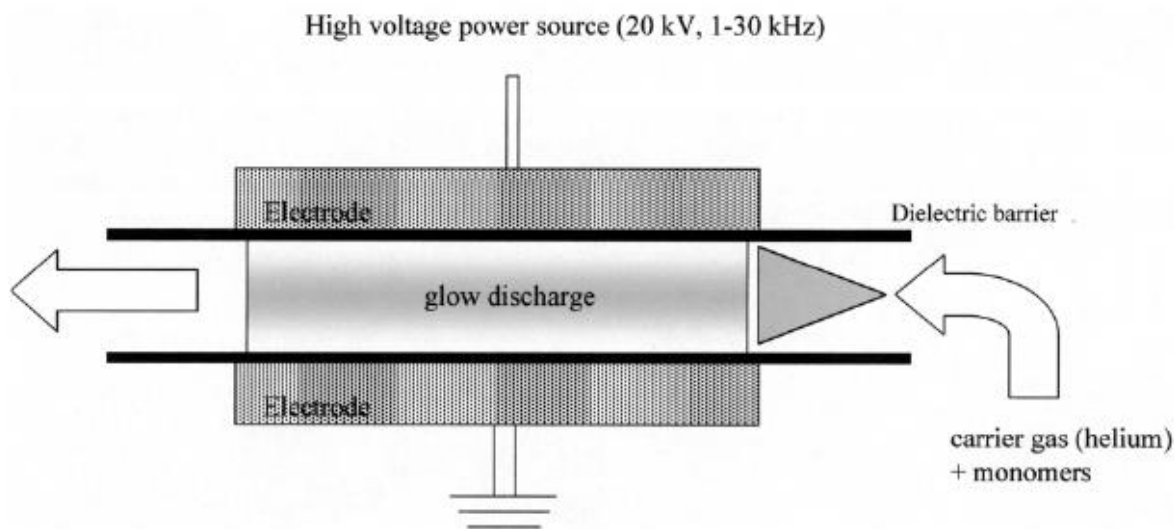


Figure 3.4 - Schematic representation of an atmospheric pressure glow discharge (APGD), typically used for plasma polymerization.

By eliminating the need of low pressure in the case of atmospheric pressure discharge, the cost and complexity of the glow discharge operation are greatly reduced.

3.6.5 Dielectric barrier discharges (DBDs)

Dielectric barrier discharges operate at approximately atmospheric pressure and a dielectric layer (made of glass, quartz, ceramic material or polymers) is placed between the electrodes. The voltage applied to the discharge is an a.c. voltage with amplitude of 1–100 kV and a frequency of a few Hz to MHz is. The DBD is similar to the APGD with a basic difference that the discharge in the APGD are generally homogeneous across the electrodes and are characterized by only one current pulse per half cycle, whereas the DBDs typically consist of microdischarge filaments of nanosecond duration (hence, with many current pulses per half cycle). The main application of DBDs is in the Ozone generation (ozonizers) that are effective tools and a large number of ozone installations that are used for water treatment [16] also it is used in the pumping of CO₂ lasers, thin-film deposition processes, the remediation of exhaust gases and for plasma display panels.

3.6.6 Corona discharges

Another type of pulsed d.c. discharge beside a glow discharge with two electrodes that operates at atmospheric pressure, is the Corona discharge. It has a cathode in the form of a wire [17]

where a high negative voltage (in the case of a negative corona discharge) is applied to the wire cathode. There also exists a positive corona discharge, where the wire has a positive voltage, hence acting as anode. The name ‘corona discharge’ arises from the fact that the discharge appears as a lighting crown around the wire.

3.6.7 Magnetron discharges

The magnetron discharge characterized by applying crossed magnetic and electric fields (d.c. or rf potential difference) to a glow discharge. Three different types of magnetron configurations can be distinguished, i.e. cylindrical, circular and planar magnetrons [18].

3.6.8 Inductively coupled plasmas (ICPs)

Inductively coupled plasmas (ICPs) can be classified under a wide class of plasma discharge the “Low-pressure, high-density plasmas”. ICPs are the most popular plasma sources in plasma spectrochemistry. In the inductively coupled source the plasma chamber is surrounded by a coil where the rf currents in the coil (inductive element) generate an rf magnetic flux, which penetrates the plasma region (Figure 3.5).

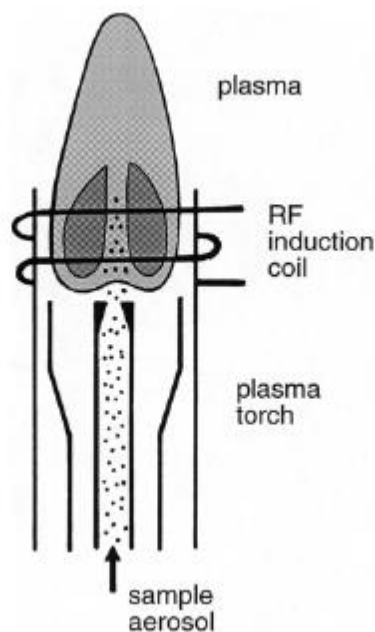


Figure 3.5 - Schematic representation of an analytical ICP torch.

The time-varying magnetic flux density induces a solenoidal rf electric field, which accelerates the free electrons and sustains the discharge [19]. Inductively coupled plasmas are used as materials processing discharges, spectrochemistry and mass spectrometric detection.

3.6.9 Microwave induced plasmas

Microwave induced plasmas (MIPs) are all plasmas that are created by the injection of microwave power, i.e. electromagnetic radiation in the frequency range of 300 MHz to 10 GHz [20]. The MIPs includes cavity induced plasmas, free expanding atmospheric plasma torches, ECRs, surface wave discharges (SWD), etc. These different plasma types operate on a pressure ranging from less than 0.1 Pa to a few atmospheres, a power between a few W and several hundreds of kW, sustained in both noble gases and molecular gases.

3.7 Applications of Gas Discharge Plasmas

The gas discharge plasmas have many applications ranging from industrial to chemical spectroscopy. Plasma can be classified into LTE and non-LTE plasmas. LTE discharges, which are characterized by rather high temperatures, are typically used for applications where heat is required, such as for cutting, spraying, welding or, as in the analytical ICP, for the evaporation of an analyte material. Non-LTE plasmas, on the other hand, are typically used for applications where heat is not desirable, such as for etching or the deposition of thin layers. The following is a list of some of the applications of plasma discharge:

- Surface modifications: Deposition of thin films, Etching, Plasma-immersion ion implantation, Surface activation and functionalization of polymers, Plasma polymerization, Cleaning of surfaces, Ashing (mainly used to remove organic fragments from inorganic surfaces), Oxidation, Surface hardening.
- Lamps: Electroded low/high pressure and Electrodeless lamps
- Plasma displays: Plasma display panels (PDPs) and Plasma addressed liquid crystal (PALC) technology
- Lasers: Atomic lasers, Ion lasers and Molecular lasers
- Ozone (O₃) generation
- Environmental applications: Destruction of hazardous wastes

- Biomedical applications: Improving the biocompatibility of materials and plasma sterilization of biological samples.
- Particle sources

3.8 Gas Discharge Tube

The Gas-Discharge tube consists of a glass tube with two electrodes on its closed extremities. At low pressure (between 5 and 15 torr) if we apply a high voltage (in the range of 1000 to 5000 volts) to the electrodes, a current flows through the gas and the gas begins to glow with specific spectrum. The voltage across a discharge tube will accelerate a free electron up to some maximum kinetic energy. The voltage must be large enough so that this energy is more than that required to ionize the atom. The flow of ions through the tube excites the gas atoms by collisional excitation. The plasma that is formed from the charged ions and electrons allows the current to pass between the tube's electrodes causing that light emission to occur.

The color of the emitted light is determined by the energy of the emitted photon. The energy of the light is related to its wavelength by the equation $E = hc/\lambda$, where λ is the wavelength, h is Planck's constant, and c is the speed of light. The color of the light emitted which is in the visible spectrum is a characteristic of the atom species present. The identity of the gas in the tube determines the color of the glow. Neon emits a red glow; helium produces pale yellow, and argon yields blue.

The emitted radiations along the Electromagnetic Spectrum that can be easily detected are (Figure 3.6):

- ✓ Vacuum ultraviolet (VUV, 120–185 nm).
- ✓ Ultraviolet (UV, 185–400nm).
- ✓ Visible (VIS, 400–700 nm).
- ✓ Near infrared regions (NIR, 700–850 nm).

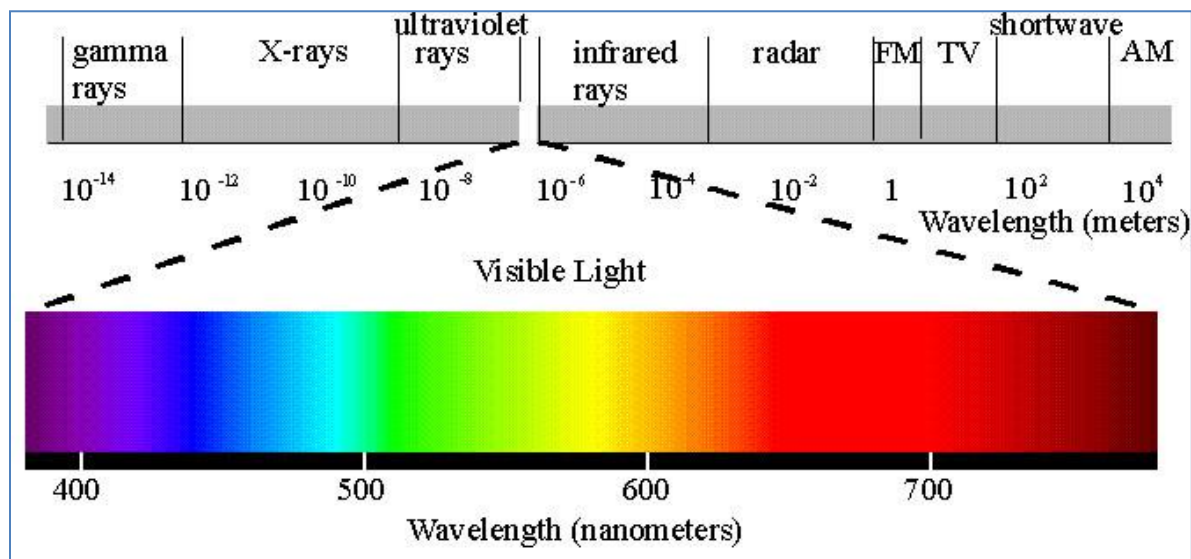


Figure 3.6 - The Electromagnetic Spectrum

In the other electromagnetic radiation in the infrared, microwave, and radio wave regions, the detection systems are less sensitive.

3.9 Glow Discharge Optical Emission Spectroscopy

Glow Discharge Optical Emission Spectrometry (GD-OES) has been used for years to determine the plasma parameters, such as its composition, temperature and electron density. In a glow discharge, the characteristic spectrum emitted by the glow discharge source is measured by the spectrometer. Besides measurements of electrical discharge parameters and photo-documentation, optical emission spectroscopy (OES) in UV-visible regions is widely used for plasma diagnostics as non-invasive and in situ method.

Discharge plasmas present considerable interest for a wide range of environmental, bio-medical and industrial applications, such as air pollution control, waste water cleaning, bio-decontamination and sterilization, material and surface treatment, electromagnetic wave shielding, carbon beneficiation and nanotube growth, and element analysis. Optical emission spectroscopy provides valuable information on excited atomic and molecular states, enables to determine the rotational, vibrational, and electronic excitation temperatures of the plasma and

thus the level of non-equilibrium and the gas temperature, and sometimes even the electron temperature [21, 22].

(OES) in UV–visible regions is used to identify many species (radicals and atoms or molecules) that is applied in the air or water pollution control processes and in biological and medical applications in order to understand the mechanisms of bio-inactivation and of the plasma [23]

One of the most important applications of (GD-OES) Provides rapid, direct bulk analysis and depth profiling analysis of solids: metals, powders, polymers, glasses and ceramics. For this the cathodic sputtering is used to remove material layer by layer from the sample surface. The atoms, removed from the sample surface, migrate into the plasma where they are excited through collisions with electrons or meta-stable carrier gas atoms. The characteristic spectrum emitted by this excited atoms is measured by the spectrometer.

The detection of the spectrum of the glow was made spectrometers. This is done by splitting light into its spectral components. The basic optical system of a spectrometer consists of a slit, a collimator, a dispersing element, and a focusing objective. Light passes through the slit and enters the collimator. A collimator is straightens out light coming in at various angles so that all of the light is travelling the same direction. Next, light enters the dispersing element, like a prism or diffraction grating, which spreads light of multiple wavelengths into discrete colors. The colors are then quantified using photometric sensors like photo multiplier tubes (PM) but the use of solid state detectors, CCD's and photo diode array's have become a common alternative for PM tubes.

3.10 The Plasma Parameters:

Electrons have far lower masses than ions, they have far higher typical speeds at fixed temperature and are much more easily accelerated; i.e., they are much more mobile. As a result, it is the motion of the electrons, not the ions, that is responsible for the transport of heat and electricity through plasma. In studying the discharge plasma, certain parameters should be defined and studied in order to understand the processes that are taking place inside the discharge tube.

3.10.1 Electron temperature:

The "ion temperature" may be very different from (usually lower than) the "electron temperature" because of the large difference in mass, the electrons come to thermodynamic equilibrium amongst themselves much faster than they come into equilibrium with the ions or neutral atoms. The plasma temperature is commonly measured in Kelvin or electron volts, and is an informal measure of the thermal kinetic energy per particle. The plasma temperature generally is estimated by the relative emission intensities of spectral lines.

There are two main groups of plasmas: the high-temperature or fusion plasmas, and the low-temperature plasmas or gas discharges. Plasma can be also divided into according to their temperature distinguishing between either with local thermal equilibrium' (LTE) where temperature of all species (electrons, ions, neutral species) is the same or not. The thermal equilibrium requires high temperature to attain [12]. The gas discharge plasmas can also be classified into LTE and non-LTE plasmas.

In non-LTE plasma ($T_e \gg T_{ion} = T_{gas}$) and in LTE plasma ($T_e = T_{ion} = T_{gas}$), where T_e , T_{ion} and T_{gas} is the temperature of the electrons, ions and the gas respectively.

3.10.2 Electron density

The term "plasma density" by itself usually refers to the "electron density", that is, the number of free electrons per unit volume. The degree of ionization of a plasma is the proportion of atoms which have lost (or gained) electrons.

According to the kinetic theory of gases, the number of molecules or density in a centimeter cube is given by the relation (temperature in Kelvin)

$$N=9.65 \times 10^{18} \frac{P}{T}$$

-where N is number of molecules or density in a centimeter cube, P is the pressure in Torr and T is the temperature in Kelvin

3.10.3 Electron drift velocity

The drift velocity is the average velocity that a particle, such as an electron, attains due to an electric field. When an electron in a gas is acted upon by a uniform electric field, it will be accelerated until it reaches a constant drift velocity.

3.10.4 Electron energy distribution function

The Electron Energy Distribution Function (EEDF) a distribution $f(E)$ of electron energies, defined such that $f(E)dE$ is the fraction of electrons with energy in the interval $(E, E + dE)$ since in an electric discharge the kinetic energy of the electrons are not uniformly distributed. The Electron (EEDF) in a low pressure processing plasma is very much a 'Fingerprint' of the discharge.

3.10.5 Electron molecule collision cross section

Charged particles move under the influence of electric and magnetic fields in an electric discharge. Total probability of collisions has a value between 0-1 this means there is a collisions or not but there is also different collisions according to electrons energy so probability of that interactions depends on, number of the collisions in unit time and number of the interaction in the same time interval.

If ideal gas atom has $2.8 \times 10^{-15} \text{ cm}^2$ area and electron radius is $2.8179 \times 10^{-13} \text{ cm}$, collision has a radius of almost 3 \AA and this will sweep out a volume of gas as the atom moves. The electron molecule collision cross section gives the probability of collision processes. All types of collisions have their own characteristics – cross sections (σ).

3.10.6 Collision Frequency or Rate

Collision frequency as, its name shows, it is the frequency of collisions between electron - neutral, electron-ion and electron-electron. Hence the overall electron collision frequency, ν_c , is the sum of the electron-neutral collision frequency, electron-ion frequency and electron- electron collision frequency and it is defined as:

$$\nu_c = R = N \cdot \sigma_c(v) \cdot v ,$$

Where N is the volume density of the background medium and $\sigma_c(v)$ the cross section of the particle with velocity v for the type of collision being considered.

3.11 Conclusion

In this chapter we have seen that there are many excitation modes for gas discharge plasmas. The most known configuration is the classical d.c. glow discharge that has a wide range of applications in both atmospheric and low pressure. However, other excitation modes, such as powering with an rf generator (either in the capacitive or inductive configuration), applying a magnetic field or microwave power, etc, have been developed to increase the plasma density and the efficiency of power absorption [3].

As shown above in this chapter, different types of plasmas are used in a wide range of applications ranging from environmental applications like destruction of hazardous wastes and biomedical applications to industrial; the most important industrial application is the surface modification (Deposition of thin films, Etching, Plasma-immersion ion implantation, and surface hardening). Another very important domain where discharge plasma is used, especially for our scope of research, is in spectrochemistry. Plasma lamps and more specifically fluorescent lamps, is the oldest way of using the plasma discharge with a new types electrodeless lamps. Also, other applications like the plasma displays, lasers, ozone (O_3) generation.

The optical emission of the plasma discharge was our main interest in this research since it is considered as a finger print for a gas and an identity to both detect and analyze qualitatively and quantitatively since the emission intensity is related to the gas concentration. In the next chapter we will introduce the idea of using the glow discharge in gas sensing of multiple gases simultaneously using color processing.

3.12 References

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4. Gas Concentration Measurement Using Digital Image Processing

4.1 Introduction

Gas sensors have played a major role in many domains ranging from the industrial applications to environmental monitoring. In the past years many methods for gas detection and sensing have been developed but most with a high cost and specific to certain gases only [1]. In this chapter we are trying to search for a new sensor which will be used to determine the concentration of each single gas in a mixture of previously known components. This sensor can be used to detect different kind of gases at the same time.

The sensor is based on the analyzing of the spectra of the emissions [2] of the studied gas; the emissions will be made by means of a gas discharge tube and captured through a CCD sensor. The images are then analyzed and processed to determine the concentration of each of the multi components in the mixture. The calibration of the color imaging sensor used in the experiment results in a great enhancement of the system.

The different approaches in gas sensing domain focus on sensors that measure either a certain type of gases or a limited number of them. The exceptions are gas analyzers like the gas chromatography [3], where it can detect many number of gases at the same time. However these analyzers are bulk, expensive, hard to use, and have a long response time.

In this chapter we proposed a small, low cost with a relatively short response time sensor that is not limited to a certain gas rather to a wide range of gases and can determine the concentration of a group of gases (up to four) in a mixture.

The chapter is divided into eight parts; the first part is an introduction to the chapter, the second part discusses the previous work done in this field especially in optical gas sensors. The third part states the principle of our proposed sensor and the mathematical model of light mixing resulted from the gas discharge emissions. The approach to the gas concentration measurement is discussed in part four. The experimental system is listed in details in the fifth part where the results and their interpretation were discussed in part six. In part seven, we tried to interpret the source of the error in measurement that appeared in our experiments that's why we studied the

sensitivity of the imaging sensor to color value measurement. Finally, a conclusion and perspectives of our work were mentioned in the last part.

4.2 State of the Art

Gas sensing methods are wide and diverse due to the several physical and chemical effects that can be measured and reflect the gas characteristics [22]. Sensors like Metal Oxide Semi Conductor (MOS) gas sensors [4] are widely used in commercial sensors other new sensors like carbon nanotube based sensors [7] are relatively new. Optical methods in gases detection like ellipsometry, spectroscopy, interferometry and surface plasmon resonance (SPR) determine gas concentrations by measuring the refractive index, absorbance and fluorescence of the sensing material subjected to the gas [8]. The optical spectroscopy gives quantitative and qualitative information of gases, the emitted or absorbed electromagnetic radiation spectrum tells us about the concentration or the quantitative information, while the qualitative information is related to the wavelengths of the spectrum. Mainly three different techniques are used: atomic absorption spectrometry (AAS), optical emission spectrometry (OES) and atomic fluorescence spectrometry (AFS). These techniques are often used in chemical laboratories as analyzers, also they have been used in instruments for air pollutant measurements [9]. Small sized OES based sensor for exhaust emission has been reported [10] and another handheld micro system to analyze chemicals both in vapor and liquid phases using discharge spectroscopy was presented in [11].

The first optical gas sensors were based on the absorption spectrum difference measurement like the infrared IR gas detectors which have been in use for long time ago, they have long life time with greater stability over time. Their disadvantages are that they can only detect gases that are strongly absorbent in the infrared spectrum like hydrocarbons, they require a relatively large volume of gas for response testing and their ambient temperature is limited to 70°C.

Optical spectroscopy gas detection techniques are rapid and often provide highly selective means of measuring gas concentration with good sensitivity they also have a good precision, their disadvantages are in being expensive and the measured gas must have a significant and distinct absorption, emission or scattering in a convenient region of the optical spectrum in order to be detectable [12]. Optical fiber based gas sensors offers some important advantages, their sides are coated with a fluorescent dye encapsulated in a polymer matrix, when interacted with gases the

dye's optical properties such as intensity, spectrum, lifetime or wavelength shift in fluorescence are changed [5]. Optical fiber based gas sensors have small size and light weight, remotely operated, they have an electromagnetic immunity which enable them to work in high noise environment, and they are also passive devices and require no electric power in the sensing zone which makes them reliable in environments with flammable gases [6].

All of the previous methods relies on a high cost systems to analyze the spectrum of the emissions however in our proposed sensor we use the digital image processing to analyze the color of the emission that decrease the cost of the system in general and the overhead calculations and processing required.

4.3 Principle

The principle of our proposed sensor relies on the idea of optical gas emission under electric discharge. Simply saying, when an electric current is passed through a certain type of gas, the gas emits light. The color of the emitted light depends on the kind of the gas; so this color is considered as the gas identity. For example the color of Helium in the discharge tube is Pink.

The color of the emitted light is determined by the energy of the emitted photon. The energy of the light is related to its wave-length by the equation $E = hc/\lambda$, where λ is the wavelength, h is Planck's constant (6.63×10^{-34} J sec), and c is the speed of light (3.00×10^8 m/sec). Therefore, only certain wavelengths of light are emitted by gases in a discharge tube.

4.3.1 Spectrum Addition of the Emission of a Mixture of Two Gases

Theoretically when two or more light sources are mixed, their spectral power distributions add and hence their intensities add. Let's consider the case of a mixture of two gases where it's under an electric field that causes the breakdown of the two gases that emit photons. Let $S_1(\lambda)$, $S_2(\lambda)$ be the spectrum of the emission of gas1 and gas2 respectively. Then theoretically the total spectrum S_T of the gas mixture will be the sum of the two spectrums:

$$S_T(\lambda) = S_1(\lambda) + S_2(\lambda)$$

The intensity of an emission of a certain gas depends on the number of photons emitted that depends on the density and temperature of the gas [13] and hence at constant temperature the intensity is proportional to the gas percentage in the mixture.

Consider the partial spectrum $S_i(\lambda)$ of a certain Gas_i in a mixture, $S_i(\lambda)$ will vary proportionally with the gas partial pressure p or its percentage in that mixture. Taking $S_{Ref}(\lambda)$ as the reference spectrum at a certain pressure then we can say:

$$S_i(\lambda) = p_i S_{Ref}(\lambda)$$

Where p_i is the percentage of the Gas_i in a mixture of gases that also corresponds to its partial pressure

The total spectrum $S_T(\lambda)$ resulted from the mixing of two spectra $S_{p1}(\lambda)$ and $S_{p2}(\lambda)$ of two gases with different percentages will be:

$$S_T(\lambda) = S_{p1}(\lambda) + S_{p2}(\lambda)$$

$$\mathbf{S}_T(\lambda) = \mathbf{p}_1 \mathbf{S}_1(\lambda) + \mathbf{p}_2 \mathbf{S}_2(\lambda) \text{ (equ. 1)}$$

Where $S_i(\lambda)$ is the reference spectrum of the emission of Gas_i.

4.3.2 Emission Measurement

Measuring the gas electric discharge emissions with a spectrometer gives a detailed measurement at each wave length. However using imaging techniques gives a less details at specific number of channels according to the type the imaging sensor. The trichromatic imaging sensor in the visible spectral region contains three channels x, y and z that gives integrated values describing the spectrum at three interlaced wavelength bands.

The response at any pixel of the imaging system sensor is:

$$x = \int_{\lambda} X(\lambda) S(\lambda) d\lambda$$

$$y = \int_{\lambda} Y(\lambda) S(\lambda) d\lambda$$

$$z = \int_{\lambda} Z(\lambda)S(\lambda)d\lambda$$

Where $X(\lambda)$, $Y(\lambda)$ and $Z(\lambda)$ are the color matching functions of the sensor and λ is the wavelength in the visible region [14].

Then the sensor's response to the emission of the mixture at channel x is:

$$x_T = \int_{\lambda} X(\lambda)(S_1(\lambda) + S_2(\lambda))d\lambda$$

$$x_T = \int_{\lambda} X(\lambda)S_1(\lambda)d\lambda + \int_{\lambda} X(\lambda)S_2(\lambda)d\lambda$$

$$x_T = x_1 + x_2$$

And the same apply for y and z channels:

$$x_T = x_1 + x_2$$

$$y_T = y_1 + y_2$$

$$z_T = z_1 + z_2$$

This is also known from Grassman's law [15] where in a trichromatic imaging system the matching between the spectrum and the three channels (x,y and z) is linear; that implies if we multiply the SPD of an emission with a constant and non negative number K the response on the three channels is respectively K_x , K_y and K_z .

The total spectrum resulted from the mixing of two spectra $S_{p1}(\lambda)$ and $S_{p2}(\lambda)$, the response of the imaging sensor on the channel x is:

$$x_T = \int_{\lambda} X(\lambda)S_T(\lambda) d\lambda$$

$$x_T = \int_{\lambda} X(\lambda)(p_1 S_1(\lambda) + p_2 S_2(\lambda)) d\lambda$$

$$x_T = p_1 \int_{\lambda} X(\lambda) S_1(\lambda) d\lambda + p_2 \int_{\lambda} X(\lambda) S_2(\lambda) d\lambda$$

$$x_T = p_1 x_1 + p_2 x_2 \text{ (equ. 2)}$$

Also the same apply for the three channels x, y and z:

$$x_T = p_1 x_1 + p_2 x_2$$

$$y_T = p_1 y_1 + p_2 y_2$$

$$z_T = p_1 z_1 + p_2 z_2$$

4.3.3 Case of Mixture of Four Gases

This formula for gas concentration measurement is not limited to 4 gases. The limitation in the maximum number of gases comes from the number of channels of the imaging sensor. Where the following formula generally apply:

$$\text{Number of Gases} = \text{Number of channels} + 1$$

In order to increase the number of gases detected we can increase the number of channels, this can be done using spectral imaging.

Spectral imaging can be seen as a generalized processing of color images with a number of channels much larger than three. Starting from three-component RGB color space, a migration to SI can be performed by involving more than three color filters or tunable filters.

We can generalize equ.2 to the case of mixture with more than two gases; let's take the case of four gases then

$$x_T = p_1 x_1 + p_2 x_2 + p_3 x_3 + p_4 x_4$$

$$y_T = p_1y_1 + p_2y_2 + p_3y_3 + p_4y_4$$

$$z_T = p_1z_1 + p_2z_2 + p_3z_3 + p_4z_4$$

These will form a system of three equations with four unknowns, the fourth equation is the sum of all partial pressures which is equal to total pressure or the sum of the percentages of each gas in the mixture that is unity.

$$p_1 + p_2 + p_3 + p_4 = 1$$

4.4 New approach for gas Concentration Measurement

The previous equations model the mixing of the emission of a mixture of four gases with various concentrations (p_i $i=1,\dots,4$). Suppose that we already know the gases in the mixture and their colors x, y and z , the total color can be measured using an imaging sensor then we can measure the concentrations by solving the following system for p .

$$\begin{pmatrix} x_1 & x_2 & x_3 & x_4 \\ y_1 & y_2 & y_3 & y_4 \\ z_1 & z_2 & z_3 & z_4 \\ 1 & 1 & 1 & 1 \end{pmatrix} * \begin{pmatrix} p_1 \\ p_2 \\ p_3 \\ p_4 \end{pmatrix} = \begin{pmatrix} x_T \\ y_T \\ z_T \\ 1 \end{pmatrix}$$

This system is a linear system of equations in the form of $A*x = b$. However the exact solution can't be calculated directly because of the nature of the physical values that are noise prone and therefore we use the Least-squares solution [16].

In Least-squares method we find the vector x that is n -by-1 vector that minimizes the sum of squared errors $(b - A*x)*(b - A*x)$ where: A is m -by- n , and b is m -by-1. And b can also be an m -by- k matrix. Using this approach we find the percentages of the four gases.

The system used in our case has a single sensor for the three channels and uses a Bayer Type filter [17] where in this filter the Y channel which is the green color filter and has a ratio of 2:4

with respect to the other color filters. Most digital cameras use a single sensor and cover that sensor's surface with a mosaic of colored filters called a color filter array, or (CFA) [19].

Color matching functions may vary from sensor to sensor and their response may not be linearly proportional to the light captured [18]. To estimate the “missing” color values for each pixel we examine the color values of neighboring pixels. This process is called CFA interpolation [19]. To overcome these problems we introduce a method for the color calibration of the imaging sensors. There are many methods for color calibration used for digital color sensors [20] that rely on a simple principle of calculating a 3x3 matrix M that will relate the theoretical results that are calculated using the mathematical model with the experimental ones. Our goal will be to calculate a 3 x 3 matrix M that converts the three channel values results from the experiments (which we'll call $[C]_{Exp}$) into calibrated values (which we'll call $[C]_{CAL}$)

$$[C]_{CAL} = [M] * [C]_{Exp}$$

To calculate the calibration matrix M we apply the following procedure:

1. First we take two colors C_1 and C_2
2. Add them theoretically and get C_{CAL}
3. Measure the resultant color experimentally and get the C_{Exp} .
4. Now we introduce the matrix M that calibrate the image sensor as: $C_{CAL} = [M].C_{Exp}$
5. Repeat the procedure at least 4 times and form a system of equations where the unknowns are the coefficients of M .

The more experiments the more equations are obtained and thus a more precise matrix M is obtained.

By introducing M to the system above we obtain the following:

$$[p] = [M]^{-1} [C]_{Exp}^{-1} [C_T]$$

4.5 The Experimental System

An experimental system is done in the laboratory at the Lebanese university faculty of Engineering III for the aim of testing and verification of the theory proposed above. The experiment it is divided into four parts: the Mechanical system which consists of the pneumatic

system that prepares the gas sample for testing, the electrical system that is responsible for the high voltage and electronics control unit and finally the optical system that takes the emissions spectrum.

4.5.1 Mechanical System

The mechanical system consists of components that are responsible for preparation and transporting of the gas studied from the bottle to the discharge tube. It includes a vacuum pump, the mixing gas bottle and solenoid valves.

4.5.1.1 The Vacuum Pump

A vacuum pump of 0.25KW is used in our experimental system. It is responsible for decreasing the pressure in the discharge tube in order to obtain an emission. The final vacuum pressure obtained is 0.02 mbar or -98.8 KPa (relative).

4.5.1.2 The Gas Bottle

In the gas bottle is used to hold the gas sample we want to measure, it is directly connected to the discharge tube and separated by solenoid valves. It is also used to mix different kind of gases at certain concentrations in order to perform a controlled experiment test.

4.5.1.3 Solenoid Valves

These valves are used to control the flow of the tested gas from the bottle to the discharge tube and to the vacuum pump (figure 4.1).

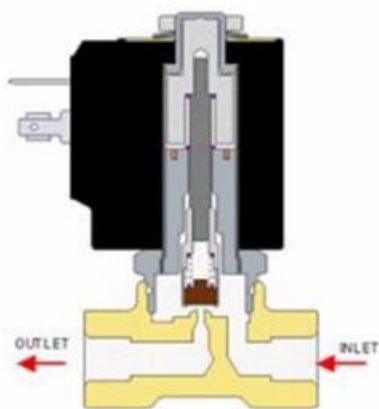


Figure 4.1 The solenoid valve used in the experimental system.

We used normally closed valves with these features:

- Maximum allowable pressure: 50bar
- Opening time: 10ms
- Closing time: 10ms
- Fluid temperature: 0°C +130°C

4.5.2 Electrical System

4.5.2.1 Transformers

For the gas in the discharge tube to breakdown and emits radiations, a relatively high potential difference is required between its electrodes. In order to obtain this high voltage we use a transformer with these specifications (figure 4.2):

- Primary voltage: 220V
- Secondary voltage: 1200V
- Frequency: 50 Hz

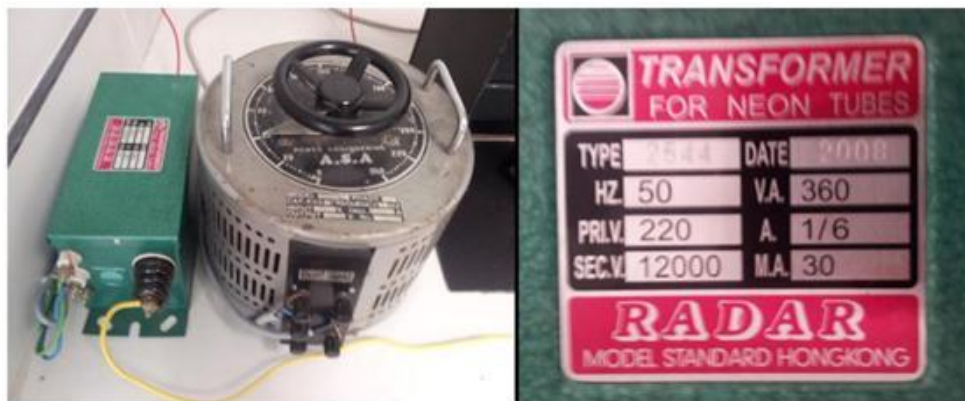


Figure 4.2 The step up transformer and the variable step down transformer used in the experiment.

We also used a step down variable transformer (0-220V) to control the input of the transformer which allows us to vary the output voltage from 220V to 12000V.

4.5.2.2 Electronic Control Unit

The control unit consists of an electronic board (figure 4.3) that is used to control the entire process. It includes a micro controller that gives control signals to the solenoid valves, the pump, relays, camera, and reads the pressure from the pressure sensor and sends it back to a computer. The control board is also connected to the computer through serial port and can receive inputs from the computer to control the different components where a semi-automatic test can be made.

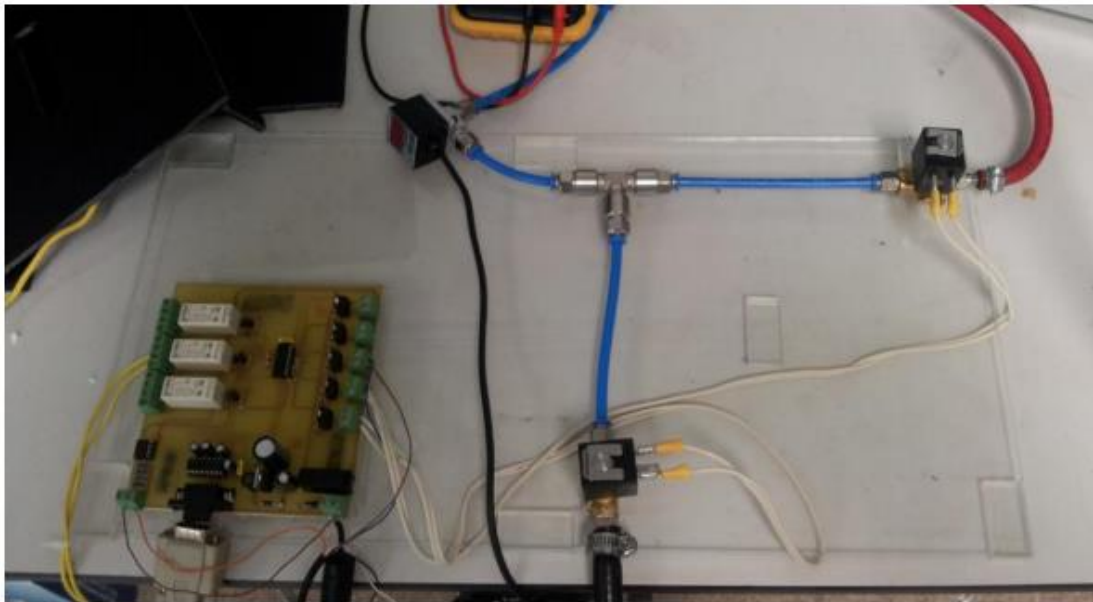


Figure 4.3. The control unit used in our experiment to control the process.

4.5.3 Optical System

The optical system consists of a discharge tube (figure 4.4) with a black box to place the tube inside where no interference can be made and a camera that is used to capture the emission of the tube.

The camera used in the experimental system is a CMOS based imaging sensor and it is connected to the computer and placed inside the black box. Once the optical emission is made the image acquisition can be made but the right time for capturing the image is choose at the lowest pressure the gas is in the discharge tube.



Figure 4.4 The discharge tube used in our experiment. The length between electrodes is 150mm.

4.6 Operation Mechanism of the Experimental System

The experimental system (figure 4.5) works in two modes: automatic and semi automatic mode. The last is used to give the operator the ability to control the right time for capturing the gas emission spectrum or the number of times gas is introduced to the discharge tube that can decrease the impurities in the tube due to previous experiments or the air that normally fills the tube. In both modes the following steps are made:

1. The gas to be tested is entered to the discharge tube. Then vacuum is applied to decrease the pressure in the tube.
2. A high voltage is applied to on the discharge tube that cause the gas to breakdown and emission occurs.
3. The emitted light is captured through a CMOS sensor and the image is send to a computer for processing.
4. In the image captured the region of interest is selected manually and the average colors are calculated inside a window of 10x10 pixels where a filter to remove outliers pixels inside the window is applied that reject any pixel less than a certain value.
5. The Average colors are calculated using this formula

$$i = \frac{\sum_{x=1}^{10} \sum_{y=1}^{10} I(x, y)_i}{\text{Number of Pixels}}$$

Where:

- i is the channel x, y and z .
- $I(x, y)_i$ is the intensity of the pixel at coordinates (x, y) of channel i .

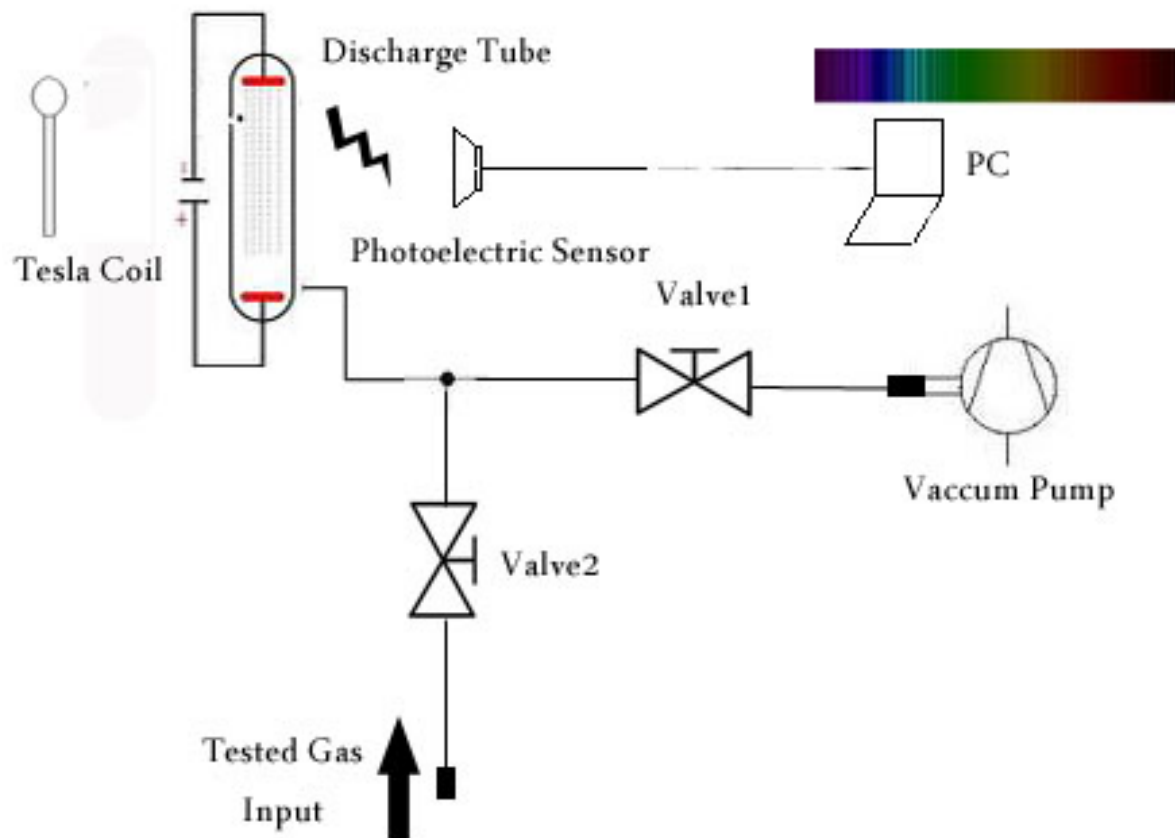


Figure 4.5 - Experimental System: Gas is entered to the discharge tube and submitted to high voltage to obtain emissions that are captured through the Photoelectric sensor and then sent to processing.

4.7 The Software and the User Interface

To perform several operations like: controlling the valves and the pump, image capturing and other things, we had developed software using C# to interface the hardware and the control board with a computer. In figure 4.6 the interface is shown, the imaging sensor images are shown in the interface where the user can select the right time to save the image of the glow of the discharge tube.

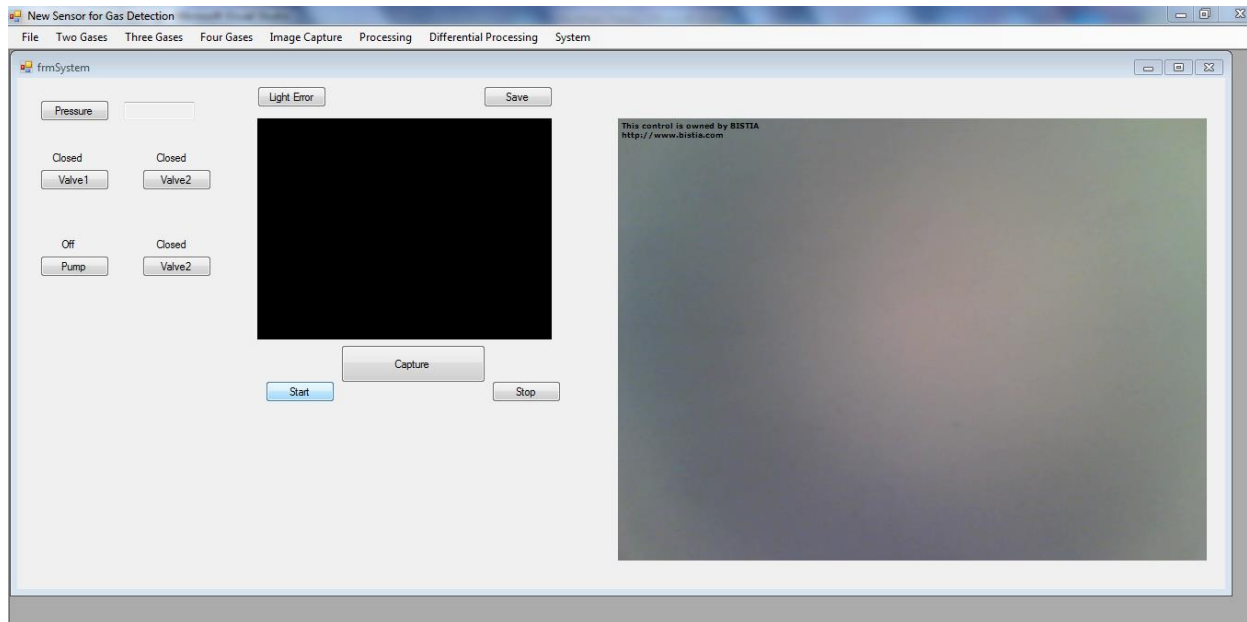


Figure 4.6 The Software interface developed.

The software developed also includes a visual interface to simulate the color mixing of two, three and four colors with different percentages (figure 4.7, 4.8) and the decomposition of a mixture of colors to its basic component percentages (figure 4.9).

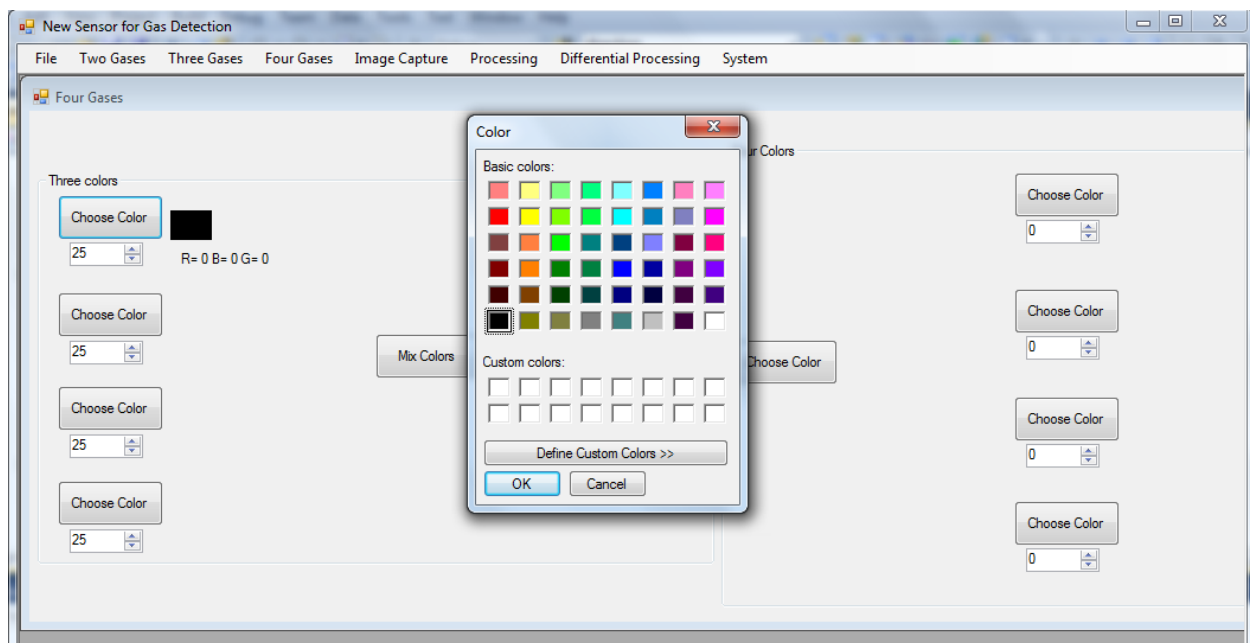


Figure 4.7 Simulation of color mixing and decomposition



Figure 4.8 Mixing of two and three colors with their respective percentage

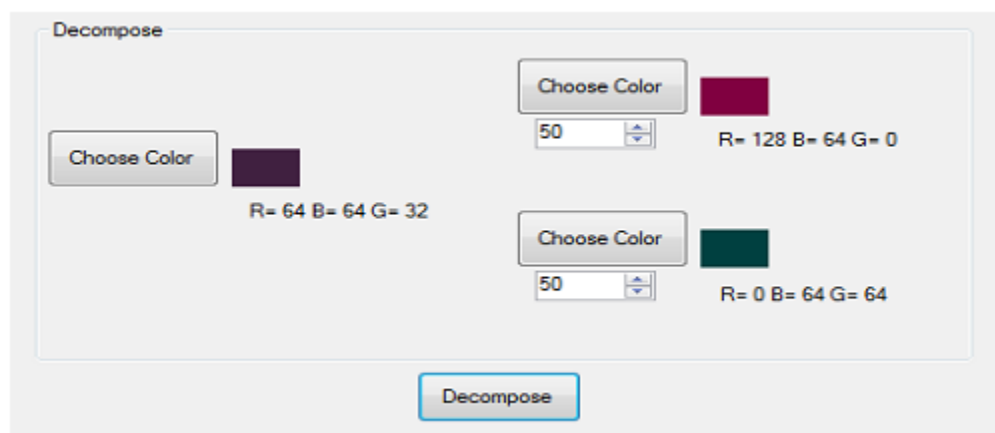


Figure 4.9 Decomposition of a color mixture of two colors to its basic components' percentages

Color measurement is done by taking the average value of pixels in a window of specified size (figure 4.10). This value is used for later for determining the concentration of the gases.

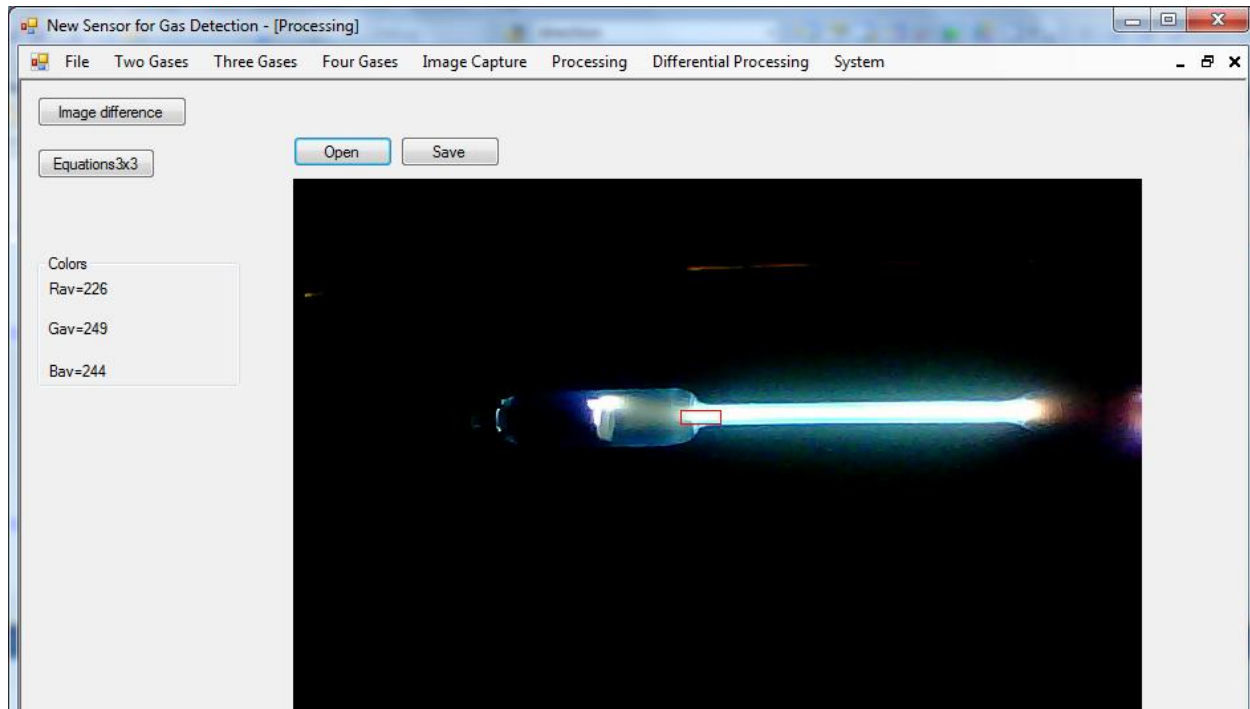


Figure 4.10 Measurement of the Color of an Emission. The Value is The Average of the Colors in a Specified Window Shown in Red.

The software developed also measures the sensitivity of the imaging sensor (figure 4.11). This sensitivity is measured for the aim of interpreting the errors in measurements. A detailed explanation of this will be introduced in paragraph 4.9.

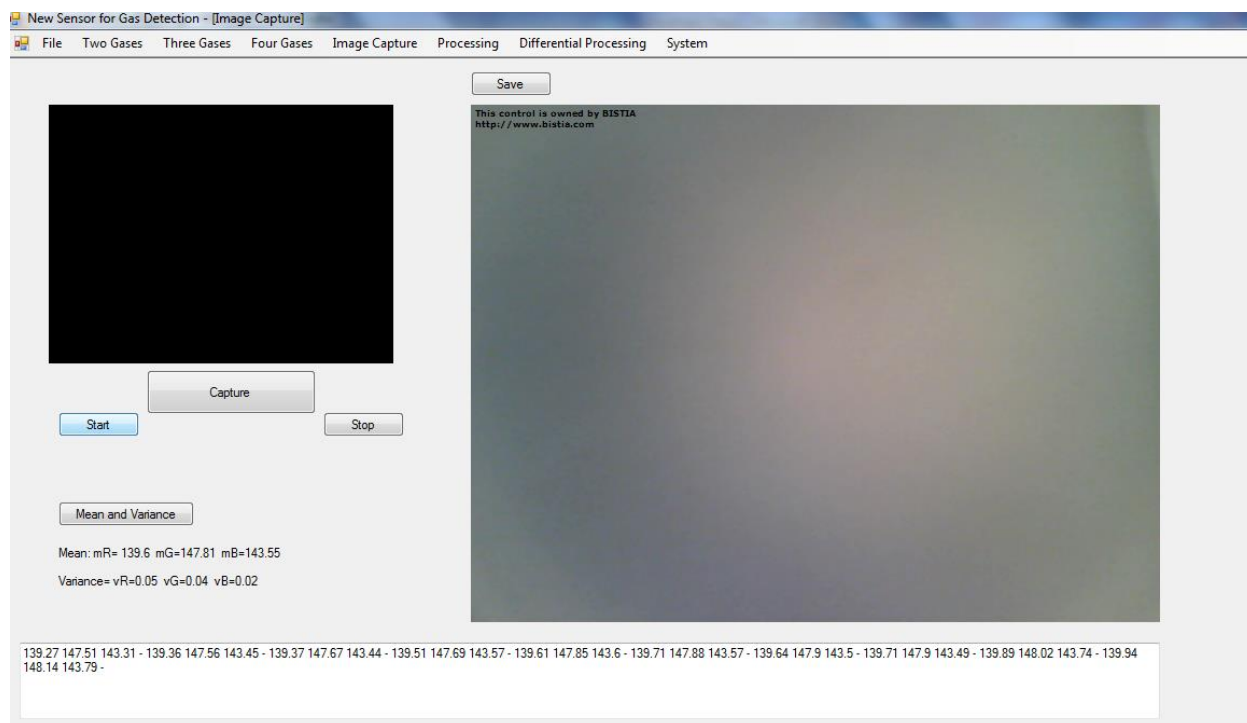


Figure 4.11 Measurement of the Sensitivity of the Imaging Sensor

4.8 Results and Discussion

Using the experiment system described above we had made tests on a group of gases (O_2 , CO_2 , Ar and He) and the colors of the three channels (x, y, z) are calculated. The tests are made on mixtures of two, three and four gases. For the mixtures of two gases we calculate the (x, y, z) values of the mixture, varying the percentages of each gas from 10% to 90% and measuring their output. These experiments includes pairs of (O_2 , CO_2), (Ar, O_2), (CO_2 , He) and (O_2 , He). A theoretical result is also calculated using the supposed mathematical model for color mixing and then the error on each channel and the average error is calculated as:

$$E_i = i_M - i_{theo}$$

Where: - E_i is the error on channel i.

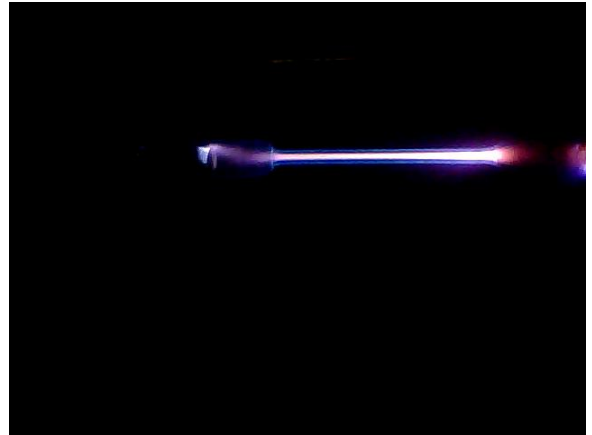
- i_M is the value of channel i measured experimentally.

- i_{theo} is the value of channel i calculated using the mathematical model.

The same is done on mixtures of three gases including the following: (Ar, CO₂, He), (O₂, CO₂, He), (Ar, O₂, He) and on the four gases (Ar, CO₂, O₂, He).

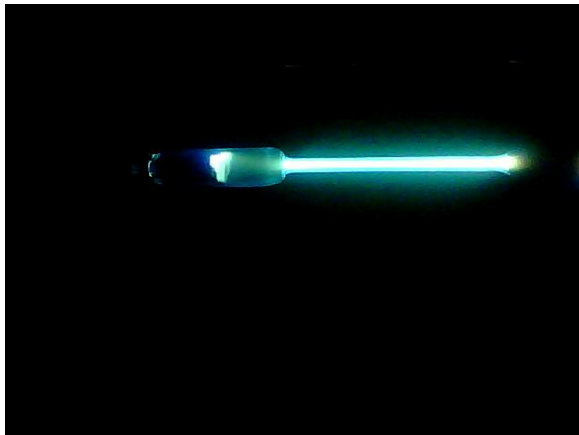


Figure 4.12. O₂(20%)+Ar(80%)



4.13. O₂(80%)+Ar(20%)

Figure



4.14. AR(20%)+He(40%)+CO₂(40%)



Figure 4.15. AR(33%)+He(33%)+CO₂(33%)

Figure

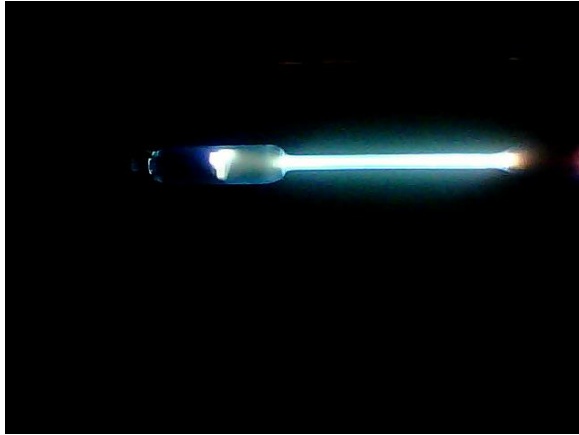


Figure 4.16. AR(40%)+He(40%)+CO2(20%)

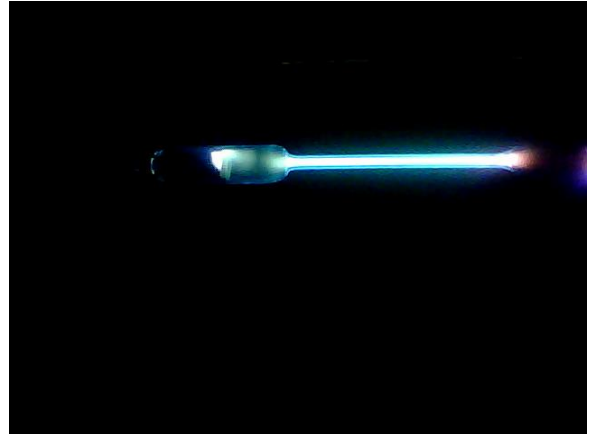


Figure 4.17 AR(10%)+CO2(20%)+O2(10%)+He(60%)

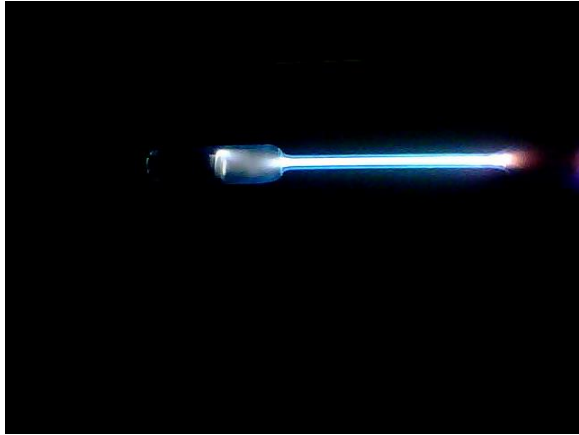


Figure 4.18 - AR(20%)+CO2(10%)+O2(10%)+He(60%)

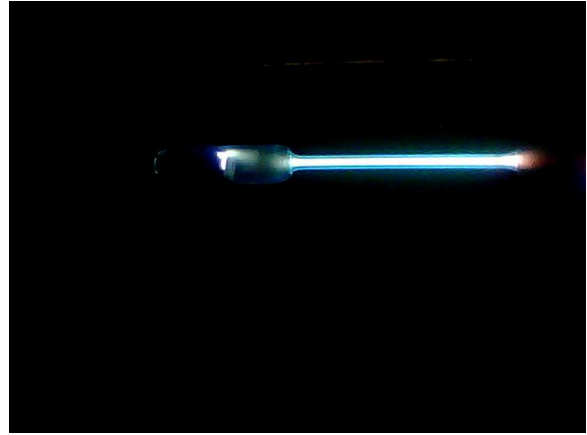


Figure 4.19 - AR(20%)+CO2(20%)+O2(30%)+He(30%)

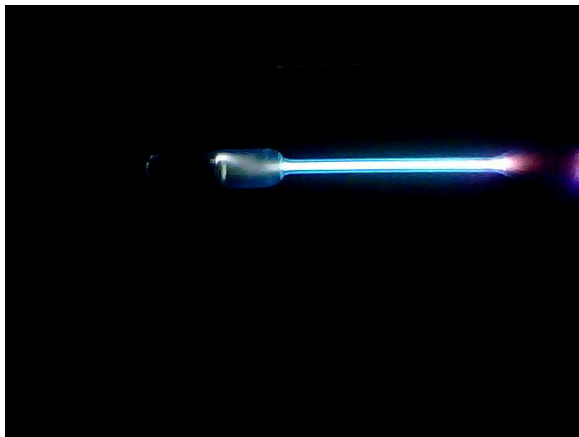


Figure 4.20 - AR(25%)+CO2(25%)+O2(25%)+He(25%)

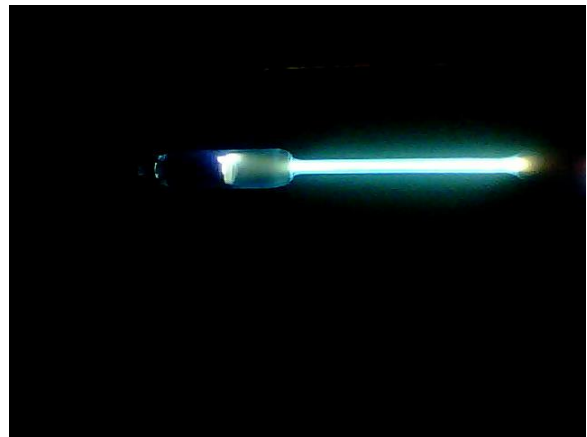


Figure 4.21 - AR(40%)+CO2(10%)+O2(10%)+He(40%)

The results obtained showed deviations that are mainly on the Y channel, where E_Y is the big especially in the mixture of four gases. We suppose that these errors are due to the imaging system used in our experiment. The results for the mixture of the four gases are:

$$E_X = 3.33\% \quad E_Y = 22.46\% \quad E_Z = 6.92\% \quad \text{Total} = 10.91\%$$

$$\text{Total Error} = 10.91\%$$

In our experiment we calibrate the imaging sensor using twenty nine experiments and after color calibration we validate on five experiments. The results obtained are:

- From $E_1 = 10.57\%$ To 2.8943%
- From $E_2 = 9.85\%$ To 6.4111%
- From $E_3 = 12.63\%$ To 5.3660%
- From $E_4 = 14.82\%$ To 3.0711%
- From $E_5 = 8.45\%$ To 3.9938%

The average Error after calibration is equal to 4.3473%

The results are considered to be promising after calibration of the imaging sensor. The average error is decreased from 10.91% to 4.3473% which is a decrease of 60% .

4.9 Sensitivity of the Imaging Sensor to Color Value Measurement

The measurement of the spectrum of the emission is done using an imaging sensor in our experiment we use a CMOS digital camera with three channels for red, green and blue. The accuracy of the plasma color measurement depends on several factors like the color consistency emission source, the sensitivity of the imaging sensor and the different parameters of the experiment that affect the emission these parameters which can be presented as the leakage of the experimental system that causes the pressure to increase with the entrance of the air to the gas discharge tube. This leakage can be in the solenoid valves used, the vacuum pump or in the connectors. For that, in order to test the measurement accuracy of our system, we took ten measurements of a steady emission source, with time interval of 200ms between each two consecutive frames taken for the color measurement, and calculated the average value of the three color channels x, y and z for each frame. The distribution plots of the measurements of three channels are below:

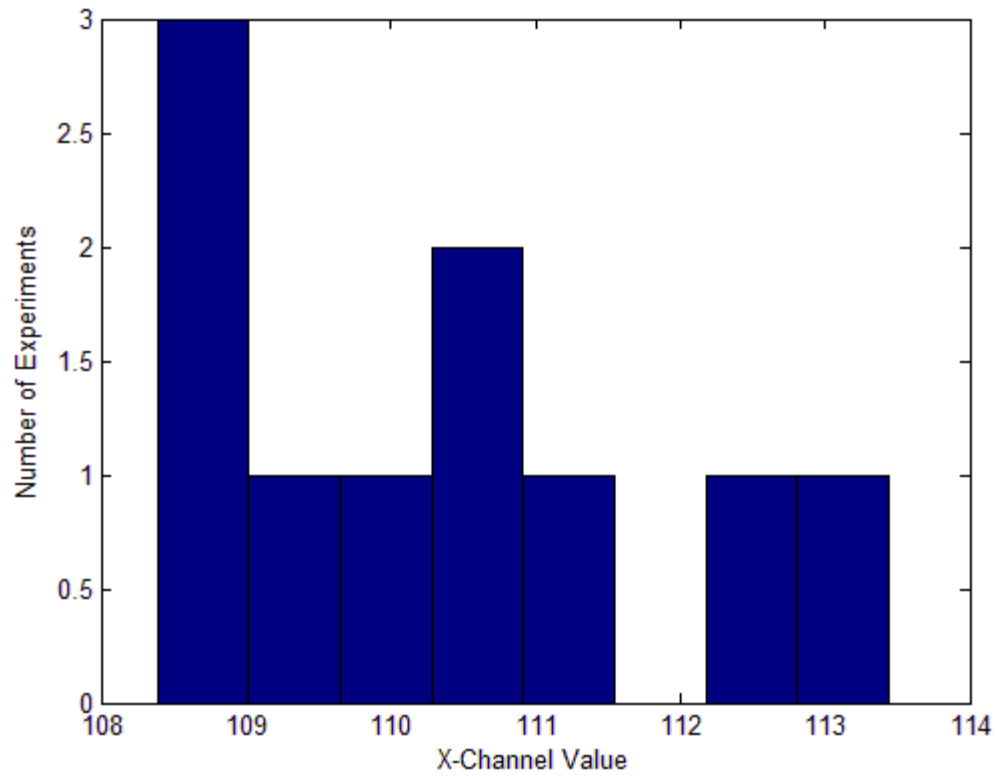


Figure 4.22. The distribution of the ten color measurements at the X-channel

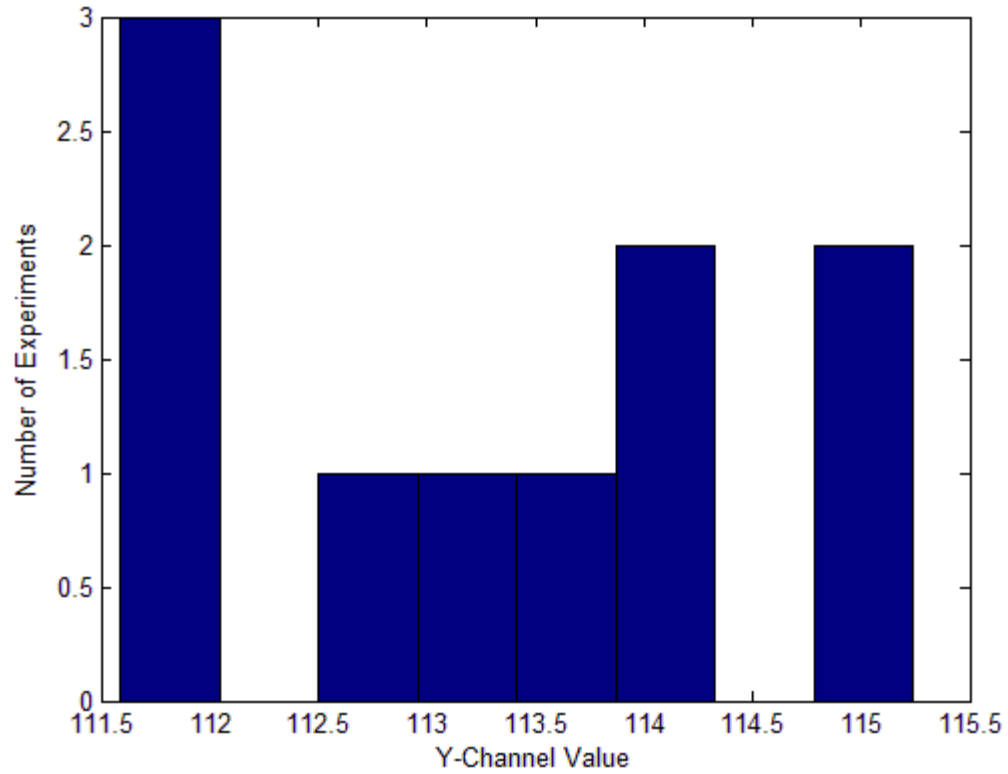


Figure 4.23. The distribution of the ten color measurements at the Y-channel

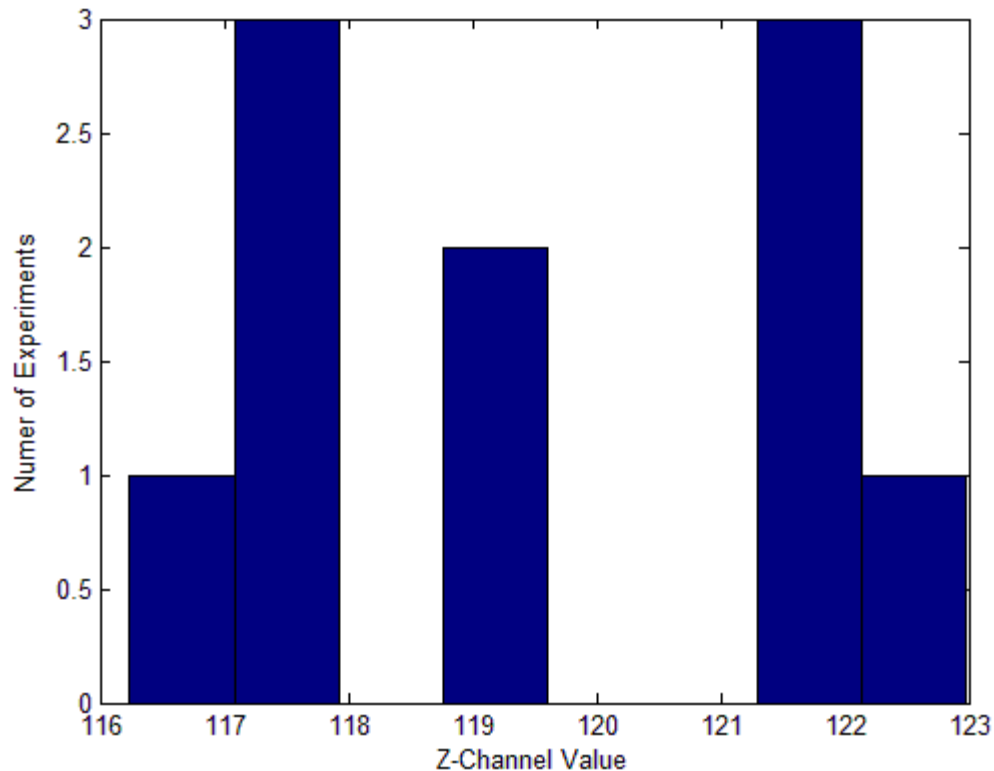


Figure 4.24. The distribution of the ten color measurements at the Z-channel

To calculate the mean m and variance σ^2 of the three channels of the imaging sensor the following procedure is done:

- Let $m_i = 0$ and $\sigma_i^2 = 0$. (Where m_i is the mean and σ_i^2 is the variance of the channel $i=X, Y$ or Z)
- Take j consecutive image of a static light source (gas emission) where no moving objects of variable lighting occurs at a time difference $\Delta\tau$.
- Calculate $C_{i,j} = \sum(I_{i,1}) / N$, where N is the total number of pixels, $C_{i,j}$ is the color value of channel I and image j .
- Calculate $m_i = \sum(C_{i,j}) / j$ and $\sigma^2 = \sum(C_{i,j} - m_i)^2 / j$

The procedure can be done as many times as possible to get an accurate mean m and variance. In our experiment we tested on 10 frames and the results were:

	x	Y	Z
Mean	110.29	113.34	$m_z=119.57$
Variance	2.86	1.7	5.57
σ	1.69	1.30	2.36

Table 4.1 - Mean m and Variance V of the distribution of the color measurement error.

The values of the variance show a drift in the measurement in the channel x, y and z, those drifts are caused by the imaging sensor and light source variation which can interpret the error obtained in the measurement done for the concentration of gases. However modeling this error in the sensor measurement and using a filter can enhance the accuracy of the system.

4.10 Conclusion and Perspectives

In this chapter we have introduced a new method for gas sensing and concentration measurement. Our proposed method relies on the principle of plasma emissions that are considered as a finger print of the gas that emits it. In the case of multiple gases emission, the spectrum of the summation of each partial emission of each gas alone is the total spectrum. The mathematical model of the color mixing of gas emissions according to the percentage of each gas is introduced. Then using digital image processing the percentages of each gas in a mixture of up to four gases can be calculated by applying the inverse of the color mixing model. The sensor is not limited to four gases only and it can be easily extended to more than that by using more than 3 channels sensor or tuned color filters. Also the calibration of the imaging sensor played an important role in enhancing the accuracy of the system; a method depending on previous measurement was introduced and the errors obtained after calibration were about 4% which is considered to be promising. However, the modeling of the noise in color value measurement as a

Gaussian random variable has shown that the mean of the measurement is close to the error obtained in the experiments.

The accuracy in measurement can be enhanced by using more dynamic range imaging sensors like the logarithmic CMOS imaging sensors [21]. Also minimizing the sensor can result in farther enhancements of the whole process and that by the ability of achieving a plasma emission at atmospheric pressure and at lower voltages, thus removing the need of the vacuum pump and Tesla coils which in turn decrease in the cost and power consumption of the sensor.

4.11 References

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5. Conclusions

Gas sensing plays a major role in a wide range of applications from domestic to industrial domains. The recent trends in gas sensing research are focusing on investigating novel technologies and approaches in addition to improving the conventional state-of-the-art sensor technologies.

Measuring the concentration of each gas in a mixture of multiple gases with an appropriate level of accuracy is a key to significant saving in time and costs, and help decision makers analyze and evaluate important information for operational scenarios that would enhance system designs. Also the ability of measuring concentrations of several gases simultaneously with minimum amount of time spent on measurement process is an important factor in realizing many real-life projects like pollution monitoring or real time industrial control systems.

Existing gas sensing methods primarily used a single sensor for each type of gas or group of gases. However, as the number of gases to be measured in an operation increases, the task of identifying, measuring concentrations, and processing data becomes time consuming, labor intensive, high cost and often impractical. In an effort to remedy this situation, this research studied the shortcomings of existing approaches and proposes a new method for gas concentration measurement of multiple gases simultaneously to improve the current methods and also discuss the miniaturization potential of each technology with its pros and cons.

This dissertation documented the research that led to the design and implementation of a new method for multiple gas concentration measurement that offers high potential for significant improvement in many scientific and engineering domains such as pollution monitoring, industrial and mechanical engineering, and manufacturing. For example, using our proposed sensor in analyzing the emissions of internal combustion engines can allow the monitoring of these emissions and the engine performance in a relatively low cost transducer that may be developed in the future. Our method can also be applied to atmosphere monitoring, hazardous gas detection or many other fields that require the measurement of concentrations of multiple gases. The applications and potential of our proposed method are thus vast and applicable to several engineering domains.

The application of image processing techniques for gas sensing, analysis, and sensor design in the engineering is relatively new compared to the notable amount of material based like solid state gas sensors' research conducted for diverse applications in fields such as manufacturing, automotive, medical, military, and atmospheric monitoring. As noted in Chapter 1, previous studies have also explored the application of image processing for plasma emissions spectroscopy for a limited number of goals and also for gas sensors applications.

All prior research and applications of gas sensing, however, have focused on developing domain specific platforms intended for very specific purposes, like detection or concentration measurement of certain gases, thereby limiting their widespread applicability and reusability.

In addition, as noted in Chapter 1, prior research in gas sensing:

- Did not consider using same sensor for measuring multiple gases simultaneously in a real time scenario.
- Did not afford unrestricted mobility to the gas sensor to be used on-site in applications that require dynamic way of measurements like in moving vehicles.
- Did not consider the cost and operation costs of using multiple sensors to measure multiple gases in the same application.
- Did not consider problems associated with using gas sensors in unprepared environments.

This research successfully addressed the abovementioned limitations. In this dissertation, the design and development of an optical-based physical gas sensing technique, image processing and algorithms, and a powerful data analysis approaches together with their practical implementation inside an experiment were discussed.

The designed sensor provides a convenient method to automatically analyze a mixture of gases of any size theoretically (tested on four gases in our experiment) at the operations level using the optical emission color processing technique through a simple model and software. The results of the research have been validated by making several tests in the laboratory on the experiment developed for testing the proposed technique. Each Chapter in this dissertation described the details of individual scientific questions successfully addressed, major challenges involved, and algorithms and methods studied, adapted, developed, and implemented in achieving a particular research objective.

The following list summarizes the individual research challenges successfully addressed and described in the preceding Chapters:

- Review of Recent Trends in Gas Sensing Technologies and their Miniaturization Potential (Chapter 2): reviewing and studying the recent trends in gas sensing and classifying them into four classes and comparing between them to find the best candidate for miniaturization.
- Optical Emission of Gas Discharge Tubes and Plasma (Chapter 3): Establishing a link between theory of plasma emissions, spectrum analysis and color mixing of the gas in the discharge tube
- New Optical Gas Sensor for Gas Concentration Measurement Using Digital Image Processing (Chapter 4): Proposing a method that uses digital image processing to model the color mixing of the emissions of the gases and applying the inverse model to get the percentages of each gas in a mixture.

In Chapter 2, the details of an overview about the state of the art and novel technologies and methods used in gas sensing were presented. Although the main focus of this Chapter was on previous work done in gas sensing field, It also discusses the miniaturization potential of some of the methods that are promising in the ability of their miniaturization but suffer from different problems. These problems were described and discussed. A comparison was also done among the miniaturized sensors in terms of different parameters like sensitivity, selectivity, cost and other terms. The primary contribution of the research presented in Chapter 2 was in the comparison that yielded a classification of these sensors into four classes, where each class contains the methods with similar pros and cons. However, no single technology was found to be the perfect candidate for the miniaturization and a trade-off must be made according to the type of application.

In Chapter 3, the details of gas discharge plasmas and parameters were discussed. In addition, methods and types of discharge were described. The results of these discussions were used to introduce the plasma emissions spectroscopy that were then applied to the gas sensor proposed. The primary contributions of the research presented in Chapter 3 were the introduction of the hardware apparatus that have been used to be conveniently extended and reused in the sensor,

thereby saving significant time and effort that would otherwise be required to reimplement low level hardware interfacing software.

In Chapter 4, a new method for gas sensing and concentration measurement was introduced. The proposed method relies on the principle of plasma emissions that are considered as a fingerprint of the gas that emits it. The mathematical model of the color mixing of gas emissions according to the percentage of each gas was developed and then using image processing the percentages of each gas in a mixture can be calculated by applying the inverse of the color mixing model. The sensor is not limited to four gases only and it can be easily extended to more than that by using more than 3 channels sensor or tuned color filters. The primary contribution of the research presented in Chapter 4 is the main contribution of this dissertation and was a flexible and dynamic methodology to facilitate the tasks of spectrum spectroscopy by using the color mixing model of the spectrum and an imaging device to capture the color of the plasma emission in the gas discharge tube instead of a spectrometer. This led to the described method to measure the concentration of multiple gases in mixture simultaneously. Validation tests evaluating the research components described in the Chapters of this dissertation were presented. In addition to validating aspect of the research during its progress, the calibration of the imaging sensor that played an important role in enhancing the accuracy of the system was also introduced in this work.

A simple simulation tool of the color mixing model was designed and the tests of the color mixing in real experiment were made. The comparison between them as a theoretical and experimental results determine the error in measurement of the sensor. Tests on mixtures of two, three and four gases were made. The calibration of the imaging sensor method depending on previous measurement was introduced and the errors obtained after calibration were about 4% which is considered to be promising. However, the modeling of the noise in color value measurement as a Gaussian random variable has shown that the mean of the measurement is close to the error obtained in the experiments.

The primary contribution of this research to the body of knowledge is that the method designed in this work for gas sensing can measure the concentration of multiple gases at the same time using a relatively cheap technology. This was achieved by providing an effective spectrum

emission spectroscopy means using digital image processing to gain a better understanding of the underlying processes in color mixing of a mixture of gases subjected to an electrical field in a gas discharge tube. The proposed method allows the user to use one sensor for multiple gases which can decrease the cost and overheads of using a sensor for each type of gases. The although the sensor proposed was tested only on four gases, it can be easily extended to larger number sing an imaging sensor with more than three channels like in multi spectral imaging. The results of the experiments made on this method are promising and if the sensor parameters are tuned perfectly a much enhancement in the accuracy and a lower margin in the error could be realized. The designed sensor and the theory of the sensing mechanism are generic and extensible to more than four gases where the sensor is modular and can be readily modified to match lower or bigger number of gases that can be measured by changing the imaging sensor only. Thus the sensor can be used in other engineering and scientific domains such as medical, transportation, pollution measurement, space exploration and many other domains that also experience a need a concentration measurement of multiple gases.