Journal of Current Medical Research and Opinion
Received 28-06-2024 | Revised 29-06-2024 | Accepted 20-07-2024 | Published Online 22-07-2024
DOI: https://doi.org/10.52845/CMRO/2024/7-7-30 ISSN (O) 2589-8779 | (P) 2589-8760
CMRO 07 (07), 3337-3358 (2024) www.cmro.in
Original Research

Manufacturing and Studying the Characteristics of the Toxic Gas Sensor

Zainab Amer Talib Sahib [1], Zahraa Thaer Jabbar [2], Tuqa Adnan Abd AL-Nabi [3], Sabreen Rashid Abd Al-Hussein Farman [4], Dhelal Khudher Salman [5]

[1]University of Kufa, College of Science, General Physics, Iraq

[2,3,4,5] Hilla University College, Medical Physics, Iraq

Abstract:

Physics of thin films An essential subfield of solid-state physics is thin-film physics. The thickness of a thin film can be anything from tens of nanometers to one micron, and it can consist of a single or many layers of atoms of a certain substance. Prepare a solid substance into a thin film by depositing it onto a solid foundation (substrate) in very thin layers using physical or chemical processes, or electrochemical reactions. Research into the characteristics of NiO thin films informed the development of the gas detector in this study. It is dangerous for people's health and safety when combustible and poisonous gases like CO, CO_2, CH_4, NO_2, etc. are present in the air. This calls for novel uses for gas sensors, such as tracking gases with potential environmental hazards, developing gas analyzers, sensors, and response/ recovery times. Excellent selectivity, rapid response, low operating temperature, little energy consumption, and long-term stability. Since metal oxide semiconductors (MOSs) are so sensitive to even trace amounts of gas, modern methods rely on them for accurate gas detection.

Key words: Toxic Gas Sensor, Characteristics, Thin-film physics

Introduction

A good understanding is provided of many of its physicalproperties, which differ from those of its constituent materials in their bulk state. [1, 2]. Research and studies on semiconductor materials have continued rapidly due to their physical properties, especially their electrical properties, which have a high possibility of modification and diversity ofthese properties. On the other hand, semiconductor materials have entered the field of study and application and have taken up a large andincreasing area because they have excellent properties, which has led tothe development of this science and the expansion of its applications in various scientific and technical fields [3,4] Thin films are of industrial and technological importance. They are involved in most applications, including: electronic applications such as magnetic memory devices, integrated circuits, detectors and transistors. [5] Optical applications: include the manufacture of solar cells, photodetectors, the manufacture of optical fibers, photography, the manufacture of ordinary and thermal mirrors, and reflective and non-reflective coatings [6]. As for magnetic applications such as electronic computers and laser CDs [7] .

1.1 Metal oxide gas sensor

MOS-based sensors work on the principle of changes in their resistance when exposed to target gases or moisture. Oxidizing gases such as NO2, Cl2,F2, and O3 increase the resistance of n-type semiconductors and

decrease the resistance of p-type semiconductors; While reducing gases such as H2, NH3,CH4, and CO do the opposite [9]. n-type MOS samples generally show a higher gas response than p-type; However, p-type membranes have their own advantages such as high catalytic properties, low humidity and operating temperature dependence [10]

The sensing performance of a MOS gas sensor strongly depends on the operating temperature, humidity, crystal structure and surface properties. Some limitations such as high operating temperature, low responsiveness, lowselectivity, high response time and recovery time are associated with gas sensors [11]. Many efforts have been made to improve sensor performance byusing traditional manufacturing methods to produce low-cost, highly responsive sensors. Researchers have focused on studies to devise a highly sensitive gas sensor with low response time and recovery time by fusing twoor more metal oxides together to create MO-MO composite materials that exhibit higher response than individual materials [12] .

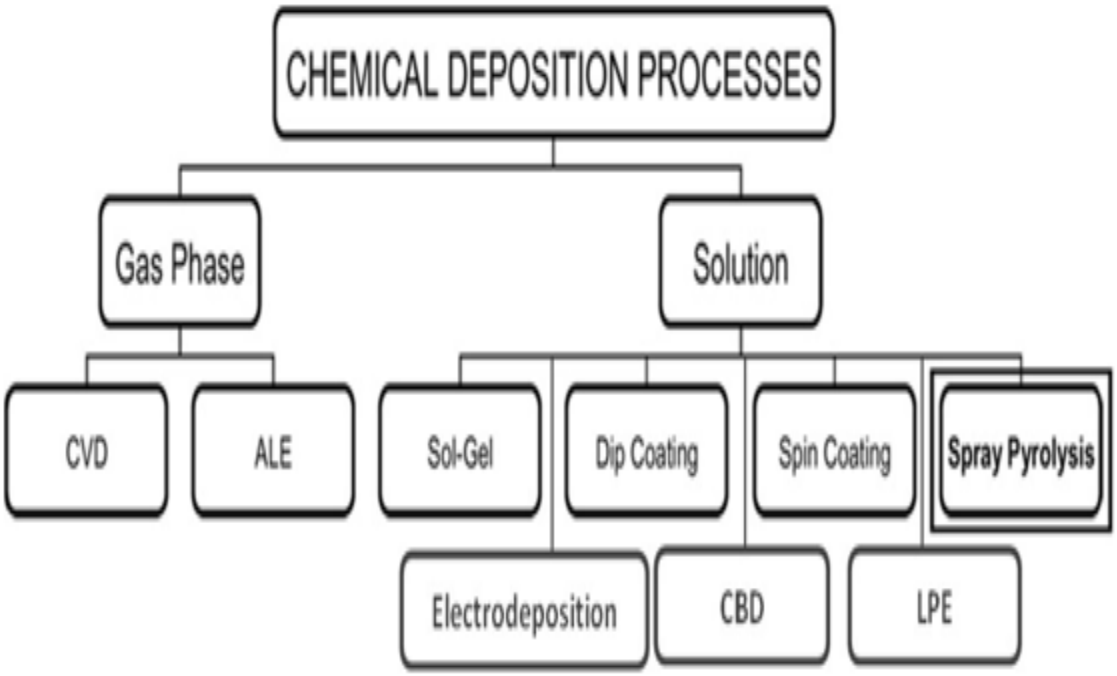
The sensing performance of a metal oxide based gas sensor can also be improved by doping the metal oxide with metals such as platinum, aluminum and palladium. AM Soleimanpour et al. [12] showed a significant increase inthe response of NiO film grafted with Pt nanoparticles even at low operating temperatures.

In this study, it is clarified how gas sensors respond, discusses how gases are absorbed on the surface of semiconductor materials and their effect on the properties of the semiconductor, and also focuses on the efficiency of the gas sensor made of nanomaterials in the form of thin films of NiO and processed under different conditions. Solution concentration used to prepare membranes for sensing different gas concentrations and different operating temperatures. [13].

1.2 Thin film deposition methods

Over the years, various materials have been manufactured in the form of thin films due to their technological importance. There is a very wide rangeof applications and extends from coating several square meters on window glass. Based on the nature of the deposition process, the techniques used forthin film deposition can be classified into two groups, namely physical and chemical deposition processes. Methods include physical evaporation deposition (PVD), pulsed laser ablation, and molecular beam sputtering.

Figure 1.1: Schematic diagram of some chemical deposition processes.



While chemical methods include methods of deposition of gas and liquidphases, as shown in Figure (1.1). Gas phase methods are chemical vapor deposition (CVD) and atomic layer enlargement (ALE), thermal spray deposition, sol-gel, electrophoretic deposition and chemical bath deposition[14].

Nickel oxide thin films have been prepared by different techniques including: electron beam evaporation, magnetron sputtering, chemical precipitation, sol-gel solution and spray pyrolysis technique (SPT) [15]. Among the various methods, spray pyrolysis is the method through whichfilms can be coated over a large area and this method is simple, low-cost and widely applicable. It gives high product purity for deposition of metallic and non-metallic materials [16].

In the present work, a thermal sputtering method was used to form NiOthin films.

1.3 Basic properties of nickel oxide (NiO)

Nickel oxide (NiO) is a p-type semiconductor and is well known for its excellent electrical and optical properties and chemical stability. It hasa wide band gap of 3.6-3.8 eV and a weak absorption band in the visible region. It is in the form of a greenish-gray powder, depending on the method of preparation. It is a transition element and an antimagnetic substance. The Néel temperature is 523 K (which is the temperature thatcharacterizes antiferromagnetic materials). Below this temperature, the sublattice atoms are spontaneously magnetized in a ferromagnetic latticemanner, a Curie temperature of less than 2000 K [17] .

The antiferromagnetic arrangement of nickel oxide is related to the symmetry properties of the crystal (body-centered cubic, face-centered cubic structure, perovskite). Its high chemical stability and thermodynamics, is very resistant to oxidation [18]. Table (1.1) showssome general properties of nickel oxide.

There are many kinds of ways to prepare NiO. Among these, the most well-known method is thermal spraying of Ni 2+ compounds such as hydroxide, nitrate and carbonate, which results in a light green powder. Heating in oxygen or atmospheric air results in black NiO powder. The color change from green to black is due to the presence of Ni 3+ resultingfrom vacant sites in Ni [18].

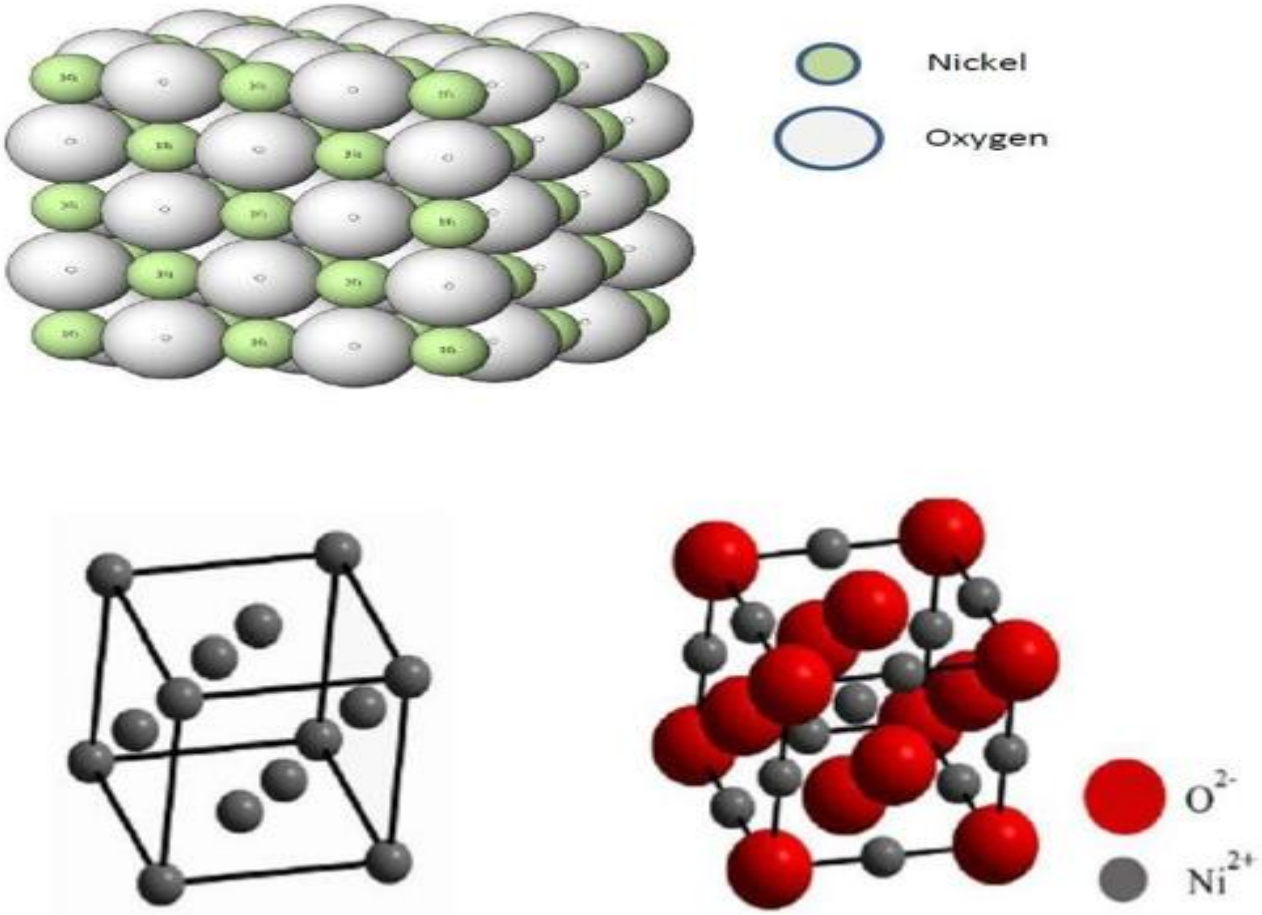
The stable crystal structure of nickel oxide at high temperature is polymorphic bencinite. By cooling the crystal, the structure transforms into a diamond shape. It should be noted that these crystal structures are formed during thermodynamically stable transitions. Different manufacturing techniques produce heterogeneous structure [19].

Crystallographic and structural properties

The structure of NiO is similar to that of sodium chloride (NaCl), which is known as the rock salt structure as shown in the figure). 1.2) It has a cubic structure of type (FCC) This cubic structure consists of two identical sublattices A and B, such that each atom of sublattice A has onlyneighbors belonging to sublattice B and vice versa. The anionic sublattice (O 2) and cationic sublattice (Ni 2+) have an FCC structure. The (100) plane is a mixed plane composed of 50% nickel and 50% oxygen while the (111) plane is alternately pure Ni and pure O. Face

(111) is a polar face (unstable) vs. Face (100) is a non-polar face (stable)The interplanar spacing between two different planes is 0.12 nm and is approximately doubled between the nature of two similar planes[20].

Crystalline solids exhibit periodicity in their crystal structure. Perfectstoichiometric metal oxides are insulators but by introducing various defects inside the crystal, their electrical, optical and mechanical properties change. It should be noted that the presence of defects depends on the method of growth. [20]



الشكل 1.2: التركيب البلوري ألكسيد النيكل ، ألسود للنيكل]20[.

1.5 Nickel oxide gas sensors

Many researches have been published on NiO gas sensor. Some research is on the manufacturing techniques, electrical and optical properties, and gas sensing properties of NiO gas sensor. Research shows that nickel oxide gas sensors are capable of detecting wide types of gases such as 2H, 3NH, 2NO, alcohol and 4CH. The response is excellent, and the operating temperature depends on the surface characteristics and the type of gas. [21]

1.6 Objective of this study

This study aims to achieve the following objectives:

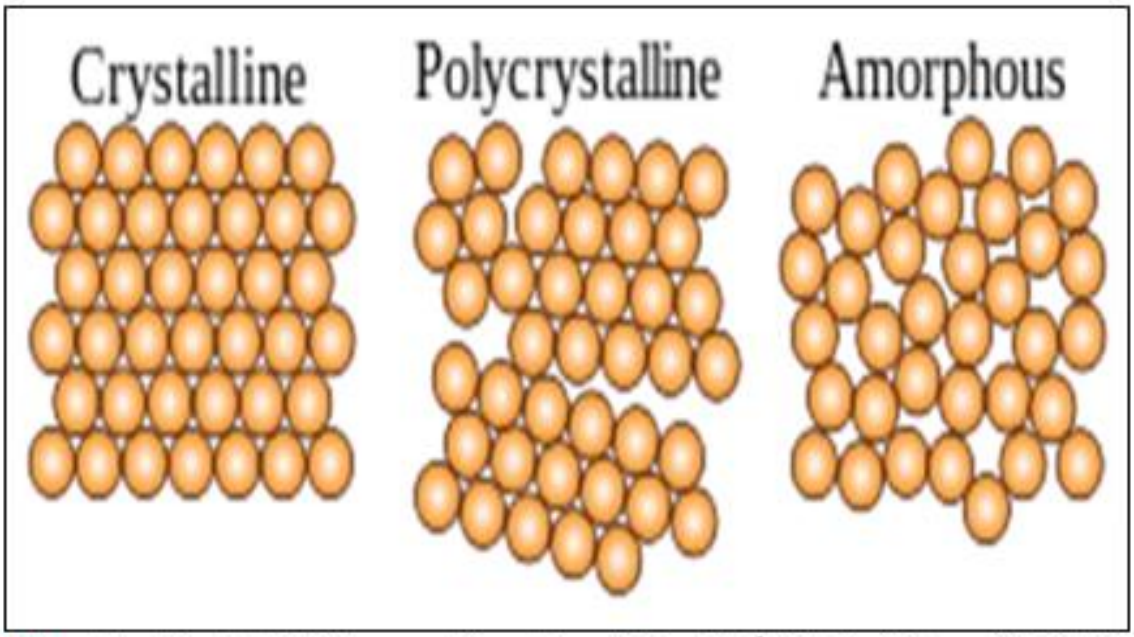
- Installation of a homemade device that allows the preparation of thinfilms of metal oxides by the thermochemical spray method.
- Preparing nickel oxide nanomembranes and studying their structuralproperties.
- Manufacture of a sensor that works as a chemical sensor based on changes in electrical resistance. This device was then used to study theallergic properties of nickel oxide films prepared for some toxic and flammable chemical gases.

An overview of the theoretical side of this studyand the ideas, scientific explanations, relationships and laws used to interpret the results obtained.

2.1 Classification of materials and characteristics of crystal structure. Crystalline materials can be divided into three types: monocrystalline,

polycrystalline and amorphous. The single crystal has a band arrangement and the arrangement of atoms extends throughout the total volume of the substance, and the bond length and angles between them are equal.

Polycrystalline materials are a combination of an array of randomly oriented crystals separated by well-defined boundaries. These crystals are known as grains and are known as grain boundaries. Non-crystalline or amorphous solids are characterized by a random arrangement of atoms or molecules [22]. Figure (2.1) shows the three structural forms.



الشكل (2.1) رسم تخطيطي لثلاثة أنواع من الترتيب البلوري (بلوري ، متعدد البلورات ، غير متبلور. [22]

2.2 Thin film characterization techniques

Nanostructured semiconductor materials are manufactured by various physical and chemical methods. The structural and electronic properties as well as the distribution of the primary particles depend greatly on the method of preparation. Once a suitable material has been installed, the first goal is to perform characterizations of that particular material. In order to do this in a systematic way, we need a variety of characterization techniques.

The different characterization techniques used are:

- Weight difference method for calculating film thickness.
- X-ray diffraction (XRD) technique.
- Atomic force microscopy (AFM).
- **Scanning electron microscopy (SEM).**
- Ultraviolet-visible spectroscopy (UV-Vis); In this research we will use only two techniques:

2.2.1 Weight difference method for calculating

Film thickness is one very important feature to determine. The reasonis that many membrane properties depend on the thickness of the membrane. There are different methods for measuring thickness, including the visual method (Michelson) and the weight difference method. In this work, the second technique was used.

The weight difference method is simple and available. You only need an accurate electronic scale, and the thickness is measured in this way using the following formula [23]:

$$t = \frac{m}{A} \quad \text{.....(2.1)}$$

Where (t) is the film thickness, (Δm) is the weight gain, (A) is the area ofthe coated pattern and (ρ) is the density of NiO which equals 6.67 g/cm3.

2.2.2 X-ray diffraction (XRD) technique

X-ray diffraction (XRD) is one of the most useful characterization methods because it can provide a great deal of information about the deposited material. X-ray diffraction can be used to study the crystalline properties of the prepared thin films such as determining the crystal structure, crystal orientation, crystal quality, and crystal sizes. [24]

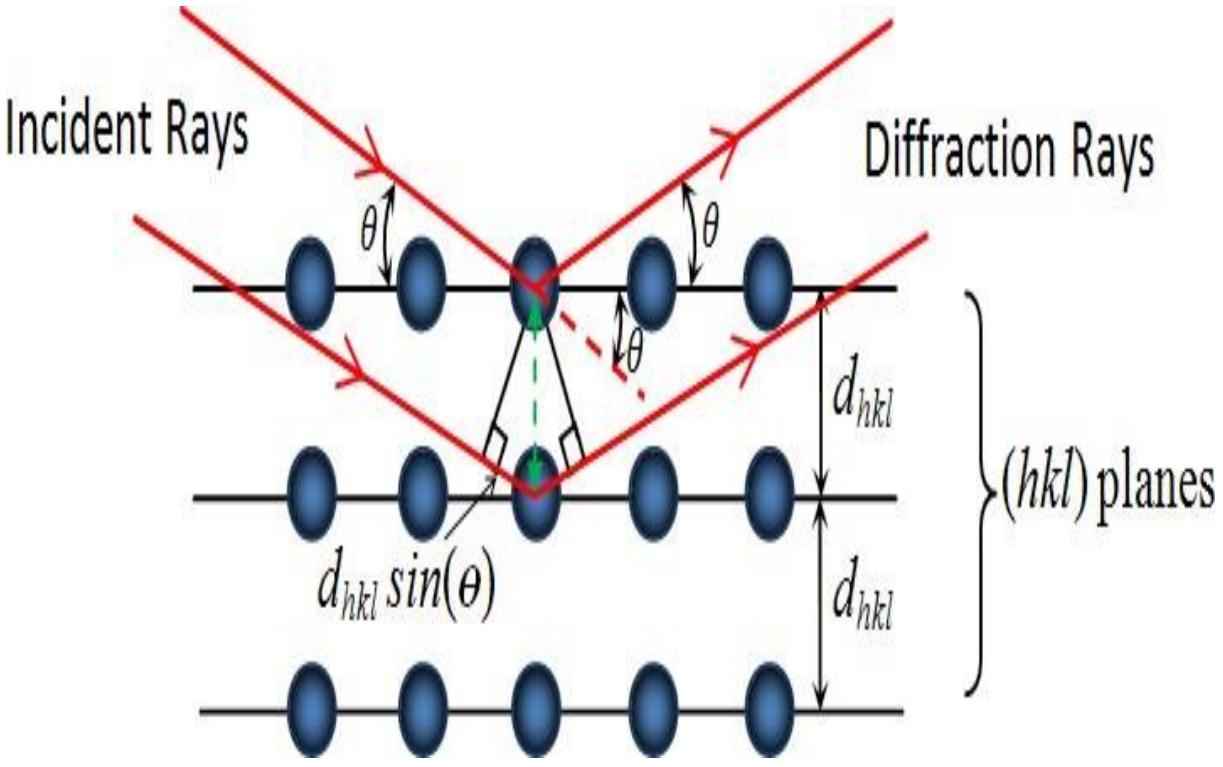
Two important advantages of X-ray diffraction for thin film analysis are[25]:

.1 The wavelengths of X-rays are of the order of atomic distances in thematerial, which particularly qualifies their use.

2. X-ray techniques are non-destructive and leave the examined specimen intact without damage. X-ray diffraction was used to determinethe crystalline phases of materials based on Braque's law. As shown i ngure 2.2, the case where diffraction occurs in a crystalline materialsatisfying Bragg's law is described as [25]

$$n\lambda = 2d_{hkl} \sin\theta_{hkl} \quad \text{.....(2.2)}$$

Where (λ) is the wavelength of the , and n is an integer. Waves satisfying this condition interfere constructively and give rise to a reflectereflected wave of large intensity.



الشكل 2.2: رسم تخطيطي لحيود االشعة السينية حسب قانون براك.]25[

The diffraction pattern is obtained by measuring the intensity of waves scattered by the material as a function of the scattering angle. Strong peaks, known as Bragg peaks, are obtained in the diffraction pattern at points where the scattering angles satisfy the Bragg condition and give information about the crystal structure, orientation, and averagecrystalline size of the films. [26]

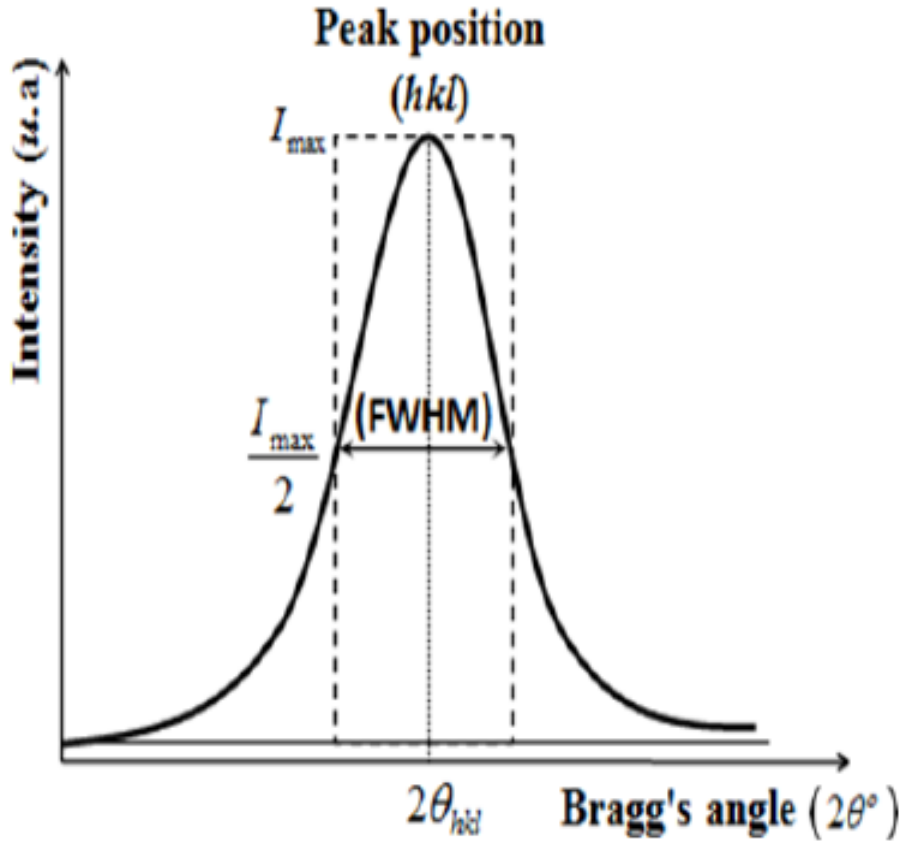
Experimentally obtained diffraction patterns of the sample are compared with standard patterns of potential elements and compoundspresent in the sample. Based on this comparison, conclusions can be drawn.

Crystal size 2.3.2.1 From the X-ray diffraction pattern, the view at a peak known as the mid- peak can be used)FWHM((See Figure 2.3) to calculate the crystal sizes in a given direction for a(hkl) using Scherar's formula [26], which is

□2.3□ ..... 0.9□ □ *D*

given as follows *hkl* □*hkl* cos □ :

hkl



Where (hklD) is the crystalline size taken from the peak (hkl), (λ) is the wavelength of the X-ray beam, (hklβ) is the midpoint of the maximum intensity (hkl).

2.2.2.1 Lattice constants

The values of the empirical lattice parameters (hkl a) for cubic systemscan be calculated from the following equation using the Miller coefficients (hkl) and the atomic level spacing (hkld) [27].

$$d_{hkl} = \frac{a_{hkl}}{\sqrt{h^2 + k^2 + l^2}} \quad \text{.....(2.4)}$$

The lattice constants in the cubic structure are equal, that is, a=b=c.

2.3 Characteristics of gaseous sensor

In this section, the properties of gaseous sensors and sensingmechanisms in metal oxides are presented Responsiveness, operating temperature, response time and recovery timeare very important characteristics of the sensor. These characteristics determine whether the sensor can be used for commercial use or not.

Other properties of sensors are stability and selectivity.

A gas sensor is a system that converts chemical information, whicharises from the physical and chemical interactions of gaseous samples with the sensor, into a usable electrical signal .

A gas sensor consists of two main parts: a sensing element (the sensitive metal oxide membrane) to recognize the gas it is interacting with and a conversion system (transducer) that converts the interaction between the gas and the sensing element into a signal, usually an electrical signal. [28]

2.4 Physical and chemical properties of NO 2 gas.

One of the most dangerous air pollutants is continuous exposure toNO2 gas, even if the concentration is low at the ppb level, as it causes emphysema, chronic bronchitis, and respiratory tract irritation. Therefore, many countries have tried to control the concentration of nitrogen dioxide in the air, which is 21 ppb) and have their own annual ambient air quality standards. [29] Nitrogen dioxide (NO2) is volatile and its pungent odor can cause severe damage to the respiratory system even at remarkably low concentrations. Mostly, NO2 is created in multiple ways such as fossil fuel burning, automobile exhaust, and emissions from chemical industries. A diesel-powered vehicle generatesa large amount of nitrogen dioxide which becomes a major concern. In addition, the volatile gas can cause acid rain when exposed to photochemical reactions with water.[30] Inhalation of nitrogen dioxide gas even at low concentrations results. Too low leads to nose or throat discomfort, fatigue, eye soreness, and lung tissue inflammation Therefore, it is very necessary to develop high-response and selectiveNO2 sensors for air quality monitoring. Nitrogen dioxide is a reddish-brown, non-combustible, toxic gas thathas a strong, suffocating odor and the symbol NO Which leads to the formation of fog, and this oxide is emitted into the atmosphere through natural sources such as: [31] Decomposition of nitrogen-containing compounds in soil by bacteria andspores. Due to various human activities, such as the formation of fuel in cars and power plants, where large quantities are produced in a narrow space, which leads to high local concentrations, which makes it a polluting and harmfuleffect on the environment. Although the total amount of NO x gases emitted into the atmospheric airis about 1/6 the amount of carbon dioxide emitted into the air, the disadvantages of NO x gases are 22 times the harmful effects of CO gas. It ismore toxic because it converts intermediate moisture into nitric acid, the inhalation of which causes major damage to the lungs and respiratory system,as well as the breakdown of nitrogen oxides in the presence of oxygen and light to produce ozone gas, and these gases cause serious damage to the respiratory system [32].

2.5 Gas sensor metrics

The efficiency of a gas sensor is measured in several ways. In the literature, the “3S” paraeters are often referred to as sensitivity, stability, and selectivity.[33] Among these parameters, sensitivity is the most

common. Selectivity is a key element in creating a commercially viable device. Some issues must be addressed, such as sensitivity, operating temperature, responsetime, and recovery time. All these factors are very important to produce a microsensor or microsensor array. These parameters are specified in this research, most of which will be applied[34].

2.5.1 Sensitivity (S)

The sensor's response when a certain type of gas is introduced. (S) Themost general concept of sensitivity applied to solid-state chemically resistant gas sensors is the change in electrical resistance (or conductivity) upon exposure to a reducing or oxidizing gas relative to theinitial state (the ratio of change in resistance upon exposure to gases relative to resistance in air). For p-type semiconductors (NiO) and reducing gases such as HS, theresponsivity S is given as: [34]

$$S = \frac{R_g - R_a}{R_a} \quad \text{.....(2.4)}$$

Where aR is the resistance of the membrane in air, and gR is the resistance of the membrane when exposed to gases. For n-type semiconductors such as (ZnO) and reducing gases, the response is,

$$S = \frac{R_a - R_g}{R_a} \times 100\ \% \quad \text{.....(2.5)}$$

The response of a gas sensor is affected by several factors such as filmthickness, crystal size, porosity, relative humidity, gas exposure time, andoperating temperature. Smaller grain size tends to increase the responsiveness of the sensor, which is attributed to the large sensing active surface due to the high surface-to-volume ratio and thus the interaction between gas molecules and crystals increases [34] .

2.5.2 Selectivity

Selectivity is defined as the ability to distinguish specific gas typesfrom background atmospheric gases. This is important as metal oxide-based sensors face significant challenges and show poor discriminationbetween gas types. Selectivity was defined as the percentage of sensitivity to a particular gas. [34]

$$SEL_{A/B} = \frac{}{GASB}$$

During this study, only one gas was added in the context of dry air, so this ratio does not explain the ability of the sensor to select specific types of gasesfrom a complex gas mixture. Selectivity has also been used to describe the ability of a sensor (or array) to detect and discriminate certain types of gases in a mixture containing multiple analyte gases. As with sensitivity, there are many factors that contribute to the selectivity of a sensor (e.g. temperature, gas flow rate etc. [35].

2.5.3 Stability

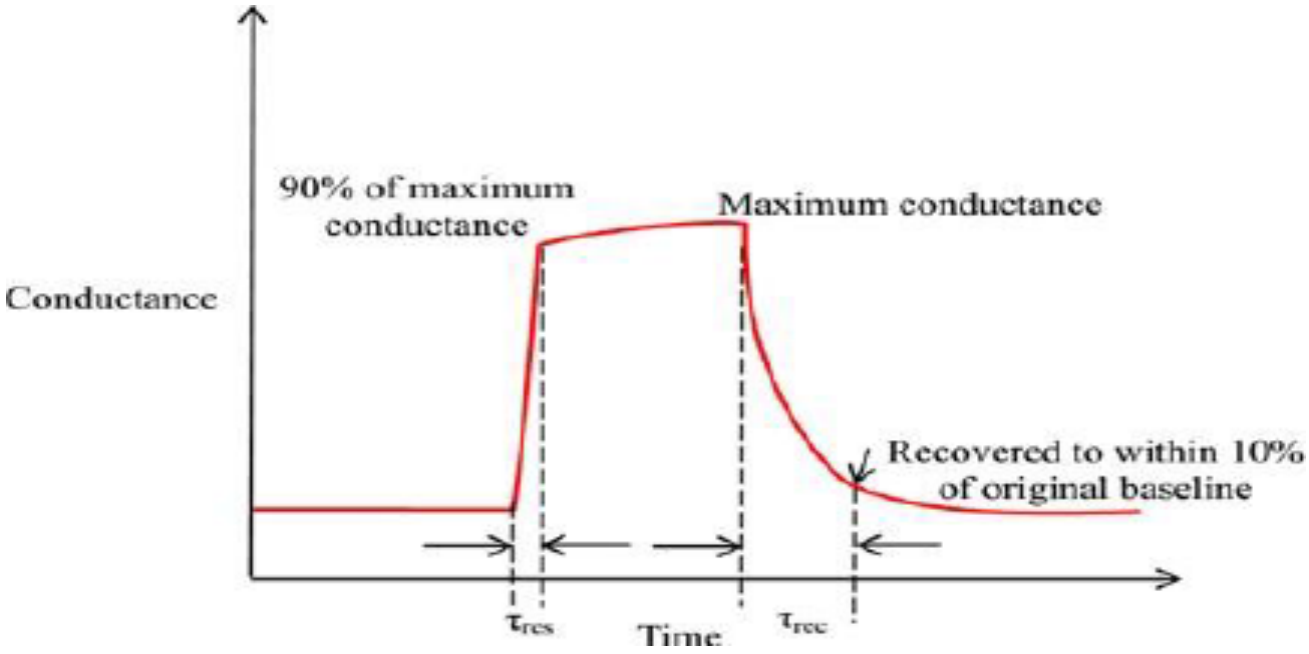
Stability is the ability of a sensor to maintain sensitivity to certain gastypes over time. Stability is calculated as shown in the following equation. [35]

$$D = \left| \frac{G_t - G_{t_o}}{t_1 -} \right| \quad \text{.....(2.36)} \ .$$

2.5.4 Response and recovery time

The response time of a gas sensor (τ res) is defined as the time it takes for the sensor to reach 90 percent of the maximum/minimum conductivity value when the reducing/oxidizing gas is introduced [36]. Likewise, when the reducing or oxidizing gas flow is removed, the recovery period is described asthe period necessary to recover within 10 percent of the original baseline.

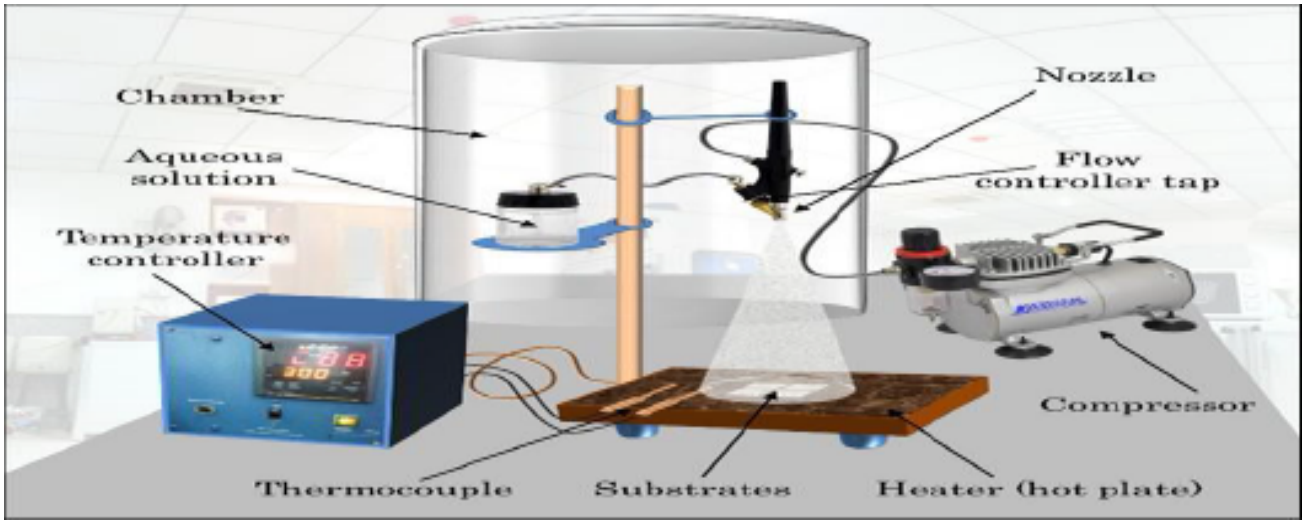
Figure 2.4 shows how this is measured from sensor data that plotsconductivity as a function of time [37].



On the other hand, all the tools and devices used in thiswork and the gas sensors manufactured from NiO will be explained and described

3.1 Thermal chemical spraying technology (SPT)

Thermochemical sputtering technique is the most popular today due to its applicability for producing a variety of conductive and semiconductor materials [38]. The basic principle involved in the thermal spraying technique (SPT) shown in Figure (3.1) consists of a sprayer (nozzle), solution, heater, substrate, temperature controller, air compressor and another gas source. Thin film deposition using this technique involves spraying a metal salt solution onto a preheated substrate. Droplets impact the surface of the substrate, spreading as a thin film. The shape and size of the film depends on the temperature of the substrate**.**



3.2 The influence of some main factors on the quality ofdeposited films.

This section discusses the influence of some key SPT parameters on theproperties of deposited films:

3.3.1 Effect of substrate temperature

The substrate surface temperature is the main parameter that determines the shape and properties of the film. By increasing the temperature, the form can change from a microscopic structure withcracks and defects to porous [39].

3.2.1 Effect of solution concentration

The concentration of brine used for spraying is the second importantvariable. The solvent, salt type, salt concentration, and additives affect the physical and chemical properties of the prepared samples. Many properties of the deposited film can therefore be changed by changing the composition of the solution. Such as film thickness, chemical composition, electrical and optical properties [40].

Effect of the distance between the spray nozzle and the substrateIf the distance between the sprayer nozzle and the substrate is changed, there are three types of processes that may occur during deposition. In Process 1, the droplet splashes onto the substrate, evaporates, and leaves a dry precipitate in which decomposition occurs. In process 2, the solvent evaporates before the drop reaches the surface and the precipitate hits the surface where decomposition occurs. In process 3, the solvent evaporates as the drop approaches the substrate, then the solid melts and evaporates (or sublimates) and the vapor diffusesto the substrate to undergo a heterogeneous reaction there.

3.3 Preparation of NiO thin films

3.3.1 Preparation of spray solutions to prepare NiO thin films

In this study, thin films were prepared using thermal spraying technology. Because of its simplicity, this technique is particularly attractive because it is fast, has simple instrumentation, and is suitable forproducing films of large areas [41].

iO thin films were fabricated on a glass substrate (25 mm × 25 mm

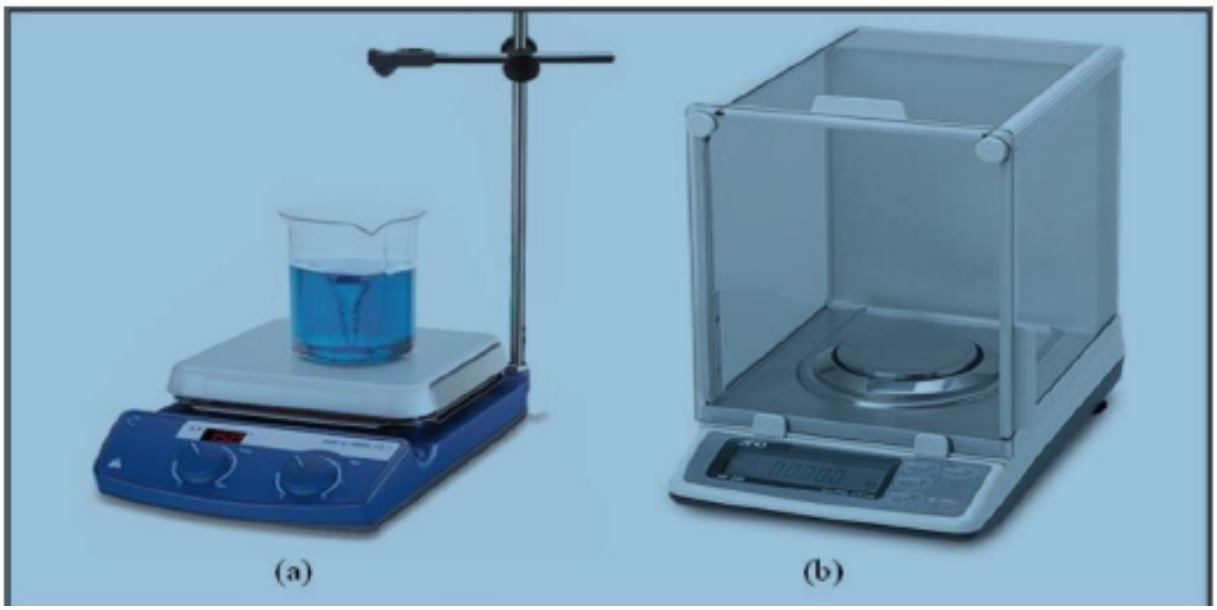
× 1 mm). Different concentrations of NiO solution were prepared by dissolving:6H2O)3(Ni(NO) in distilled water, with continuous stirring for one hour at room temperature to obtain a homogeneous solution using a magnetic stirrer (IKA® C-MAG HS7) as in Figure (3.2: a).

It weighs 0.29079 gm, 0.87238 gm, 1.445397 gm, 2.03555 gm and2.9079 gm of dehydrated nickel nitrate: 6H2O)3(Ni(NO). Each weightwas dissolved in 100 ml to produce concentrations of (0.01, 0.03, 0.05,

0.07 and 0.1 Molarity) An accurate electronic balance (HR-200 A&D Co.) was used as shown in Figure (3.2: b). The weight of 6H2O) 3(Ni (NO) required for each concentration was determined using the following equation [42]:

$$M = \frac{W}{M_W} \times \frac{1000}{V} \qquad (3.1)$$

Where M: is the molar concentration, W: the weight of the substance, MW: the molecular weight, V: the volume of distilled water.



3.3.2Thin film deposition

Figure (3.1) shows the spray system used in this work. Air gas is used as the carrier gas and an air compressor is used to atomize the mist. During spraying the substrate temperature is ~420±5°C. In order to avoid cooling ofthe substrate, spraying is done at intervals of about 12 seconds, followed by a wait of about 2 minutes, with a spray rate of 5 ml/h. The distance between the substrate and the spray nozzle was maintained at 30 cm in order to deposit thin films with uniform thickness.

Film thickness was determined using the gravimetric method as discussed in Chapter 2. Films deposited on clean glass slides had their masspreviously determined. After deposition, it was weighed again to determine the amount of material deposited. By measuring the surface area of the deposited film, taking into account the density of the material, the thicknesswas determined using equation (2.1) and ranged from 350 to 400 nm.

Compositional measurements (X-ray diffraction analysis)

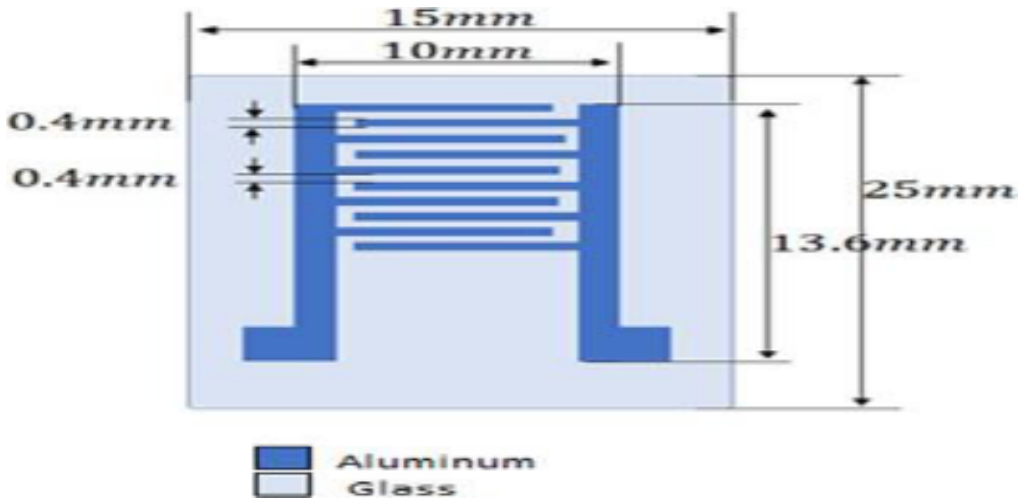
Philips In the range of 20°–80° in the American Standard for Testing and Materials (ASTM)[43] cards of NiO the general structure of the thin films including the diffraction peaks, which show the peak positions and phase concentrations, and the corresponding atomic distance spacing (Å d hkl) , lattice constants, crystal size, and relative intensity (oI/I). Using the Scherrer equation, the strongest peak of the films was used to determine the average crystal size .

Gas sensor checks:

The sensitivity of gas sensors depends mainly on the grain size of thematerial exposed to the gas [44]. The grain size on a substrate of a givenmaterial is known to depend on the settling capacity of the substrate. It is believed that substrates with lower surface tension result in smaller grain size. Glass, which has the lowest surface tension, is best for obtaining thesmallest grain size for the NiO thin film [45].

Al Intergrade Electrodes (IDE):

He used thermal evaporation technology (Edward unit type E306A),which is used through a metal mask to thermally evaporate the aluminumlayer on the NiO sample. Figure (3.3) shows the overlapping metal electrode masks (8 and 10 fingers) used in this work.



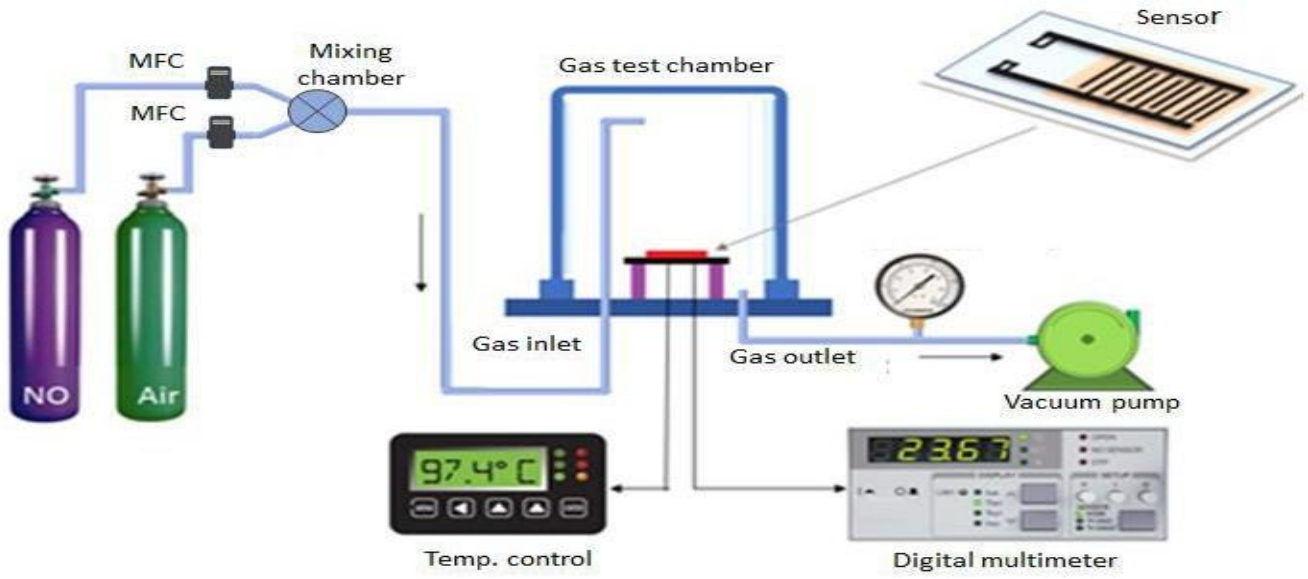
Gas sensor inspection system:

Figure 3.4 shows a schematic cross section of the gas sensor test rig. Itconsists of a cylindrical vacuum-tight stainless steel test chamber with a diameter of 163 mm and a height of 200 mm, with the base rotatable and sealed with an O-ring. The effective volume of the chamber is 4173.49 cc. It has an inlet to allow test gas to flow, and an air intake valve to allow air toevacuate.

Another third port is given to measure the pressure rate inside the chamber. A multi-electrode feed at the base of the chamber allows electrical connections to be made to the heater assembly and sensor electrodes. The heater assembly consists of a hot plate and a k-type thermocouple inside the chamber to regulate the operating temperature of the sensor.

There is also a multimeter connected to the PC that is used to measure the change in conductivity of the sensor subjected to a pre-determined mixing ratio between air and gas. The chamber can be emptied to approximately vacuum (1−3 bar) using a rotary pump. Gas mixing valves are integrated to control the mixing ratios of test carrier gases, and through the flow meter and valve arrangement, the air and test gas feed into the mixing gas accumulator. This mixing scheme is designed to ensure that the gas mixture entering the test chamber is mixed in a way that gives true sensitivity.

For gas sensing tests, the chamber was equipped with a 500 W electricceramic heater with computerized control. The chamber is supplied witha mixture of the target gas (NO2) and the air is adjusted in controlled proportions via two control valves/mass flow at 1000 cubic meters per minute during the test. A current source (2400 Source Meter, Keithley, Cleveland, Ohio, USA) was used to follow and record the changes in electrical



resistance of the samples during the sensing test and convert them into an electrical signal.

Results and Interpretation

Results and interpretation of experimentalmeasurements of NiO films that were prepared by thermal spraying on a glass substrate deposited at a substrate temperature of 420 degrees Celsius, the distance between the nozzle and the substrate is 30 cm, and the thickness of the films varies between 280 - 300 nanometers with focus. The composition of NiO films was tested for different concentrations(0.01, 0.03, 0.05, 0.07, 0.1 M). The characteristics of the gaseous sensor were also tested for different gas (NO2) and operating temperature of the sensor and the results we obtained are discussed.

4.1 Structural characteristics (X-ray diffraction analysis)

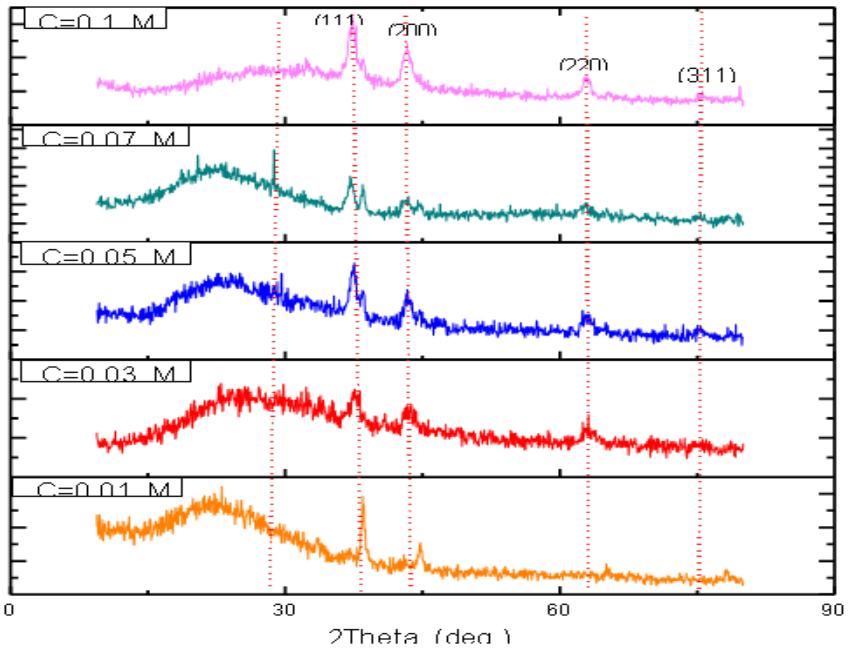
The structural and lattice parameters of NiO films can be found by X-ray diffraction (XRD), which records the intensity as a function of theBragg diffraction angle between 20 and 80 degrees.

Figure (4.1). It can be seen that all samples for all concentrations showed three main peaks at about 37.7°, 44.7° and 63.2° which correspond to Miller coefficients (111), (200) and (220) respectively, andthis is in agreement with the ICC [43] data card number. Diffraction (ICDD) (04–0835) which corresponds to JCPDS (No. 47-1049) for nickebxide .

This pattern indicates that the formed film is polycrystalline with a cubic NaCl type (a=b=c) facet centered (FCC)) with a principal directionin the (111) plane [46] . No other clear peaks belonging to impurities or nickel metal appear. Thethin film with a Nr concentration of 0.1 M has a higher and sharper diffraction peak (111), which indicates an improvement in the crystallinity of this film compared to other models deposited at lower concentrations. It should be noted that other peaks appear at equals (200)and (220).

Weak peaks indicate that these films have a textural composition, and that the composition depends on the concentration of the spray solution used. These results attest that the texture composition of membranes is higher when the molar concentration is smaller. This can be attributed tothe smaller nickel nitrate hydrate flux, which allows a better ordered growth process for the films. On the other hand, sharp peaks can be clearly seen, indicating significant crystalline order in this specific direction [47].

The results obtained fit well with published studies [48,49]. Average crystal sizes (D) estimated using the highest peaks, we observethe crystal size increasing from 10.67 nm to 28.46 nm as the molar solution concentration increases from 0.01 mol/L to 0.1 mol/L, with which the crystal size is likely affected, which could It is attributed to thedecrease in voids and defects in the crystal structure.



The presence of nano-sized grains in polycrystalline materials to high density of grain boundaries. It is known that grain boundaries act as sites of electron transfer (oxygen uptake), leading to improved sensor efficiency. However, the sensitization mechanism is related to the grain density [50], since the electrochemical processes and corresponding optical absorption mainly occur at the grain boundariesand on the grain surfaces [51].

4.4 Gas sensor measurements

The basis of the work of the gas sensor is to convert the interaction withthe gas into an electrical signal. NiO is a metal oxide that can perform thisconversion. Due to the effect of the presence of gas molecules and their interaction with the surface of the membrane, this affects the electrical resistance of the membrane [52].

The sensor measurements are examined for samples with different concentrations when exposed to a gas with a concentration of 77 cubic centimeters of gas and at different operating temperatures ranging from (50, 100, 150, 200, 250, 300) degrees Celsius to find the sensitivity of the sensor to the gas, the morphology of the membranes, the voids for oxygen,and the size of the particles. , and the nature of the gas are the key points of the gas sensing phenomenon [53].

4.4.1 Sensitivity and operating temperature

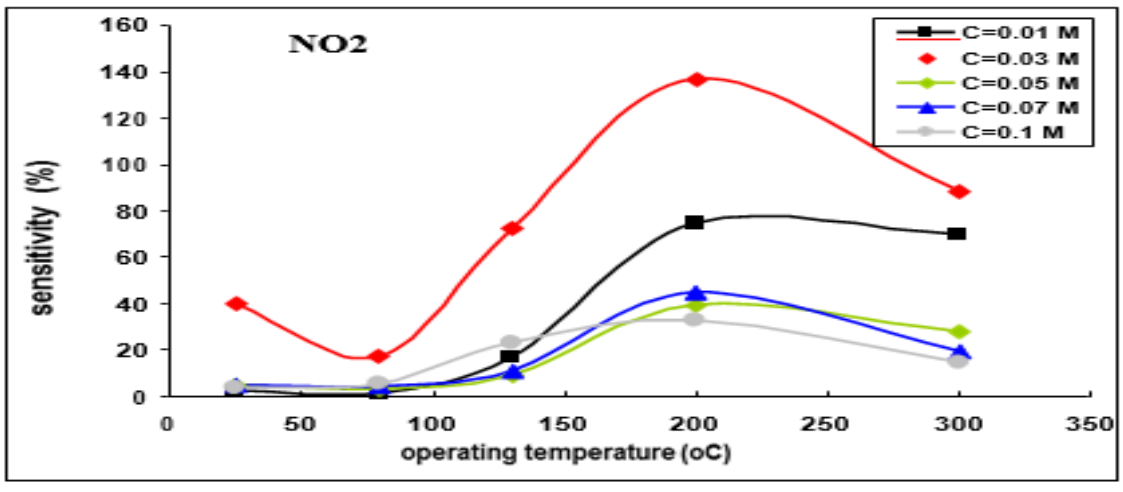
The temperature at which a chemical reaction takes effect is called theoperating temperature. Figure (4.2) shows the variation of sensitivity with operating temperature, as it is clear that sensitivity increases with increasing operating temperature. The best temperature that achieved maximum responses was found as shown in the figure around 200°C for NO2 gas. The sensitivity increases due to the increased rate of surface interaction with the gas .

The best sensitivity was obtained at a spray solution concentration of 0.03M, where its value was about 136%. This may be due to the small crystal size, large numbers of oxygen voids and surface morphology, which are the main factors responsible for increasing the sensitivity of the gas sensor [54]. For this reason, the effect of spray concentration on sensitivity was studied with the aim of finding the optimal concentration.

At low temperatures, the response of the sensor is limited by the speedof the chemical reaction. Gas molecules cannot have enough energy to become active, so the sensitivity of the sensor is limited. At a higher temperature, the diffusion speed of gas molecules is restricted. The increase in sensitization with temperature can be attributed to the fact that the thermal energy obtained was high enough to overcome the activation energy barrier for the reaction and the significant increase in electron concentration resulting from the sensing reaction.

At some intermediate temperatures, the speed values of the two operations become equal, at which point the response of the sensor has reached a maximum.[55] It has been observed that as the operating temperature increases further, the response decreases, which can be attributed to a decrease in the adsorption of gas molecules on the surface.For NiO thin films.

Table (4.3) shows the operating temperature values of the gas sensor and its change with concentration



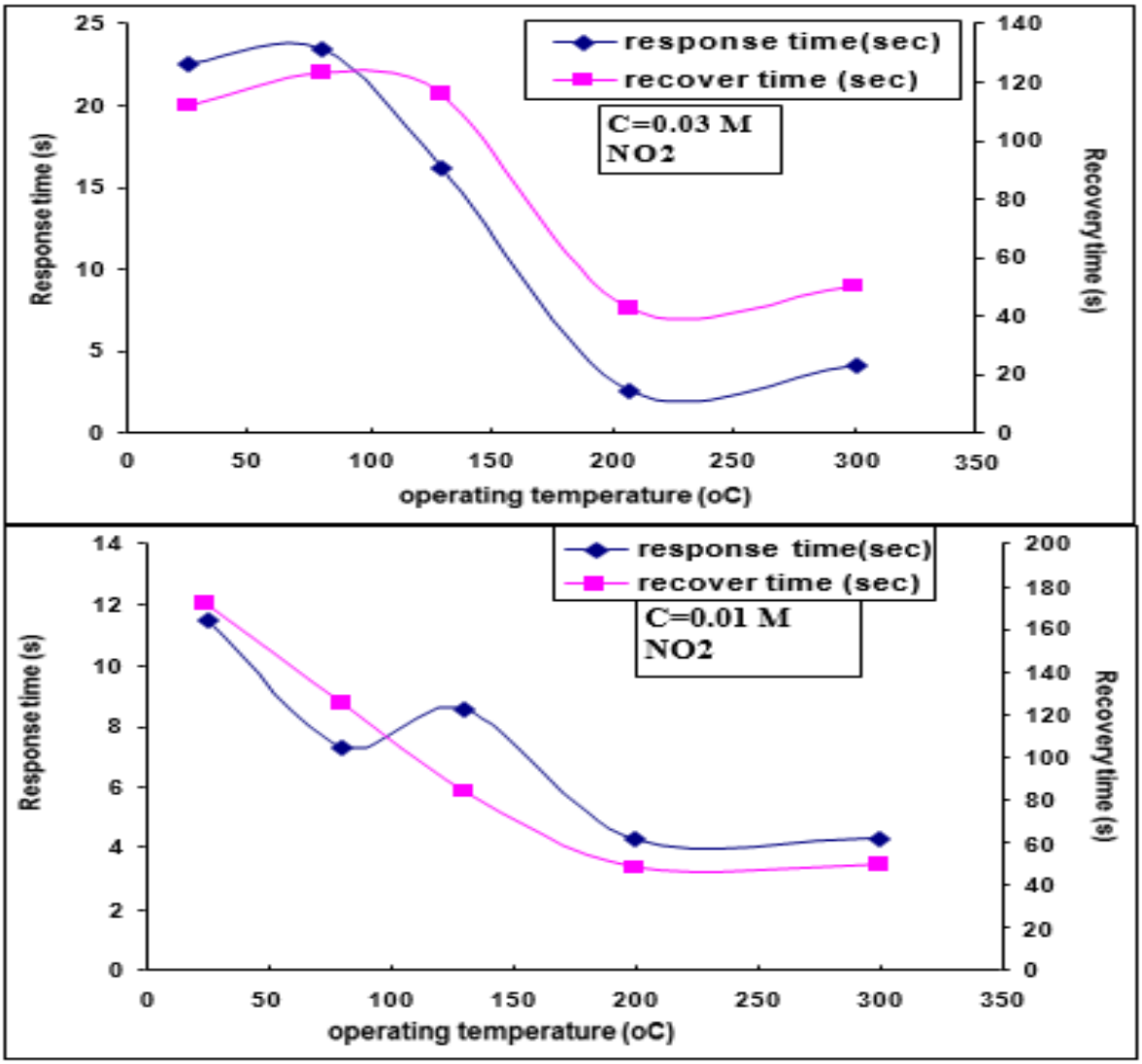
4.4.1Response and recovery time

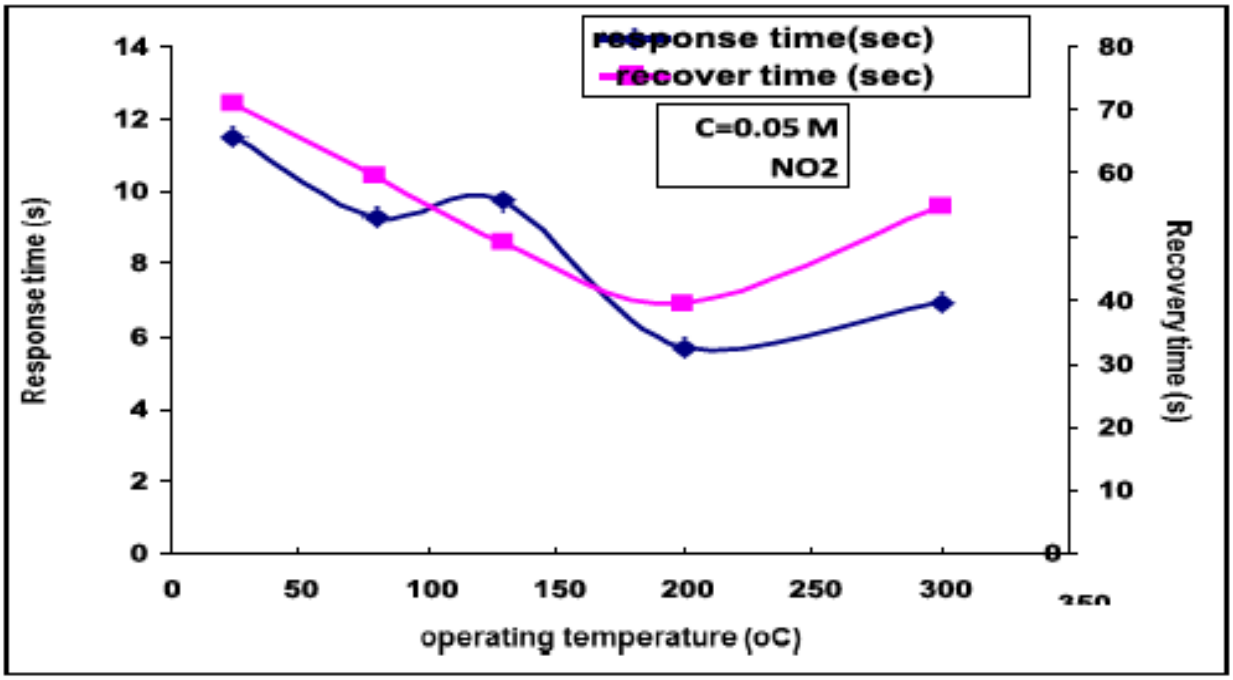
The response time is the period of time during which the resulting signal is approximately 90% of the final value when the sensor is exposedto the gas concentration and the recovery time is the time required to return to the initial value of approximately 10% of its value. The responsedepends in particular on the characteristics of the sensor such as crystal size and electrode geometry. electrode position, etc. A faster response time indicates that the sensor is excellent.

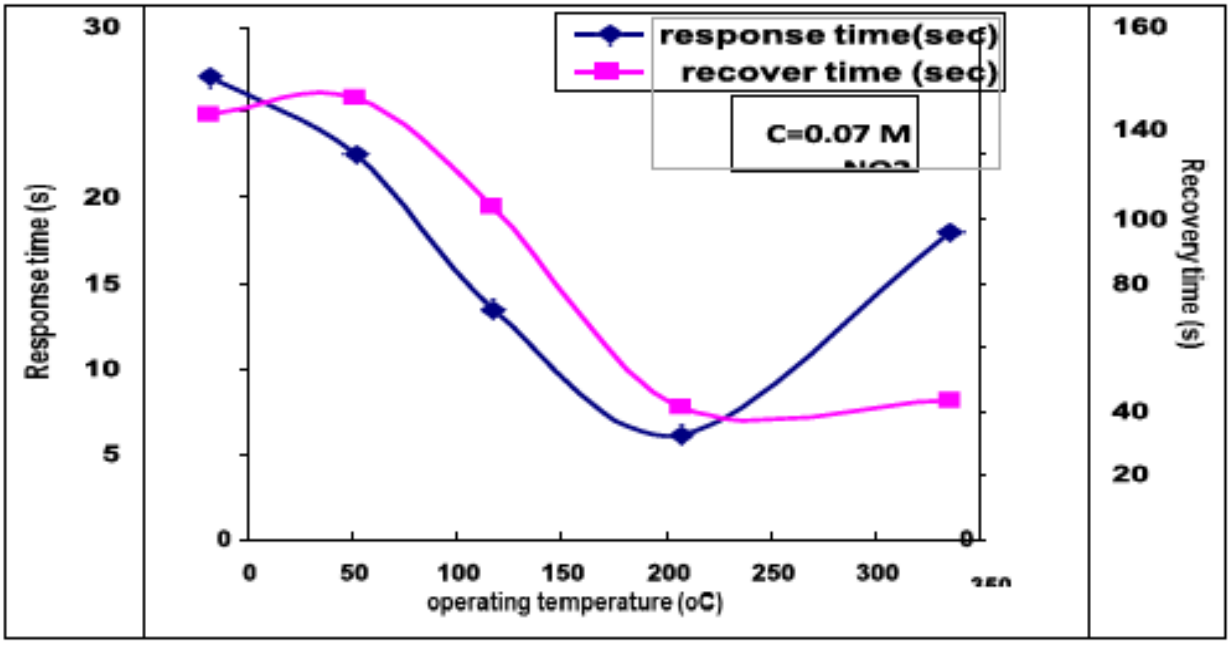
Figure (4.3) shows the "response time and recovery time" of thesensor; With operating temperature

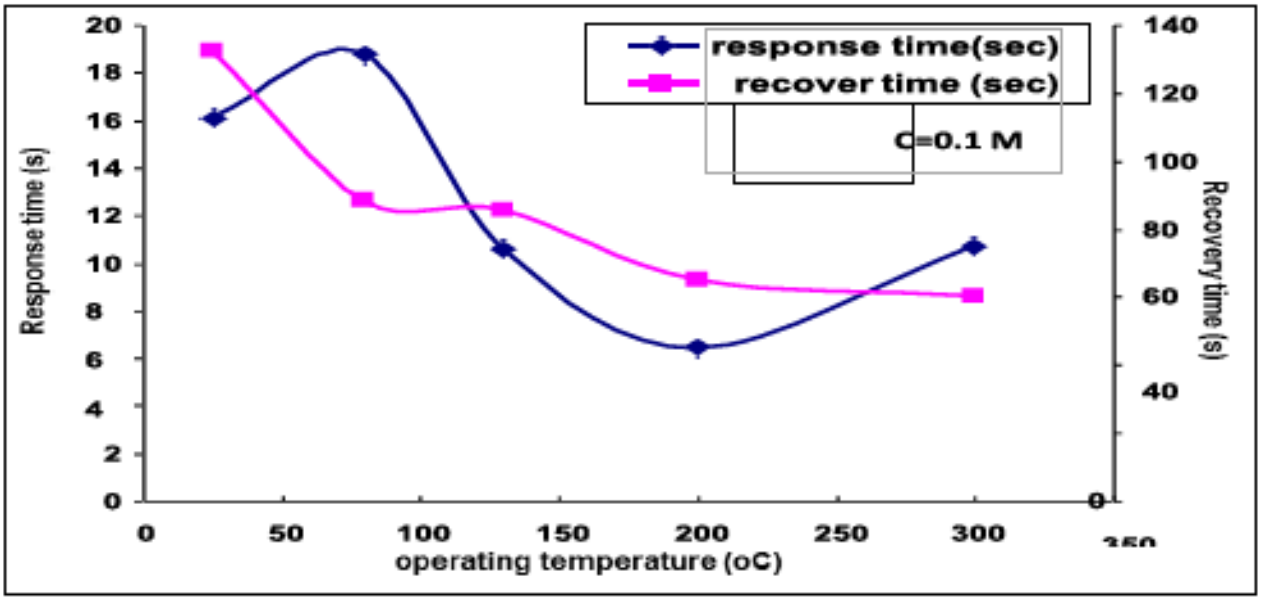
We note that the response time* of the sensor decreases with increasingoperating temperature, and the lowest value of the response time for thesensor manufactured from NiO is about 2.68 seconds at the operating temperature of 200 degrees Celsius, and the recovery time at the same operating temperature is about 75.6 seconds for the sample with a molarconcentration of 0.03 M when exposed to NO2 gas. .

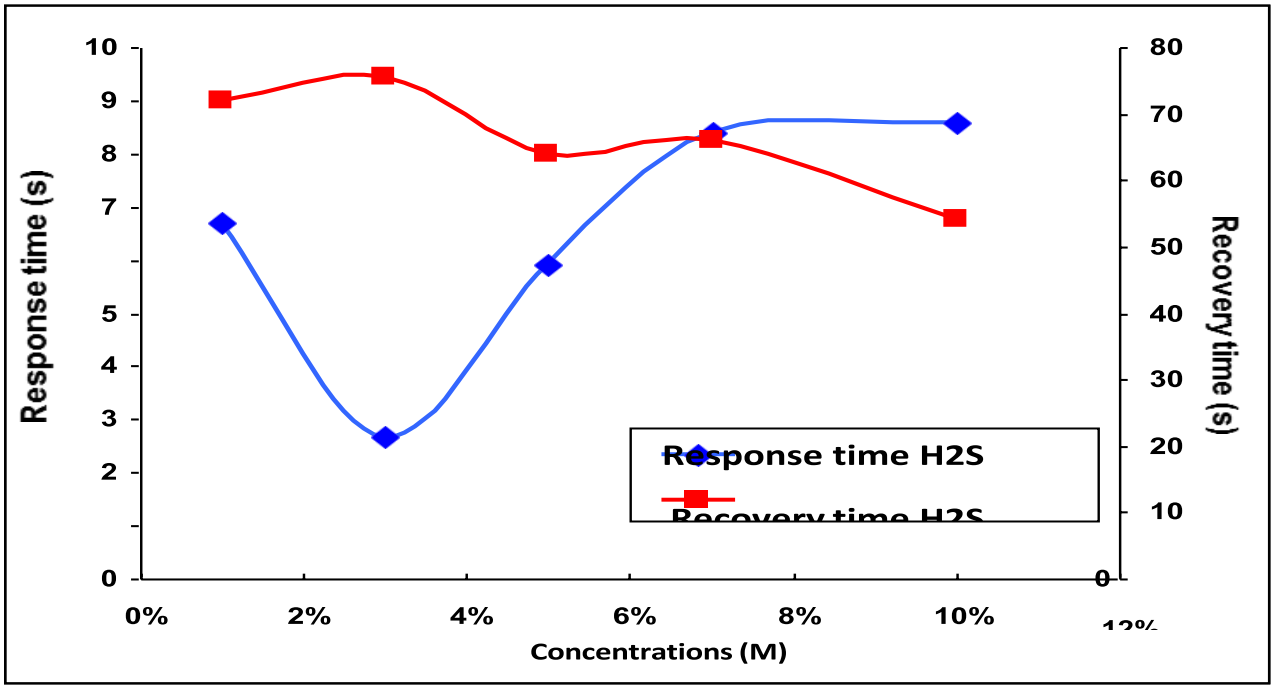
Therefore, we attribute the rapid response to the 0.03 M concentration to a decrease in activation energies, and this decrease in energy can be linked to the increase in oxygen vacancies resulting in the lattice. [56] NiO and oxygen adsorption increases with electrons in the near surface region, creating a surface electron depleted layer. This led toan increase in the number of active sites for adsorption and a rapid response time for the sensors. Also, the response time as mentioned above depends on the size of the crystals that occur at low concentrationsas shown in the XRD results. Therefore, reducing the thickness of the film may be a suitable way to improve the response time, as the change inresponse and recovery times with concentration appeared in Figures (4.3)and (4.4), and all sensor parameters are mentioned in Table (4.2).




response time(sec)
recover time (sec)
C=0.05 M
NO2
Response time (s)
Recovery time (s)
operating temperature (oC)


response time(sec)
recover time (sec)
C=0.07 M
Response time (s)
Recovery time (s)
operating temperature (oC)


response time(sec)
recover time (sec)
C=0.1 M
Response time (s)
Recovery time (s)
operating temperature (oC)



Conc (M)	S NO2 %	Operating temp NO2 (°C)	Response time NO2 (Sec)	Recovery time NO2 (Sec)
1%	78	210	4.3	47.7
3%	136	210	2.56	42.5
5%	40	210	5.68	39.3
7%	45	210	6.1	41
10%	33	210	6.4	65.1

Conclusions

The basis of this research is the improvement and characterization of nanostructured NiO thin films and their application in the field of gas sensing. Nickel oxide films were successfully prepared using thermal spray technology at different concentrations on glass substrates at temperatures around 420°C. In order to determine the optimal concentration for sample preparation, the effect of some preparatory variables such as the molarity of the solution and the thickness of the films on the structural properties was studied. And find which of these concentrations improves the properties. The most important results obtained can be summarized as follows: From the results of Gas sensor devices. From the gas sensor measurements: it can be concluded that the NiO gas sensors showed high sensitivity to gas. Also from the study it can be concluded that the optimal operating temperature is 200 degrees Celsius for all concentrations, and increasing concentrations did not affect the operating temperature. The most important conclusion is that we note that the concentration of 0.03 M for NiO membranes is much better than other sensors with concentrations higher and lower than this concentration, which means that despite the good sensitivity and good response and recovery time, the concentration of 0.03 M for the sensors is the best in general, as we obtained the best time. The response and recovery are within 2.86 seconds and 75.6 seconds respectively and the sensitivity is about 136% for NO2 gas for concentration 0.03 M. Therefore, NiO metal oxide is practical and suitable for obtaining a fast and sensitive gas sensor capable of detecting toxic and

flammable gases. We conclude that the results obtained confirm that NiO membranes have a promising future in the field of gas sensing.

Future work

Based on the results of this study, the following future studies areproposed: Study the effect of doping with elements such as Co or Cu to improvethe properties of NiO thin films and sensors manufactured from them. The use of doped and undoped NiO thin films in photoelectricapplications such as photodetectors and solar cells. Preparing NiO thin films using another technique, such as chemicaldeposition, and comparing their results with the results of other techniques. Study of the current-voltage (I-V) properties of films deposited onanother semiconductor to prepare a PN junction. Using NiO membranes as a photocatalyst and antibacterial.

References:

1. Jilani, Asim, Mohamed Shaaban Abdel-Wahab, and Ahmed Hosny Hammad. "Advance deposition techniques for thin film and coating,Modern Technologies for Creating the Thin-film Systems and Coatings , 2, (2017),P.p 137-149.
2. Tripathy, Sumanta Kumar, B. Nagarjun, and V. Siva Jahnavy. "Optical and structural characteristics of copper doped tin oxide thin film prepared by thermal evaporation method." International Journal of Engineering and Innovative Technology (IJEIT), Vol. 3, (2013).
3. K.O. Ukoba, A.C. Eloka-Eboka, F.L. Inambao, Review of nanostructured NiO thin film deposition using the spray pyrolysis technique, Renewable and Sustainable Energy Reviews, 82, (2018),P.p 2900–2915.
4. Jeun, Jeong-Hoon, and Seong-Hyeon Hong. "Porous SnO_2 Films Fabricated by Anodic Oxidation and RIE Process and CuO AdditivesEffect on Gas Sensing Properties." Nanotechnology,18 , (2009), P. 065707.
5. S.Palanichamya, J.Raj Mohamedb, K.Deva, Kumarc, P.S.Satheesh Kumara, S.Pandiarajand, L.Amalraj ,"Physical properties of rare earth metal (Gd3+) doped SnO_2 thin films prepared by simplified spray pyrolysis technique using nebulizer.", Optik, Vol.194, (2019),p.162887.
6. Zhan, Zili,;Wang, Wei-Ning1; Zhu, Liying; An, Woo-Jin; and Biswas, Pratim, Morphology control of SnO_2 thin film gas sensorsby a flame aerosol reactor (2010).
7. Yousif, Salam Amir, and Jenan Mohamed Abass. "Structural, Morphological and Optical Characterization of SnO_2: F thin filmsprepared by Chemical spray Pyrolysis." International Letters of Chemistry, Physics and Astronomy, Vol. 13, (2013):P.p 90-102.
8. Dilip L.Kambleab, Namdev S.Haralec, Vithoba L.Patilc, Pramod S.Patilc, Laxman D.Kadam , "Characterization and NO_2 gas sensing properties of spray pyrolyzed SnO2 thin films." Journal of Analytical and Applied Pyrolysis, Vol. 127, (2017), P.p 38-46.
9. Tang-Yu Lai, Te-Hua Fang, Yu-Jen Hsiao, Ching-An Chan, "Characteristics of Au-doped SnO_2–ZnO heteronanostructures for gas sensing applications." Vacuum, Vol.166, (2019): P.p155-161.
10. Maziarz, Wojciech. "TiO_2/SnO_2 and TiO_2/CuO thin film nano- heterostructures as gas sensors." Applied Surface Science, Vol.480,(2019): P.p 361-370.
11. Chatchawal Wongchoosuk, Anurat Wisitsoraat, Adisorn Tuantranont, Adisorn Tuantranont, Teerakiat Kerdcharoen, Teerakiat Kerdcharoen , "Portable electronic nose based on carbonnanotube-SnO_2 gas sensors and its application for detection of methanol contamination in whiskeys." Sensors and Actuators B: Chemical, Vol. 147, No.2 (2010): P.p 392-399.

12. V. M. Aroutiounian, "Semiconductor metal Oxide hydrocarbon gasSensors", International Scientific Journal for Alternative Energy and Ecology, Vol. 47, No. 3, (2007), P.p33-42.
13. Wang, P. Yang, X. Wei1 and Z. Zhou, "Preparation of NiO two- dimensional grainy films and their high-performance gas sensors for Mammonia detection", Nanoscale. Res. Lett, Vol. 10, No.119, (2015), P.p 1- 6.
14. D. Farrukh, R. M. Kevin and E. S. Mohammed, "Morphology and property control of NiO nanostructures for supercapacitor applications", Nanoscale Research Letters, Vol. 8, No. 1, (2013), P.p 1-7.
15. J. S. Anandh, M. Haris and P. Immanuel, "Structural and Optical Properties of Pure Nio and Li-Doped Nickel Oxide Thin Films bySol-Gel Spin Coating Method", International Journal of Science and Research, Vol. 23, (2014), P.p58-87.
16. A. G. Attieh, M. S. A. Wahabab, A. A. Farghalibc and P. M. Z.Hasana, "Structural optical and photo-catalytic activity of nanocrystalline NiO thin films", Materials Research Bulletin, Vol.7, (2016), P.p71-75.
17. D. Farrukh, R. M. Kevin and E. S. Mohammed, "Morphology and property control of NiO nanostructures for supercapacitor applications", Nanoscale Research Letters, Vol. 8, No. 1, (2013),P.p 1- 7.
18. D. G. Enrico and M.Alessandro, "Sol-Gel Thin Films for PlasmonicGas Sensors", Sensors, Vol. 15, No. 7, (2015), P.p16910-16928.
19. J. Zhang ,Qin Z, Zeng D ,Xei C, Metal-oxide-semiconductor based gas sensors: screening, preparation, and integration. Phys.Chem. Chem. Phys,19 (2017): P.p6313- 6329.
20. Laifa Sang, Guogang Xu, Zhiwei Chen, Xinzhen Wang, Hongzhi Cui, Gaoyu Zhang, Yajie Dou "Synthesis and characterization of Au-loaded SnO2 mesoporous spheres by spray drying and their gas sensing property." Materials Science in Semiconductor Processing,Vol. 105 (2020): P.104710.
21. C.Wang, et al., Metal Oxide Gas Sensors: Sensitivity andInfluencing Factors. Sensors ,10, (2010): 2088-2106.
22. A.M. Soleimanpour, et al., Surface and gas sensing properties ofnanocrystalline NiO thin films. Applied Surface Science 276 (2013):P.p 291-297
23. R. Pearce, T. Iakimov, M. Andersson, L. Hultman, A. L. Spetz, and R.Yakimova, “Epitaxially grown graphene based gas sensors for ultra sensitive NO_2 detection,” *Sensors Actuators, B Chem.*, 2011.
24. G. Williams and G. S. V. Coles, "The Gas-Sensing Potential ofNanocrystalline Tin Dioxide Produced by a Laser Ablation Technique", MRS Bulletin, Vol. 24, No. 6, (1999), P.p 25-29.
25. David C. Look, D. C. Reynolds, C. W. Litton, R. L. Jones, D. B. Eason, and G. Cantwell, "Characterization of homoepitaxial p-typeZnO grown by molecular beam epitaxy", Applied Physics Letter, Vol. 81, No. 10, (2002),P.p1830-1832
26. M. Reddya, A. S. Reddyb and P. S. Reddya, "Annealing effect on the physical properties of dc reactive magnetron sputtered nickeloxide thin films", Physics Procedia, Vol. 49, (2013), P.p9-14.
27. P.J. Kelly and R.D. Arnell, "Magnetron sputtering: a review of recent developments and applications", Vacuum, Vol. 56, (2000),P.p159-172.

28. M. Leskelä, and M. Ritala, "Atomic layer deposition (ALD): from precursors to thin film structures". Thin Solid Films, Vol. 409, No.1, (2002),P.p 138-146.

29. D. Perednis and L. J. Gauckler, "Thin film deposition using spray pyrolysis", Journal of Electroceramics, Vol. 14, (2005), P.p 103- 111.

30. S. A. Mahmoud, S. Alshomer and M. A. Tarawnh, "Structural andoptical dispersion characterization of sprayed Nickel Oxide thin films", Journal of Modern Physics, Vol. 2, (2011), P.p1178-1186.

31. R. C. Korošec and P. Bukovec, "Sol-Gel Prepared NiO thin filmsfor electrochromic applications", Acta Chim. Slov, Vol. 53, (2006), P.p136-147.

32. F. Y. Yang, Kai Liu, Kimin Hong, D. H. Reich, P. C. Searson and C. L. Chien" Large magnetoresistance of electrodeposited Single-Crystal Bismuth thin films", Science, Vol. 284, No. 5418, (1999),P.p1335-1337.

33. J. C. Osuwa and G. I. Onyejiuwa, "Structural and electrical properties of annealed Nickel Oxide (NiO) Thin Films preapared by chemical bath deposition", Journal of Ovonic Research, Vol. 9,No.1, (2013),P.p 9-15.

34. Y.Z. Liu, C.C. Wang and M. Chu, "Low threshold 1.3-μm InGaAsP/InP lasers prepared by a single-step liquid-phase epitaxy", Journal of Applied Physics, Vol. 63, (1988), P.p 2151-2151.

35. D. J. Estes and M. Mayer, "Electroformation of giant liposomesfrom spin-coated films of lipids", Colloids and Surfaces B: Biointerfaces, Vol. 42, (2005),P.p 115-123.

36. P. Baudry, A. C. M. Rodrigues, M. A. Aegerter and L. O. Bulhões,"Dip-coated TiO2- CeO2 films as transparent counter-electrode fortransmissive electrochromic devices". Journal of Non-Crystalline Solids, Vol. 121, (1990),P.p 319-322.

37. D. Y. Jianga, J. M. Qina , X. Wangb, S. Gaoa, A. C. Lianga and J. X. Zhaoa, "Optical properties of NiO thin films fabricated by electron beam evaporation", Vacuum, Vol. 86, No. 8, (2012),P.p1083-1086.

38. H. Ivan, L. Jozef, S. Helmut and V. Peter, "properties of sputteredNiO thin films", Journal of Electrical Engineering", Vol. 53, No. 11-12, (2002),P.p 339-342.

39. V. Julijana, P. G. Margareta, N. Metodija and S. Nace, "Studies on electrochromism of chemically deposited Nickel Oxide thin films",Silpakorn University Science and Technology Journal, Vol. 5, No. 1, (2011), P.p 34-42

40. C. K. Romana and B. Peter, "Sol-Gel Prepared NiO Thin Films forElectrochromic pplications", Acta Chimica Slovenica, Vol. 53, (2006), P.p136-147.

41. J. H. Ahmed, "Study of optical and Electrical Properties of NickelOxide (NiO) Thin Films Deposited by Using a Spray Pyrolysis Technique", Journal of Modern Physics, Vol. 5, (2014), P.p 2184-2191.

42. Hotovy, V. Rehacek, P. Siciliano, S. Capone, L. Spiess, Sensingcharacteristics of NiO thin films as NO_2 gas sensor. Thin solid films, 418, (2002), P.p 9-15.

43. Y.ZhO, H. Wang, C. Wu, Z.F. Shi, F.B. Gao, W.C. Li, G.G. Wu, B.L. Zhang, G.T. Du , Structures, electrical and optical properties of nickel oxide films by radio frequency magnetron sputtering. Vacuum, 103, (2014), P.p 14-16.

44. M. V. Nikoli´c, V. Blagojevi, K. M. Paraskevopoulos, T. T. Zorba , D. Vasiljevi-Radovi, P. M. Nikoli and M. M. Risti, "Far infrared properties of sintered NiO", Journal of the European CeramicSociety, Vol. 27, (2007), P.p 469–474.

45. H. Benzscour, "Synthèse d'un oxyde transparent conducteur (OTC)par pulvérisation chimique (ZnO, NiO)", Magistere Thesis, Badji Mokhtar University, (2008), Algeria.

46. S. Perusin, "Conséquences de l'oxydation haut température sur l'injection de défauts et le comportement mécanique des matériauxmétalliques", Doctoral Thesis, Toulouse University, (2004), France.

47. J. D. Desai, S. K Min, K. D. Jung and O. S. Joo, "Spray pyrolyticsynthesis of large area NiOx thin films from aqueous nickel acetate solutions", Applied Surface Science, Vol. 253, No. 4, (2006), P.p 1781-1786.

48. P. D. Hoon, "Optimization of nickel oxide-based electrochromicthin films", Doctoral Thesis, Bordeaux 1 University, (2010), France.

49. P. Puspharajah, S. Radhakrishna, and A. K. Arof, "Transparent conducting lithiumdoped nickel oxide thin films by spray pyrolysis technique", Journal of Materials Science, Vol. 32, (1997), P.p 3001-3006

50. M. Soleimanpour, "Synthesis, fabrication and surface modification of nanocrystalline nickel oxide for electronic gassensors", Doctoral Thesis, Toledo University, (2013), U.S.A

51. V. Marcio, P. S. Renan and I. C. Susana, "Synthesis and characterization of stable Co and Cd doped nickel hydroxidenanoparticles for electrochemical applications", Ultrasonics Sonochemistry, Vol. 16, No.1, (2009), P.p 35-40,

52. P. S. Patil, L. D. Kadam, "Preparation and characterization of spraypyrolyzed nickel oxide (NiO) thin films", Applied Surface Science,Vol. 199 ,(2002), P.p 211-221.

53. W.D. Callister, Fundamentals of materials science and engineering-An intergrated approach. 2005, John Wiley & Sons, Inc, Second edition.

54. Crystal Structure Gallery, National Institute of Advanced IndustrialScience and Technology (AIST). Available at: https://staff.aist.go.jp/nomurak/ common/ STRUCIMAGES/ NiO.gif.

55. H. Benzscour, "Synthèse d'un oxyde transparent conducteur (OTC)par pulvérisation chimique (ZnO, NiO)", Magistere Thesis, Badji Mokhtar University, (2008), Algeria.

56. S. Benhamida, "Caractérisation Des Couches Minces D'oxyde De Nickel (NiO) Ela oré Par Spray Pyrolyse", Doctoral Thesis, BiskraUniversity, (2018), Algeria.