A Dissertation

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Synthesis, Fabrication and Surface Modification of Nanocrystalline Nickel Oxide for
Electronic Gas Sensors

by

Amir Masoud Soleimanpour

Submitted to the Graduate Faculty as partial fulfillment of the requirements for the
Doctor of Philosophy Degree in Engineering

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An Abstract of
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Recently, metal oxide gas sensors have attracted much attention in connection with monitoring of combustible and toxic gases because of their higher sensitivity, fast response and recovery times, low power consumption, and low fabrication cost. Nickel oxide (NiO) is a wide band gap and p-type semiconductor with stable chemical and physical properties. NiO has been recognized as one of the most promising material for optical, electrical and gas sensor application owing to its electronic and catalytic properties. NiO is synthesized using different techniques, such as pulsed laser deposition, RF sputtering, electrochemical deposition and sol-gel. The focus of this research was to synthesize and characterize the gas sensing behavior of nickel oxide metal oxide gas sensors.

Thin films of nickel oxide synthesized by a sol-gel method have fine nanostructured grains with a high surface to volume ratio, which is beneficial for gas sensor applications. The effect of thickness, fabricating technique, operating temperature, post laser irradiation and metallization on the gas sensing behavior of nickel oxide have been studied. The microstructure, optical and electrical properties of coated film were
studied by XRD, SEM, TEM, EDAX, XPS, UV-Vis spectrometer. The gas sensing properties of NiO based sensors were studied for different explosive and hazardous gases as a function of gas concentration and operating temperature.

The dependence of fabrication method, film thickness and operating temperature on the hydrogen gas sensing behavior of NiO thin films was investigated. It was observed that the samples with multi-step annealing possessed smaller grain size, higher porosity and higher gas sensing performance. The sample with lower thickness showed better gas sensing performance in all operating temperatures. Moreover, the operating temperature was an important parameter for nickel oxide thin film, and the maximum gas sensor response was recorded at 175°C for hydrogen gas. The effect of post laser irradiation on the gas sensing property of NiO was investigated using Nd:YVO₄ laser with a wavelength of 532 nm in different power levels. After laser irradiation, the microstructure, crystallinity and conductivity of the thin films were changed. Results indicated that the irradiated sample with specific power showed better gas sensing performance for hydrogen. Also, the gas sensor response decreased using laser irradiation on the sample. As a result, laser irradiation is an additional tool for tuning the gas sensing behavior of nickel oxide gas sensor. Later, the nickel oxide film was tested for other reducing gases, such as CH₄, NH₃, and in a mixed gas environment at different operating temperatures. These measurements were conducted to study the selectivity of nickel oxide gas sensor. It was found that the NiO thin film showed a relatively high response to a low concentration of ammonia gas (25 ppm) at a relatively low operating temperature. Instead, the sample showed a relatively low response to methane gas compared to hydrogen and ammonia in the same concentration level. Besides, the gas response of the
device at different operating temperature was studied for reducing gases. The film showed a maximum sensitivity for methane and hydrogen gases at 175°C, and the highest response was recorded at 150°C for ammonia gas. These findings are valuable to design selective gas sensors. Finally, Pt decorated sample was tested for various concentrations of hydrogen gas at different operating temperature. The gas sensing property of the film was improved significantly due to the catalyst effect of Pt particles on the surface of metal oxide. Pt decorated sample increased the hydrogen sensing property of nickel oxide by decreasing the energy needed for splitting H₂ or O₂ molecules on the surface of metal oxide.

This study shows several important parameters for nickel oxide gas sensors and it is expected that these techniques can be used to improve the gas sensing performance of different metal oxide gas sensor devices in the future. Collected data at various operating temperatures and gas mixtures can be used to design more selective gas sensors. More detailed research is necessary to establish a general rule for other metal oxide thin films.
To my lovely parents and my supportive sister
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List of Abbreviations

°C.................................Celsius (temperature)
$\Delta H_{\text{chem}}$........Heat of adsorption - chemisorption
$\Delta H_{\text{phys}}$........Heat of adsorption - physisorption
A.................................Surface area
CH$_4$.............................Methane gas
d.................................Specific plane distance
D.................................Grain size
DC.................................Direct current
e.................................Electron
Ea.................................Activation energy
Ec.................................Energy of conduction band
EDAX............................Energy-dispersive X-ray spectroscopy
eV.................................Electron volt (energy)
FCC.................................Face centered cubic
Fe$_2$O$_3$........................Ferric oxide
FWHM............................Full width at half maximum
g.................................Gram
GID.................................Grazing incidence beam technique
GPIB.............................General purpose interface bus
H$_2$...............................Hydrogen
H$_2$O.............................Water
HCP...............................Hexagonal centered cubic
hr.................................Hour
I$_2$...............................Iodide
IR.................................Infra-red
ISI.................................International standard industrial classifications
K.................................Kelvin (temperature)
k.................................Plank's constant
KE.................................Kinetic energy
KI.................................Potassium iodide
kJ.................................Kilo joule
LEL...............................Low explosive limit
mA.................................Milli ampere
MFC...............................Mass flow controller
min...............................Minute
mm...............................Millimeter (distance)
MOGS............................Metal oxide gas sensor
MoO$_3$........................Molybdenium Oxide
mTorr........................Millitorr (pressure)
n..............................Integer
Nd:YVO$_4$....................Neodymium-doped yttrium orthovanadate
NH$_3$..........................Ammonia gas
Ni-Cr........................Nickel - chromium
NiO...........................Nickel oxide
nm............................Nanometer (distance)
NMOS..........................Nanostructured metal oxide gas sensor
NO$_2$..........................Nitric oxide (gas)
O$_2$............................Oxygen (gas)
Pd.............................Palladium
PLD............................Pulsed laser deposition
ppm............................Parts per million
Pt.............................Platinum
R...............................Resistance
RF.............................Radio frequency
RT.............................Room temperature
S..............................Response of sensor
s.............................Second (time)
S/V............................Surface to volume ratio
SCCM.........................Standard cubic centimeters per second (gas flow rate)
SEM............................Scanning electron microscope
Si.............................Silicon
SnO$_2$........................Tin oxide
TEM............................Transmission electron microscope
TGA............................Thermo gravimetric analysis
TLV............................Threshold limit value
Torr...........................Pressure
UHP............................Ultra high purity
UV............................Ultra violet
V.................................Voltage
Vap............................Vapor
Vis............................Visible
WO$_3$..........................Tungsten oxide
wt. %..........................Weight percent of total
XPS............................X-ray photoelectron spectroscopy
XRD............................X-ray diffraction
ZnO............................Zinc oxide
List of Symbols

θ...............................................Angle of incident
λ.............................................Wavelength
ν...............................X-ray frequency
τ..............................Transient time
Ω.cm..................Ohms times centimeter
Φ...............................Detector work function
Ψ..............................Psi
Δ...............................Delta
Chapter 1

Introduction

A chemical gas sensor is a device which detects various gases in different atmospheres with transforming chemical reactions to analytically detectable signal [1]. The gas sensors are usually a part of security or control systems, and are used to detect gas leakage or control the exhaust air. In particular, monitoring of explosive and hazardous gases in the air is important owing to an increase in usage of different gases in industries. Chemical sensors are classified according to their operational mechanics. However, the current commercial gas sensors suffer from severe limitations due to low sensitivity and high operating temperature [2-5]. Therefore, there is an urgent need to design a sensor with good sensitivity, stability and fast response at low cost. Metal oxides are a great candidate for gas sensor applications due to chemical stability and easy fabrication techniques. The dependence of oxide conductance on the gas environment results in their applications in gas sensor [6]. Nanocrystalline metal oxide thin films offering a combination of high response, fast response time for target gases which are beneficial for industrial applications [5, 7, 8].
Chapter one gives an overview of different gas sensing techniques which are available in the market. A detailed description about the gas sensing mechanisms and sensor characteristics, such as sensitivity, selectivity, and repeatability are provided. The most important parameters which control and affect sensor performance of the sensitive layer are reviewed. Finally, an overview of nickel oxide material, fabricating techniques, and literature review about NiO gas sensors are provided.

1.1 Optical Gas Sensing Method

Gas sensing using optical gas sensors has several advantages, such as good sensitivity, selectivity and reliability. Optical gas sensors have a long life compared to other detection methods. The general equipment consists of two main components: a light source and a detector. Usually the light source is an IR laser diode. The light source transmits light through gas environment towards the detector. Each gas absorbs light in a specific wavelength and this reduction in a light intensity can be related to the absorption of the light [9]. The exact wavelength for each specific gas can be found in online databases [10]. Due to non-contact detection mechanism of these sensors, the life cycle of these sensors is high. Due to different component requirements, such as IR light source, detector and filters, the installation expenses are high. Another drawback of these sensors is optics contamination over time [9]. Figure 1-1 shows a schematic diagram of the IR-based gas sensor.
1.2 **Acoustic Gas Sensing Method**

The acoustic based gas sensors have longer lifetime and are less dependent to environmental contamination in the system. Surface acoustic wave sensors consist of input and output transducer and piezoelectric material [9]. These sensors can be used to detect temperature, pressure, humidity and different target gases in the environment [11].

Figure 1-2 shows a schematic diagram of the surface acoustic wave sensor. A sensitive layer is coated between two input and output transducers. The input transducer makes a frequency and it can be received by the output transducer. During the gas exposure, gas molecules absorb on the sensitive layer, and the mass of sensitive layer changes, respectively [12]. Therefore, the output transducer measures the difference and calculate the gas concentration according to the calibration data.
Figure 1-2: A schematic diagram of surface acoustic wave sensor.

1.3 Electrochemical/Conductometric Sensing Methods

This set of sensors represents the majority of sensor family. There are three separate electrochemical groups which will be discussed separately in this section.

The potentiometric sensor consists of ion selective electrode, a reference electrode and electrolyte. Ion selective electrodes are selective for one specific ion. For example, glass electrode was announced in 1909 by Haber and was used to detect hydrogen ions [13]. These sensors have a good selectivity due to the nature of sensing mechanism, operating voltage and working temperature. The main disadvantage of this technique is using high voltage and temperature due to a low partial pressure of detectable gases such as H₂ [9, 13].

Amperometric sensors are commonly used to detect different analytes, such as gas components in the gas environment or liquid phase. Due to a high sensitivity and a low fabrication cost, these sensors are used in different applications such as safety
A typical amperometric sensor consists of electrolyte, counter electrode, reference electrode and working electrode. The working electrode positioned behind the gas diffusion barrier as shown in the Figure 1-3. The signal is detected due to the oxidation/reduction of target gas in contact with the working electrode. A constant bias is applied to the electrode to detect measurable change in the current flow caused by gas reaction. The sensitivity of the sensor depends on the diffusion rate of gas molecules into the sensor. Therefore, the response signal has a slight delay for the gas molecules to diffuse inside the diffusion barrier [15]. Therefore, disadvantages of these sensors are long response time and their complex design structure [9, 15].

![Figure 1-3: A schematic diagram of amperometric sensor.](image_url)

The conductometric semiconductor gas sensors are being used in a variety of different industries such as environmental monitoring, public security, automotive applications and air conditioning in public places. The electrical conductivity of these sensor changes as a function of reaction to different target gases. These sensors have several advantages such as low fabrication cost, high sensitivity, and good
reproducibility. It should be mentioned that these sensors are sensitive to humidity, operating temperature and cross sensitivity. The gas sensing performance of these sensors can be changed by altering substrates, thickness and operating temperatures. The common operating temperature of metal oxide gas sensors is in the range between 200 to 600°C. These MOGS have been extensively used to measure and monitor trace amounts of different gases such as H₂, NH₃, and CH₄ [16]. Metal oxide gas sensors have been considered as an alternative replacement for current expensive analytical techniques such as optical spectroscopy and gas chromatography as a result of low cost and high sensitivity to different gases [17, 18]. In the following section, more detailed information will be provided for metal oxide gas sensor devices.

1.4 Metal Oxide Gas Sensors

In the early 60s, the absorption and desorption of gas molecules on the surface of metal oxide semiconductor has been introduced, and first metal oxide gas sensor was announced to the market [16]. Metal oxide thin film such as ZnO and SnO₂ were introduced as gas sensing devices. Demands for these MOGS grew due to rises of applications over time [9, 19]. There are extensive research studies on different metal oxide gas sensor to improve three characteristics of the sensor: sensitivity, selectivity and stability even at low operating temperature. There are two types of semiconductor metal oxide; the majority of charge carriers in n-type and p-type semiconductors are holes and electrons, respectively. Due to different charge carrier type, metal oxide performs differently to reducing/oxidizing gases. Table 1.1 shows a typical behavior of both types of gas sensors.
Table 1.1: Different types of metal oxide semiconductor.

<table>
<thead>
<tr>
<th>Type</th>
<th>Carrier type</th>
<th>Oxidizing Gas</th>
<th>Reducing gas</th>
</tr>
</thead>
<tbody>
<tr>
<td>n-type</td>
<td>Electrons</td>
<td>Conductivity decreases</td>
<td>Conductivity increases</td>
</tr>
<tr>
<td>p-type</td>
<td>Holes</td>
<td>Conductivity increases</td>
<td>Conductivity decreases</td>
</tr>
</tbody>
</table>

In spite of extensive research, the effect of different fabricating parameters and post processing techniques on electrical, optical and gas sensing properties is still unclear for some metal oxide thin films. To design a high performance sensor, it is necessary to study the effective parameters on the gas sensing property of the sensor. Recently, advances in nanotechnology attracted more research studies in the field. Nanomaterials have a large surface to volume ratio; the high surface area provides a change in gas sensing properties of the material.

Korotcenkov and Fin et al reported several detailed overview studies for several metal oxide gas sensors [16, 20-22]. These articles present effective parameters which have an influence on the gas sensing properties of different n-type metal oxide gas sensors. Currently, there are extensive researches on different metal oxide gas sensors such as NiO, ZnO, Mn₂O₃, SnO₂, Fe₂O₃ and MoO₃ [16, 21-23]. Researchers have been studying different techniques such as doping, addition of noble metal to improve the selectivity and stability of metal oxide thin films [24]. The performance of different thin films can be optimized by altering the microstructure of thin film [25].

In this study, nickel oxide has been selected as a gas sensing material among other metal oxides that can be used for gas sensors. Figure 1-4 shows the number of citations with a keyword “Nickel Oxide” in the last 20 years. The number of citations has
increased enormously in recent years, implying an increase in the number of research studies in the field.

![Graph showing the number of citations with the keyword “nickel oxide” in the last 20 years.](image)

Figure 1-4: Number of citations with the keyword “nickel oxide” in the last 20 years, (ISA knowledge website).

Due to an increase in atmospheric pollution, there is a need to fabricate sensitive devices to detect and measure different hazardous gases. Currently, standard air pollution measurements are based on expensive optical spectroscopy and gas chromatography techniques. These techniques are large, expensive and slow in terms of reaction times [18, 26]. Therefore, there is an urgent need to design and fabricate cheap gas sensor devices to detect diverse explosive and toxic gases. Hydrogen and methane are odorless and colorless gases, which cannot be detected by human senses. Hydrogen concentration should be controlled in different applications such as hydration of hydrocarbon, desulphurization of petroleum products, nuclear reactors and turbine generators [26].
Methane concentration should be controlled in different industrial applications, due to the possibility of forming an explosive mixture in the air at levels as low as 5%. Ammonia is a colorless gas with a pungent odor. This gas is produced as a result of animal manure decomposition. This toxic gas has a threshold limit value of 25 ppm. Due to high atmospheric pollutions, detection of explosive gases, such as H$_2$, CH$_4$ and NH$_3$ is important for different industries. Table 1.2 shows the toxicity threshold limit value (TLV) and lower explosive/flammability limits (LEL) of several gases. It is shown that H$_2$ and CH$_4$ are non-toxic and have LEL of 15,000 and 40,000 ppm in a room temperature [27]. These values decrease by increasing the ambient temperature and atmospheric pressure. On the other hand, NH$_3$ has a TLV level of 25 ppm [18].

Table 1.2: The source of emission, toxicity and explosive/flammable limit value of gases.

<table>
<thead>
<tr>
<th>Gas</th>
<th>Source of emission</th>
<th>Toxicity/Threshold limit value (TLV)</th>
<th>Low explosive/ Flammable limit</th>
</tr>
</thead>
<tbody>
<tr>
<td>H$_2$</td>
<td>-</td>
<td>40,000 ppm</td>
<td></td>
</tr>
<tr>
<td>CH$_4$</td>
<td>Engines</td>
<td>-</td>
<td>1000-15,000 ppm</td>
</tr>
<tr>
<td>NH$_3$</td>
<td>Decomposition of animal manure</td>
<td>25 ppm</td>
<td>-</td>
</tr>
</tbody>
</table>

1.5 Gas Sensor Characteristics

In the following section, the gas sensing mechanism of metal oxide gas sensors will be discussed and several important characteristics of metal oxide gas sensor will be provided in detail.
1.5.1 Gas Sensing Mechanism

Gas molecules are in contact with metal oxide surface, they can adsorb with physisorption or chemisorption. Physisorption is a weak adsorption between adsorbate and adsorbent which the heat of adsorption is less than 6 kcal mol$^{-1}$. In the chemisorption process, the gas molecules interact more strongly with a solid atom and the heat of adsorption is greater than 15 kcal mol$^{-1}$. Figure 1-5 shows Lennard-Jones model for physisorption and chemisorption process. It can be seen that the heat of adsorption $\Delta H_{\text{phys}}$ is relatively smaller than $\Delta H_{\text{chem}}$. It should be noted that the heat of chemisorption is comparable to a heat of compound formation [29].

![Figure 1-5: Lennard- Jones Model for physisorption and chemisorption](image)

The sensing mechanism of metal oxide gas sensors can be explained by the adsorption of oxygen on the surface of metal oxide grains and its reaction with H$_2$ gas molecules. Semiconductor oxides such as ZnO and NiO are insulator in a stoichiometry ratio, and their non-stoichiometry semiconducting behavior attributed to the percentage of Ni$^{+2}$ vacancies in NiO or excess O$^{2-}$ ions in ZnO of the prepared sample [31, 32].
Figure 1-6 (a) shows a schematic diagram of band bending after chemisorption of oxygen ions on the surface of grain. Adsorbed ions are responsible for a change in conductivity. The negative charged ions are responsible for absorbing electrons and upward band bending around the edge of the grain. By absorbing oxygen molecules on the surface of metal oxide, they extract electrons from the conduction band Ec and electrons trap at the surface in form of ions. This mechanism causes a band bending and the electron depleted region near the surface of each grain [22, 33].

During the adsorption process at elevated temperatures, different oxygen species are formed on the surface of NiO as $O_2^-$ and $O^-$ [34]. The reaction summaries of adsorbed oxygen on the surface of NiO are listed below:

\begin{align*}
O_{2(\text{Gas})} & \rightarrow O_{2(\text{Adsorbed})} \quad \text{(1.1)} \\
O_{2(\text{Adsorbed})} + \bar{e} & \leftrightarrow O_2^- \quad \text{(1.2)} \\
O_{2(\text{Adsorbed})} + 2\bar{e} & \leftrightarrow 2O^- \quad \text{(1.3)}
\end{align*}

When oxygen species are adsorbed on the surface of NiO grains, they act as a surface acceptor and force electrons to be removed from the lattice. Further reaction of these adsorbed oxygen ions with reducing gases causes a decrease in band bending and changes the conductivity of grain.
Figure 1-6: (a) A schematic diagram of the band bending after chemisorption of charged species [23] on n-type metal oxide (b) A schematic diagram of gas sensing mechanism on the surface of metal oxide.

By introducing H$_2$ gas molecules, the electrical conductivity of film changes due to the surface reactions at the grains. The reaction summary can be expressed by:

$$H_2 + O^{-}_{\text{adsorbed}} \rightarrow H_2O_{(\text{vap})} + e^-$$  \hspace{1cm} (1.4)

The H$_2$ molecules react with adsorbed oxygen ions and form water vapor, and as a result of this reaction, electron transfer back to the film according to the reaction [35]. Therefore, the transfer of electrons to the conduction band of semiconductor changes the conductivity of the film. For p-type semiconductor, the transfer of electrons to the
conduction band makes the semiconductor less p-type, and the film resistance increases, respectively (Figure 1-6 (b)). On the other hand, for n-type semiconductor material, the resistance decreases with increasing the number of electrons in the film.

As described in the previous section, metal oxide gas sensors show a change in a resistance in contact with different target gases at different operating temperatures. To characterize and compare sensor performance, a set of parameters should be defined for each sensor. The most important sensor's characteristics and requirements are described below.

1.5.2 Sensor Response

The gas sensing property of the sensor is measured by collecting a change in resistance over two sensing electrodes under various gas concentrations. The change in the sensor resistance is attributed to ion adsorption of gas molecules, surface reaction of target gas with adsorbed oxygen on the surface of metal oxide [36]. The sensor response in percentage, S, is defined as the ratio of resistance change by introducing target gas in the air [5].

\[
S = \left( \frac{R_{\text{gas}} - R_{\text{air}}}{R_{\text{air}}} \right) \times 100
\]

(1.5)

where, \(R_{\text{gas}}\) and \(R_{\text{air}}\) are the resistance values of the sensor during gas exposure and air, respectively.
1.5.3 Response and Recovery Times

Response and recovery times are two main characteristic parameters for different target gases. Response and recovery times are time constant, which sensor needs to change to 63% of its original value.

1.5.4 Selectivity

Cross sensitivity refers to a behavior of a sensor in a mixed gas environment. This is an important characteristic to detect specific gas. Metal oxide gas sensors are sensitive to different gases, and this behavior makes the selectivity of the sensor a big challenge. There are different techniques to improve the selectivity of metal oxide gas sensors. For example, sensor response and recovery times can be compared as an effective parameters to detect different target gases. Also, filters can be used to make the sensor more selective in different applications [37]. For instance, SiO$_2$ layer on top of the sensor selectively allows H$_2$ molecules to diffuse through the layer [9].

1.5.5 Repeatability

In an industrial application, the sensor repeatability is important. This property is vital for commercialized products, which need to work for several thousands of cycles in ambient conditions [38]. The sensor has to show reproducible data for a certain period of time. Degradation of sensor performance can be caused due to a polluted sensing environment or changes in the microstructure at high working temperature.
1.6 Surface Modification

Semiconductor metal oxides have been used extensively for detection of different gases at high temperatures [23]. There are several parameters which affect the performance of the sensor such as adsorption, catalytic ability and thermodynamic stability. Figure 1-7 shows different diffusion mechanisms in bulk and inter-grain conditions.

Figure 1-7: Different parameters during the gas sensing behavior of metal oxide gas sensor [22].
Metal oxide thin films are fabricated by dry/wet techniques. The microstructure of fabricated thin film is closely associated to the fabrication process. By altering deposition parameters, the microstructure changes and the gas sensing performance of film changes respectively. Grain size and porosity are two important parameters for metal oxide gas sensors [21, 22]. In a porous sample, the whole volume of the film is accessible by target gas. A higher porosity means higher surface to area ratio and more exposed surface to interact with target gas. Figure 1-8 shows a schematic diagram of the porosity effect on the gas penetrability. It can be seen that porous material has higher volume accessibility to gas molecules compared to the dense sample which has a small portion of gas permeability.

Figure 1-8: A comparison of gas penetrability for porous and dense sample [22].
It has been reported that the selectivity of the sensor can be improved by controlling the porosity. Lower oxygen partial pressure in dense coatings, leads to a decrease in oxygen partial pressure and increase sensitivity towards H$_2$[39].

The grain size has an important effect on the gas sensing performance of MOGS. By decreasing the grain size, the surface to volume area increases and the exposed area will be increased which is beneficial for the gas molecules to react with the surface of the grains. Moreover, the shape and faceting of different metal oxide has an effect on the gas sensing performance of the device. Recently, several reports have been published on the influence of film shape and texture on the gas sensing performance of film. Batzill reported different surface energies for different series of planes (SnO$_2$) [40]. Golovanov et al reported variation of surface reaction with water in different SnO$_2$ crystallographic planes [41]. Kohl showed that the hydrogen molecules cannot be activated on smooth SnO$_2$ surfaces [42]. In another study, It was reported that highly oriented ZnO thin films have lower resistance [43]. Therefore, this understanding leads to an interesting research area to detect specific gas molecules and improve the selectivity of the device.

Noble metals such as Pt and Pd, are used as active catalysts. These noble metals enhance the reaction between target gas (especially hydrogen) and oxygen molecules [1]. Spill over is a term, which is used to describe the diffusion of adsorbed species from an active site (noble metal) to a non-active site. Catalysts are mostly island type on top of metal oxide thin film. These sites, enhance the speed of molecule dissociation [44]. It has been reported that noble atoms decrease the energy needed to split H$_2$ or O$_2$ atoms on the surface of metal oxide thin films [45]. Figure 1-9 shows a schematic diagram of hydrogen and oxygen adsorption at the catalyst particle.
Modification of metal oxide thin films by post processing techniques, such as light irradiation, has been reported to improve different properties of thin films [3, 7]. It has been reported that laser irradiation can be used to change the surface structure of metal oxide thin film and to increase sensor response [46]. Several appropriate uses of laser technique have been introduced, such as using a constant or pulsed wave laser with a different wavelength to get a desired property (Figure 1-10). Zhang et al. reported an improvement for WO$_3$ thin films in gas sensor response for NO$_2$ gas [46].

Figure 1-9: A schematic diagram of spill over process at the surface of nickel oxide.

Figure 1-10: A schematic diagram of laser irradiation for metal oxide thin film.
1.7 Nickel Oxide

1.7.1 General Properties

In this section, properties of nickel oxide material such as crystallographic structure, phase diagram, defect chemistry and basic properties will be discussed. Later, different fabrication techniques will be reviewed and a sol-gel method will be discussed in more detail. Finally, a literature review will be presented to clarify the current state of the art in nickel oxide gas sensor.

NiO is a remarkable p-type semiconductor with a wide band gap of 3.6-4.0 eV [47]. NiO is a promising material for different applications, such as solar thermal absorber [48], fuel cells [49], electro-chromic display devices and gas sensors [50]. Table 1.3 shows general properties of nickel oxide.

Figure 1-11 shows the atomic structure of nickel oxide crystals. Figure 1-12 shows the phase diagram of a Ni-O binary system. The stable crystal structure of nickel oxide at a high temperature is polymorph bunsenite. By cooling the crystal, the crystal structure converts to rhombohedral. It should be noted that these crystal structures form during thermodynamically stable transitions. Different fabrication techniques produce a non-stoichiometric structure, such as simple cubic in a room temperature [51].
Table 1.3: Properties of nickel oxide.

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Formula</td>
<td>NiO</td>
</tr>
<tr>
<td>Crystal structure</td>
<td>Rock salt (Octahedral)</td>
</tr>
<tr>
<td>Electron configuration</td>
<td>3d$^8$</td>
</tr>
<tr>
<td>Cation</td>
<td>Ni$^{++}$</td>
</tr>
<tr>
<td>Binding energy (O$_{1s}$)</td>
<td>530 eV</td>
</tr>
<tr>
<td>Optical basicity</td>
<td>0.915</td>
</tr>
<tr>
<td>Oxide ion polarizability</td>
<td>High</td>
</tr>
<tr>
<td>Molar mass</td>
<td>74.6928 g/mol</td>
</tr>
<tr>
<td>Density</td>
<td>6.67 g/cm$^3$</td>
</tr>
<tr>
<td>Melting point</td>
<td>1957°C</td>
</tr>
<tr>
<td>$\Delta H_f$ for metal oxide formation per oxygen atom @ 298 K</td>
<td>245.2 kJ/mol</td>
</tr>
<tr>
<td>Bandgap</td>
<td>2.0-4.3 eV</td>
</tr>
<tr>
<td>Type of conductivity</td>
<td>P-type</td>
</tr>
<tr>
<td>Resistance</td>
<td>$10^9$-$10^{11}$ ohm.m$^{-1}$</td>
</tr>
<tr>
<td>Dielectric constant</td>
<td>10</td>
</tr>
<tr>
<td>Coefficient of refraction</td>
<td>2.23</td>
</tr>
<tr>
<td>Refractive index (n$_D$)</td>
<td>2.18</td>
</tr>
</tbody>
</table>

Figure 1-11: Simple cubic structure of NiO [52].
Crystalline solids show a periodic atom in a crystal structure. A perfect stoichiometric metal oxide is an insulator and by introducing different defects inside the crystal, the electrical, optical and mechanical property of the oxide changes, respectively. There are different categories of defects inside the crystal such as: point, line, planar and bulk defects. Point defects are common in different crystals due to a small size of impurity atoms in a pure material. Interstitial, substitutional atoms and vacancies are common examples of point defects in a crystal structure. Figure 1-13 shows different point defects in a crystal structure.
Dislocations (edge, screw or mixed) are examples of line defects. Planar defects can be categorized into grain boundaries and stacking faults. The grain boundaries occur when different crystallographic planes reach together. The stacking fault structure is common in closed packed structures such as FCC and HCP, and is caused by misalignment of several layers of atoms in a preferred orientation. The properties of a sample can be altered by changing the number of defects in the crystal. Fabrication process, the annealing temperature and percentage of impurities have strong effects on the properties of the fabricated film [53].

1.7.2 Review of Fabricating Techniques

Nickel oxide thin films are fabricated using different techniques. Common fabrication methods are RF sputtering, pulsed laser deposition, electrochemical deposition, spray pyrolysis and sol-gel [54]. Other methods such as flame fusion, arc image furnace floating zone, plasma torch and solar furnace melting are not suitable to fabricate NiO films in nanometer thicknesses [55].

Sputtering and pulsed laser deposition techniques are used to fabricate large scale high quality thin film, although these techniques are expensive. In the literature,
Steinebach et al. and Masahiko et al. deposited NiO using a sputtering technique using NiO target on silica and alumina substrates [28, 56]. When the substrate temperature and atmospheric pressure (oxygen and argon) were changed, nickel oxide films exhibited different electrical, optical and gas sensing performance. In another study, Brilis et al. fabricated nickel oxide films using pulsed laser deposition on Si (001) substrate. It was shown that the film had 40% sensitivity towards 30,000 ppm of hydrogen gas at 210°C. Cantalini et al. used a sol-gel technique to fabricate nickel oxide thin film using NiCl₂·6H₂O and thermal annealing at 700°C. The sensor response towards H₂ and CO gases in dry air and different temperatures were investigated [57].

The sol-gel technique is a versatile process to fabricate ceramics, organic and non-organic nanomaterials. This process gained much more attention due to its simplicity, low operating temperature, excellent control on a stoichiometry of precursor and ability to produce uniform, homogeneous coatings over a large area [58]. The first patent based on sol-gel technique was issued in 1930 for dip coating of silicate film [59]. The sol-gel process involves a transition of solution to a gel phase. The precursor is deposited on a substrate using dip coating, roll coating and spray coating techniques. Spin coating is more common due to its application in the fabrication of thin films. Spin coating consists of pouring precursor on the substrate, and aggressive fluid removal by a centrifugal rotation [60]. Removal of the remaining liquid is called the drying process, which is used to evaporate the remaining solvent. Afterwards, it is necessary to use the annealing process to obtain the final crystal structure. The properties of the film strongly depend on the deposition parameters such as solution concentration, thickness and preheating/annealing temperatures [61, 62].
1.7.3 Review of NiO Gas Sensor

There are extensive studies on optical/electrical properties of NiO in the literature [63-68]. There are few studies on the gas sensing property of NiO [2, 3, 28, 32, 69, 70]. Table 1.4 shows a literature review of different fabricated NiO thin films which are used for gas sensor application.
Table 1.4: Comparison of different NiO gas sensors.

<table>
<thead>
<tr>
<th>Method</th>
<th>Material</th>
<th>Target gas</th>
<th>Concentration (ppm)</th>
<th>Temperature °C</th>
<th>Response</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrothermal process [71]</td>
<td>NiO - Nanowire</td>
<td>Toluene, methanol</td>
<td>~ 10-1,000</td>
<td>350</td>
<td>1-7%</td>
</tr>
<tr>
<td>DC magnetron sputtering [72]</td>
<td>NiO</td>
<td>NO₂</td>
<td>1-10</td>
<td>160</td>
<td>1-3%</td>
</tr>
<tr>
<td>Sonochemical synthesis [73]</td>
<td>NiO</td>
<td>CO</td>
<td>100</td>
<td>200</td>
<td>1%</td>
</tr>
<tr>
<td>RF sputtering [28]</td>
<td>NiO</td>
<td>H₂</td>
<td>5,000</td>
<td>600</td>
<td>55%</td>
</tr>
<tr>
<td>Citrate-gel [2]</td>
<td>Li, Ti doped</td>
<td>Chloroform, toluene</td>
<td>1,000</td>
<td>RT</td>
<td>~ 4-10%</td>
</tr>
<tr>
<td>Pulsed laser deposition [50]</td>
<td>NiO</td>
<td>H₂</td>
<td>30,000</td>
<td>80</td>
<td>12-14%</td>
</tr>
<tr>
<td>Pulsed laser deposition [74]</td>
<td>NiO</td>
<td>H₂</td>
<td>30,000</td>
<td>210</td>
<td>40%</td>
</tr>
<tr>
<td>Sol-gel [57]</td>
<td>SiO₂-NiO</td>
<td>H₂</td>
<td>850</td>
<td>300</td>
<td>~9</td>
</tr>
<tr>
<td>Magnetron sputtering [32]</td>
<td>NiO + Pt</td>
<td>H₂</td>
<td>1,000-5,000</td>
<td>320</td>
<td>5-45%</td>
</tr>
<tr>
<td>RF Sputtering [69]</td>
<td>Li doped NiO</td>
<td>H₂</td>
<td>30,000</td>
<td>RT</td>
<td>~ 0.2</td>
</tr>
<tr>
<td>Magnetron Sputtering [75]</td>
<td>TiO₂-NiO</td>
<td>H₂</td>
<td>500</td>
<td>250</td>
<td>~5-25</td>
</tr>
<tr>
<td>Magnetron sputtering [3]</td>
<td>NiO</td>
<td>NH₃</td>
<td>50,000</td>
<td>350</td>
<td>~2</td>
</tr>
</tbody>
</table>

Notes: 
- R = R<sub>g</sub>/R<sub>a</sub>
- (∆V<sub>s</sub>)
Chapter 2

Experimental and Electronic Properties of Nickel Oxide Thin Film

2.1 Introduction

This chapter provides experimental details and characterization techniques which were used in this study. The first section describes the sample preparation procedure. In the second part, different characterization techniques are discussed in detail. The surface characterization techniques are X-ray diffraction (XRD), scanning electron microscope (SEM), transmission electron microscope (TEM), energy dispersive X-ray spectroscopy (EDAX), X-ray photoelectron spectroscopy (XPS). In addition, the electronic, optical and gas sensing properties of nickel oxide thin film are presented in detail.

2.2 Sample Preparation

NiO thin films were deposited by a sol-gel processing method. The coating solution was prepared by dissolving 0.1 M nickel nitride hexahydrate \([\text{Ni(NO}_3\text{)}_2\cdot6\text{H}_2\text{O}]\) into 20 ml of equal amount of isopropanol alcohol and polyethylene glycol 200
[H(OCH₂CH₂)ₙOH]. The solution was stirred at 25°C for one hour to yield a transparent solution. Nickel hydroxide particles were produced in the solution by adding dilute ammonium hydroxide [NH₄OH] drop wise to the solution under magnetic stirring. In order to reduce the particle agglomeration, several drops of Triton X-100 were added to the solution to decrease surface tension and eliminate particle clustering. Finally, the solution was stirred for one hour, and the final solution was used for the spin coating step.

The NiO thin films were coated on alkali free glass substrates (2×2 cm²), which were cleaned with acetone and distilled water to remove any contaminated organic compounds. Then, the films were coated by using the spin-coating process. The prepared films were preheated at 350°C for 5 minutes to remove solvents after the coating of each layer. This coating process was repeated to get the desired thickness of NiO film. Then, the samples were annealed at 550°C for three hours to obtain desired structure. Figure 2-1 shows a schematic diagram of the coating procedure.

![A schematic diagram of coating procedure.](image)
The microstructure, electrical and optical properties of nickel oxide thin films were evaluated using different characterization techniques such as TGA, XRD, XPS, SEM, TEM, EDAX, UV-vis spectrophotometer and a custom build gas sensor system. A brief introduction for each characterization technique will be provided in the following section.

2.3 Thermal Gravimetric Analysis

Thermogravimetric analysis (TGA) has been carried out for as-synthesized precursor in the air using a thermogravimetric analyzer (TA Instruments Q50) at a constant rate of 4°C/min. This analysis examined the conversion process during calcinations. Figure 2-2 shows the plot of wt.% vs. temperature for precursor used in this study. Thermo gravimetric analysis was studied to understand the different stages of weight loss in a wide temperature range to select the best preheating and annealing temperature for the deposited film. The weight of the container has been monitored by placing it in a furnace and monitoring the weight (accuracy 0.1 µgr) up to 550°C with an increasing temperature rate of 4°C/min. The process depicts weight loss in three different stages up to 550°C. The overall weight loss up to 100°C (i.e., point B) is 20% which represents the weight loss of the sample due to the evaporation of isopropanol alcohol. The substantial weight loss at 160°C is due to the decomposition of polyethylene glycol 200 [76]. By further increasing of the temperature, nickel nitride and hydroxide compounds started to decompose at 320°C (i.e., point D), and total weight loss of 4 % was observed in this transition. According to the literature, polyethylene glycol 200 and nickel nitrate, start to decompose around 160°C and 350°C, respectively [76, 77], which are in an agreement with our experimental. According to our
findings, appropriate preheating and annealing temperature of 350 and 550°C were selected for this study [78].

Figure 2-2: Weight (%) vs temperature plot of the obtained precursor; the temperature is raised at the rate of 4°C/min in the air.

2.4 X-ray Diffraction

The crystal structure of NiO thin films was identified with X-ray diffractometer (XRD, PANalytical). The grazing incidence beam technique (GID) was used by a chromatized Cu Kα radiation using 40 mA and 45 kV in different two theta ranges with a low incident angle of 0.5°. The duel time and step size were varied to get the desired diffraction technique. Figure 2-3 shows a schematic diagram of the X-ray diffraction principle. Figure 2-4 shows the XRD spectra of NiO thin film deposited on alkali free glass substrate. In the XRD pattern, peaks appeared corresponding to (200), (111) and (220) planes of the NiO thin film. The XRD pattern indicated that the film had a
polycrystalline structure. The diffraction pattern depends on the orientation of the crystal lattice. Bragg’s law is used to calculate a specific distance (d-spacing): 

\[ 2d \sin \theta = n\lambda \]  

(2.1)

where, d, θ, n and λ are specific plane distance, angle of the incident beam, the integer and the wavelength. The average grain size is calculated using the well-known Scherer formula:

\[ D = \frac{0.9\lambda}{\beta \cdot \cos \theta} \]  

(2.2)

where λ, β and θ are wavelength of X-ray beam, full width at half maximum (FWHM), and diffraction angle, respectively.

Figure 2-3: A schematic diagram of X ray diffraction [79].
2.5 Scanning Electron Microscope

The surface morphology of NiO films was characterized using a scanning electron microscope (SEM, Hitachi S-4800). The SEM uses a highly focused electron beam to generate a variety of signals from the surface of the sample. The reflected electrons form an image as a result of using a software program. SEM provides rapid, high quality images with a large magnification (~300,000 ×). SEM machines are able to provide spot chemical analysis (EDAX) and compositional trace element mapping.

2.6 Transmission Electron Microscope

The crystallographic planes of samples can be characterized using a transmission electron microscope. A TEM technique uses a beam of electrons through an ultra-thin
sample to produce the image. The image forms due to the interaction of transmitting electrons with specimen’s atoms. In addition, TEM is capable of providing electron diffraction data which can be used to verify preferred crystallographic orientations in the fabricated sample. The samples were characterized using Tecnai F20. Figure 2-5 shows SEM and TEM and diffraction patterns of fabricated NiO thin films.

Figure 2-5: SEM and TEM images NiO film, (a) SEM image (b), (c) TEM images with different magnification, and (d) electron diffraction pattern of film.
2.7 X-ray Photoelectron Spectroscopy

The analysis of chemical binding energy was performed on the surface of the samples using X-ray photoelectron spectroscopy (XPS, Kratos Axis Ultra XPS) with Al Kα at 1486.6 eV and base vacuum of $2 \times 10^{-10}$ mbar. Corrections of energy shift, due to the steady state charging were made by assigning 284.6 eV binding energy to the C 1s peak [80]. It should be noted that each element has a specific binding energy. This energy is calculated using the following equation:

$$E = h\nu - KE - \Phi$$

(2.3)

where $h$, $\nu$, $KE$ and $\Phi$ stand for Planck’s constant, X-ray frequency, kinetic energy and detector work function [9]. Figure 2-6 shows the XPS analysis of as deposited NiO thin film.

![Figure 2-6: XPS spectra of NiO film (Picture in inset shows XPS spectra in the Ni 2p$_{3/2}$ range).](image-url)
2.8 Optical Properties

The optical properties of the films were measured with a double beam UV/Visible spectrophotometer (UV-1650 PC Shimadzu) in the range of 250-1050 nm. Figure 2-7 shows the optical transmittance spectra of the NiO films coated on the alkali free glass substrates. The sample exhibited transmittance larger than 65% in the visible and near IR range. The samples has an absorption edge in the 300-380 nm range. The optical gap of the film was calculated as 3.6 eV, respectively. The intrinsic band gap of NiO has been reported to be around 3.7 eV, which is very close to our measured data [63, 82, 83].

Fresnel approach was employed to theoretically estimate the optical properties and the thickness of the film [84]. A program was developed using Matlab software to theoretically estimate the refractive indices and the thickness of the NiO film based on the experimental values of the reflectance data from bi-layer (NiO/glass) substrate.

Figure 2-7: Optical transmission spectra of NiO fabricated on alkali free glass.
2.9 Ellipsometry Measurements

Spectroscopic ellipsometry measures two parameters ($\psi$ and $\Delta$) at each wavelength that are related to optical properties of the entire sample. Consequently, each of the ellipsometry spectra was fitted using a Levenberg-Marquardt regression algorithm, representing each sample with a two-layer model (i.e., Glass substrate and NiO layer). The dispersion of the index of refraction for each sample was represented using a parametric function of wavelength (i.e., Cauchy relationship). The extinction coefficient was set to zero for all models. Once the dispersion of the index of refraction was found for the film, an effective medium approximation was used to deduce the porosity [85].

Figure 2-8 (a) and (b) show $\psi$ and $\Delta$ spectra obtained for the sample at two different angles of incidence. The solid lines represent the fitting results obtained from the studied models. Once a good fit was calculated from the data, the dispersion of the index of refraction was automatically obtained through the Cauchy relationship. Subsequently, the porosity of each NiO film was calculated using an effective medium approximation [86].
Figure 2-8: Experimental and fitted ellipsometry data for NiO thin films (a) Psi (Ψ) v wavelength and (b) Delta (Δ) v wavelength.
2.10 Electrical Properties

The electrical properties of the samples were measured by collecting data over the electrodes in the temperature range of 25-250°C under vacuum conditions (30 mTorr). The conductivity varies with temperature in a classical Arrhenius form [31],

$$\sigma = \sigma_0 \times \exp\left(\frac{E_a}{kT}\right)$$  \hspace{1cm} (2.4)

where $\sigma_0$, $E_a$ and $k$ are conductivity at high temperature, activation energy and Boltzmann constant, respectively [87].

Figure 2-9 shows the change of resistance as a function of temperature for NiO films in the range of 25-300°C. The results indicated that the change of resistance with temperature had a typical Arrhenius behaviour. Generally, the resistivity of the film can be affected by an isotropic background scattering due to external surface and grain boundaries [82]. The fitted line in the picture can be converted to an activation energy using the Arrhenius equation [88]. The activation energies of sample were close to 0.22 eV. Pure stoichiometric NiO crystal is a perfect insulator; however, considerably high electrical conductivity can be achieved by increasing the number of defects in the crystal [88-90]. As mentioned earlier, the polycrystalline NiO exhibits p-type conductivity due to metal cation deficiency [3]. When the films are heated at a high temperature, the resistances of the films increase. It is important to note that the electrical property of NiO thin film strongly depends on the defects in the crystals such as interstitial defects and vacancies [91].
2.11 Lithography Process

The metal electrodes were fabricated by a photolithography process on the surface of a metal oxide semiconductor to measure electrical and gas sensing properties of the sample. Figure 2-10 shows the basic procedure for the photolithography process. At the first stage, the sample was covered with a photoresist (Microposit S1811, positive photoresist) using a spin coating technique. The spin coating process resulted in a uniform thin layer. Then, the coated sample was preheated at 70°C for 10 minutes in an oven. After the prebaking process, the photoresist was exposed to intense direct light. Then, developer chemical (MF-319) was used to remove the photoresist which was exposed to the light. Next, the sample baked at 80°C for 15 min to make a durable protective layer for a chemical etching process. In the etching process, the sample was suspended in the etching solution for a specific time to remove unwanted gold coating.
Finally, the photoresist was removed from the sample using a chemical solution (Acetone).

Figure 2-10: A schematic diagram of Lithography procedure.

2.12 Gas Sensing Measurements

In order to fabricate a sensor device, a thin layer of gold was coated on NiO films by a vacuum evaporation method. The electrodes were fabricated by a photolithography process and etching of gold with KI/I$_2$ solution. The samples were installed into a custom build Pyrex chamber (200 cm$^3$) with tungsten connecting electrodes, with inlet and outlet connectors to allow gas passage above the sample. Mass flow controllers were used to control desired gas concentrations into the chamber with digital displays. A constant flow of dry air (100 sccm) was kept constant for all tests during the experiments. Ultra high pure H$_2$, NH$_3$ and CH$_4$ were regulated by varying mass flow meters in different
concentration ranges. The experimental setup was designed to mix gases completely before inserting them into the chamber. The samples were placed on a resistive heater coupled with a DC power supply while the temperature was set to a desired temperature. A Ni-Cr thermocouple was used to monitor temperature variations of the sample. The gas sensors were tested by measuring the resistance between two gold electrodes using a high mega ohm Multimeter (Keithly-1200). The resistance of samples was collected in 1s time intervals and plotted using LabView software during the gas sensing experiment. Figure 2-11 shows the sensor testing station used throughout this research.

![Figure 2-11: A schematic diagram of NiO sensor testing instrumentations.](image)

Figure 2-12 (a) shows the dynamic response of the NiO sample for 1000-3000 ppm of H\textsubscript{2} at 175°C. The dependence of the sensor response was linear for low H\textsubscript{2} concentrations; however, and it can be seen that the sensor can be used to detect gas molecules quantitatively. Repeatability determines suitability of the gas sensor for practical applications [28, 92]. Figure 2-12 (b) shows the repeatability of the NiO sample.
for 3000 ppm of H₂ gas at 175°C. No significant change was observed after different cycles. It was found that the response and recovery times were almost constant for each cycle. A small deviation can be attributed to a small error in inserting target gases using mass flow meters.

![Graph](image1)

![Graph](image2)

Figure 2-12: (a) Dynamic response of NiO device to 1000-3000 ppm H₂ gas at 175°C and (b) Repeatability data for 3000 ppm of H₂ at 175°C.
Chapter 3

Fabrication of Porous Nickel Oxide Samples: The Effect of Fabricating Process, Operating Temperature, and Thickness

3.1 Introduction

The applications of nanocrystalline metal oxide in gas sensors have attracted much attention due to their high sensitivity, fast response and low operation temperature [5, 50, 69, 74, 93]. The working principal of metal oxide gas sensor (MOGS) is associated with a change of electrical conductivity due to adsorption/desorption of target gas in an ambient condition. Many materials have been investigated for MOGS applications [3, 5, 50, 73, 74, 93]. It is known that the gas sensing behavior of MOGS is related to the microstructure of thin films. Several approaches have been studied to improve the gas sensing behavior of different metal oxides such as ZnO and SnO$_2$ [21, 94-96]. Imawan et al. reported a low response value of 10% for 500 ppm of H$_2$ gas at different operating temperature of 200-500$^\circ$C for TiO$_2$ modified NiO film [75]. Fasaki et al. reported a gas response of 50% under 10,000 ppm of H$_2$ at 400$^\circ$C for a PLD grown NiO samples [97]. Recently, Steinebach et al. reported response values of 96.6% under
5000 ppm of H$_2$ at a high operating temperature of 500$^\circ$C for NiO thin films deposited by a sputtering method [28]. In a practical viewpoint, low operation temperature of H$_2$ sensor is required to use a sensor in the ambient conditions due to explosive and flammable nature of H$_2$ at an elevated temperature. Thus, a need for a gas sensor that can be operated at a relatively low operating temperature (<200$^\circ$C) with high sensitivity as well as fast response and recovery process is needed. It is known that MOGSs are mostly non selective for different gases. Various techniques have been used to improve the sensitivity and selectivity of sensor devices such as using filters, and catalysts [98]. Moreover, in a real application, humidity has an adverse effect on the gas sensing property of the device. Though numerous investigations have been carried out, there is only limited information about the selectivity and reliability issues of gas sensor.

NiO thin films were fabricated by a sol-gel method with special efforts to change the porosity of the coated films by a multi-step coating and subsequent annealing processes. Hydrogen sensing properties of nanocrystalline NiO thin films were investigated.

In order to enhance the sensor properties, porosity was increased by using a multi-step annealing during the calcination process. The samples were characterized for structural, electrical and optical properties. Moreover, the effects of operating temperature, humidity, thickness, grain size and porosity on the H$_2$ sensing property of NiO thin films were investigated. Also, the cross sensitivity measurements showed that the sensor could be used to monitor a target gas in a mixed gas environment.
3.2 Experimental Procedure

NiO thin films were deposited with a sol-gel process. The coating solution was prepared by dissolving 0.1 M nickel nitride hexahydrate \([\text{Ni(NO}_3\text{)}_2\cdot6\text{H}_2\text{O}, \text{Alfa}\]) into 20 ml of equal amount of isopropanol alcohol and polyethylene glycol 200 \([\text{H(OCH}_2\text{CH}_2\text{)}_n\text{OH}].\) The solution was stirred at 25°C for 2 hours to yield a transparent solution. Nickel hydroxide colloid was produced in a solution by adding dilute ammonium hydroxide \([\text{NH}_4\text{OH}].\) drop wise to the solution under magnetic stirring. In order to reduce particle agglomeration, several drops of Triton X-100 \((\text{C}_{14}\text{H}_{22}\text{O}(\text{C}_2\text{H}_4\text{O})_n).\) were added to the solution to decrease the surface tension and agglomeration of NiO particles. Triton X-100 is a surfactant compound which can be used to decrease the surface tension between two liquids, or a liquid and a solid [99]. Then, the solution was stirred for one hour before a spin coating step. The NiO thin films were coated on alkali free glass substrates \((2\times2 \text{ cm}^2),\) which were cleaned with acetone to remove any contaminated organic compounds. Then, the films were coated by the spin-coating process at a rotation speed of 1500 rpm for 30 s. The prepared films were preheated at 350°C for 5 min to remove solvents after coating of each layer. This coating process was repeated to get a desired thickness for NiO films.

Two different methods were used to fabricate samples as shown in Figure 3-1. In method-I, the samples were annealed at 550°C for 3 hours after coating all layers \((\text{N series})\) whereas in method II, the samples were annealed at 550°C after coating each layer \((\text{P series}).\) Method II was repeated for 2, 4 and 6 times to produce samples with different thicknesses. Table 3.1 shows our experimental conditions for the prepared NiO samples.
The crystal structure of NiO thin films was studied using a X-ray diffractometer (XRD, PANalytical). The grazing incidence beam technique (GID) was used with a chromatized Cu Kα radiation using 40 mA and 45 kV in the range between 35° and 45° with a low incident angle of 0.9°. The surface morphology of NiO films was characterized by a scanning electron microscope (SEM, Hitachi S-4800). The electrical properties of samples were investigated by measuring the resistance change over the electrodes in the temperature range of 25-250°C under vacuum conditions (30 mTorr). The optical properties of films were measured with a double beam UV/Visible spectrophotometer (UV-1650 PC Shimadzu) in the range of 250-1050 nm. Fresnel approach was employed to theoretically estimate the optical properties and the thickness of the sample [84]. A program developed using Matlab software to theoretically estimate the refractive indices and the thickness of NiO film based on the experimental values of the reflectance data from bi-layer (NiO/glass) substrate. The value of the thickness for P-2L sample was estimated to be 16 nm. Similar measurements were performed for all other samples. The values of the thicknesses are listed in Table 3.1.

Table 3.1: Sample numbering according to the fabricating method.

<table>
<thead>
<tr>
<th>Sample Name</th>
<th>Number of layers</th>
<th>Method</th>
<th>E_a</th>
<th>R (kΩ) at 100°C</th>
<th>Thickness (nm)</th>
<th>Surface Area (m²/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>N-2L</td>
<td>2</td>
<td>I</td>
<td>0.37</td>
<td>754</td>
<td>19</td>
<td>35.55</td>
</tr>
<tr>
<td>P-2L</td>
<td>2</td>
<td>II</td>
<td>0.44</td>
<td>276</td>
<td>16</td>
<td>51.69</td>
</tr>
<tr>
<td>P-4L</td>
<td>4</td>
<td>II</td>
<td>0.42</td>
<td>224</td>
<td>29</td>
<td>21.36</td>
</tr>
<tr>
<td>P-6L</td>
<td>6</td>
<td>II</td>
<td>0.41</td>
<td>106</td>
<td>46</td>
<td>18.58</td>
</tr>
</tbody>
</table>

In order to fabricate gas sensors, a thin layer of gold was coated on the NiO films by a vacuum evaporation method. The electrodes were fabricated by a photolithography process and etching of gold with KI/I₂ solution. Then, the sensors were installed into a
custom build Pyrex chamber (200 cm$^3$) which had an inlet and outlet connectors to flow the gas mixtures. Mass flow controllers were used to control a desired gas concentration to the chamber with a digital display. A constant flow of dry air (100 standard cubic centimeters per minute) was kept constant for all tests during the experiments. Ultra high pure H$_2$ (99.999%) was regulated by varying mass flow meters in the range of 1000 - 3000 ppm through the test. The experimental setup was designed to mix gases completely before inserting it to the chamber. The samples were placed on a resistive heater coupled with a DC power supply while the temperature was set to a desired temperature. A Ni-Cr thermocouple was used to monitor the temperature of the sample. The gas sensors were tested by measuring the resistance between two gold electrodes using a high mega ohm Multimeter (Keithly-1200). The resistance of the samples was collected in 1s time intervals and plotted using LabView software during the gas sensing experiment. The gas sensing behavior of device was measured in dry, humid (with 35% humidity) and mixed environments to investigate the effect of humidity and other gases (NH$_3$, CH$_4$) on the gas sensing property of NiO film.
Figure 3-1: Schematics of the processing steps of NiO films used in this study.

3.3 Results and Discussion

Figure 3-2 shows the XRD patterns of NiO samples. The peaks in XRD patterns can be assigned to two crystallographic planes. Two peaks at 2θ = 37.4° and 43.4° were observed for all samples and assigned to (111) and (200) of simple cubic NiO, respectively. Both N-2L and P-2L samples showed approximately same peak intensities. When the thickness was increased, the intensity of NiO peaks increased while the full width at half maximum (FWHM) values was decreased. This can be attributed to the growth of grains by increasing the thickness of films and annealing time. According to Van der drift model [78], the random orientation of particles were nucleated on the surface of sample at an initial step of coating and a preheating step. Furthermore, the nanocrystalline grains are grown during the annealing process. The average grain size (D) of films can be calculated by Scherer formula. However, due to some limiting factors, it
is difficult to evaluate the actual grain size in very thin coatings using the Scherer formula [100]. Therefore, additional SEM measurements were used to analyze the grain size and surface morphology of the samples.

Figure 3-2: The XRD patterns of NiO films prepared on glass substrates.

Figure 3-3 shows the SEM micrographs of different NiO thin films. Here, circular grains were observed for N-2L and P-2L samples. Figures 3-3(a) and (b) show two layered samples with two different fabricating methods. It can be seen that the sample P-2L had a smaller grain size and possessed more porosity than N-2L sample. As a result of smaller grain size and higher porosity, the electrical conductivity and gas sensing property of the film could change significantly. The grain size was increased by increasing the film thickness for P-4L and P-6L, and the shape of grains started to change by increasing the thickness of the film (Figures 3-3 (c) and 3-3 (d)). The average grain sizes of samples were estimated from the SEM images (using Image J software) were 27, 17, 42 and 48 nm for N-2L, P-2L, P-4L and P-6L, respectively. It can be seen that the
grain size and film thickness can be tuned by selecting an appropriate fabricating method. Metal oxide films with smaller grains were ideal for gas sensor applications. The SEM micrographs show the surface topography of the film whereas the XRD patterns show the bulk properties [22, 101, 102].

The surface to volume ratio (S/V) and the degree of porosity are two important parameters, which play important roles in the gas permeability of H$_2$ in NiO thin film. The high S/V ratio could be obtained by simultaneously decreasing the size of the grains and incorporation more porosity into the structure [23]. The porosity of N-2L and P-2L samples were estimated with an effective medium approximation using a spectroscopic ellipsometry measurement (not shown here). The best fit data indicated that the porosity of N-2L samples was 24% whereas P-2L samples was 35%. It should be noted that due to a smaller size of H$_2$ molecules, H$_2$ diffused easily into the porous spaces of the film and as a result, the interaction between the grains and target gas can be intensified [103].

![SEM images of NiO samples](image)

Figure 3-3: The SEM images of NiO samples (a) N-2L, (b) P-2L, (c) P-4L and (d) P-6L.
Figure 3-4(a) shows the dependence of conductivity for all samples in a temperature range of 25-250°C. The electrical conductivity in NiO is proportional to the transfer of positive charge from cations in the lattice [70]. The electrical conductivity was increased with increasing the temperature indicating that the NiO films had a semiconductor behavior. The multi-step annealed samples (P series) had higher resistance than typical sol-gel fabricated samples (N series). This phenomenon can be attributed to the film density and large grain boundary region in the P series (Figures 3-3(a) and 3-3(b)).

The conductivity of films increased with increasing the sample thicknesses due to a larger grain size and less number of grain boundaries of thicker samples [90]. A decrease in sheet resistance with an increasing of the thickness was also reported for SnO$_2$ gas sensor [21, 104]. The activation energy values were calculated using the Arrhenius equation [105],

The calculated $E_a$ values were 369, 437, 419 and 410 ± 5% meV for N-2L, P-2L, P-4L and P-6L, respectively. The activation energy values decreased with increasing of the number of layers (P-4L and P-6L).
Figure 3-4: (a) A semi-log plot of the conductivity (σ) versus reciprocal of the absolute temperature (1/T) of NiO films for different samples and (b) influence of grain size on potential distribution along polycrystalline grains.

Figure 3-4 (b) shows one dimensional potential distribution along the diameter of polycrystalline grain for two different grain sizes. Oxygen is physisorbed in the grain boundary regions and a space charge region (Ls) forms around the surface of each grain. It has been reported that the grain size less than 24 nm can be fully depleted by space charge carriers [22]. When grain size is less than 2Ls, the grain resistance dominates the
resistance of the whole film. The electrical conduction is dominated by the grain boundaries for samples with larger grain size (>2Ls) [33]. Since the core region of the grains has a low resistance and a space charge region has a high resistance, larger grained samples (P-4L and P-6L) shows a grain boundary controlled conduction and higher conductivity than two layered sample (P-2L).

Figure 3-5 (a) shows the optical transmittance of NiO films deposited on glass substrates. The absorption edge for NiO film was around 300 - 380 nm. These values were in agreement with the values reported in the literature [65, 96]. Both N-2L and P-2L showed transmittance values larger than 95% in the visible and IR range. P-2L showed a slightly lower transmittance due to a better film coverage on the surface. The optical transmittance of the sample was decreased with increasing the thicknesses (P-4L and P-6L). This behavior can be attributed to microstructure of prepared samples. By increasing the film thickness, grain size increased and film coverage improved. Therefore, the films showed a higher dispersion of the incident light and decreased in the light transmittance through the films. Figure 3-5 (b) shows the change of \((\alpha h\nu)^2\) with photon energy for all samples. It was found that the absorption coefficient decreased with a decrease of the photon energy. A sharp absorption edge was observed near the band gap of NiO. The optical band gap was obtained for each sample by extrapolating the straight line portion of plot at \(\alpha = 0\) for each graph. The value of the optical band gaps was shown in the inset of Figure 3-5 (b). As seen in Figure 3-5 (b), there was a slight variation of a band gap of NiO films fabricated at different conditions. The value of band gap slightly was decreased with an increase in number of layers [106]. This variation can be arisen due to
the combined effect of the (I) high density of dislocations, (II) quantum size effects and (III) change in barrier height [107].

Figure 3-5: (a) Optical transmittance spectra of different NiO films and (b) Plot of $(\alpha h\nu)^2$ and photon energy for different samples.
The gas sensing measurements of NiO samples were carried out by measuring the resistance across two electrodes for different temperatures and H$_2$ concentrations. The sensor response was calculated by the following equation:

$$S = \frac{(R_{\text{Gas}} - R_{\text{Air}})}{R_{\text{Air}}} \times 100$$

(3.1)

where, $R_{\text{Gas}}$ and $R_{\text{Air}}$ are the resistance of the sensor in target gas and air, respectively [84]. All the NiO based sensor used in this work showed a p-type conducting behavior. The increase in resistance under the exposure of H$_2$ gas was expected as a concentration of holes in the p-type semiconductor decreased due to the charge transfer between H$_2$ molecules and NiO surface in an oxygen environment.

The H$_2$ sensing mechanism of NiO film in the air can be explained by a reaction of hydrogen with a physisorbed oxygen on the NiO film [108]. NiO is a non-stoichiometry p-type semiconductor metal oxide and its semiconductor behavior was attributed to non-stoichiometry percentage of Ni$^{2+}$ and O$^{2-}$ ions in the prepared sample [31, 32, 35]. Therefore, generation of holes inside the lattice can be enhanced by adding of H$_2$ (a reducing gas). When oxygen species are adsorbed on the surface of NiO grains, they act as a surface acceptors and force electrons to be removed from the lattice. As a result, more holes are available for conduction. By introducing H$_2$ as a reducing gas to the chamber, the electrical conductivity of the film decreases. The H$_2$ molecules react with the adsorbed oxygen ions and form water vapor. This exchange reaction cause electrons transfer back to the film, hence the surface resistance increases in p-type materials [35]. It has been reported that parameters, such as thickness, grain size, porosity, film texture, active surface area, grain network, bulk stoichiometry and surface geometry are important in gas sensing property of NiO thin films [22, 109]. Among these
parameters, grain size and porosity are two main factors which affect the gas sensing parameter of the NiO thin film. With a decrease in the grain size the surface to volume ratio increases and the exposed area of the film increases, respectively [110].

Figure 3-6 (a) shows the response as a function of operating temperature for all samples for 3000 ppm of H$_2$. Although the response was high in low thickness films, the response was decreased with an increasing the thickness. At low operating temperatures the low sensor response can be attributed to the low thermal energy of H$_2$ molecules to react with adsorbed oxygen species on the surface. A rapid increase in the response values was observed at 150°C and reached to a maximum value at 175°C for two layered samples. By increasing the temperature, H$_2$ molecules absorb enough thermal energy to overcome the activation energy barrier [34]. By further increasing the temperature to 225°C, the response values decreased for all sample which can be attributed to the difficulty of exothermic reaction at a high temperature and increased the desorption rate of H$_2$ [111]. It has been reported that there is an optimum operating temperature for most of the semiconductor metal oxide gas sensors [21, 23, 72, 78].
Figure 3-6: (a) Variation of the response of the NiO samples as a function of temperature (H₂ concentration 3000 ppm) and (b) Response and recovery curves for 3000 ppm H₂ at different working temperatures.

The rapid response and recovery times are demands for a gas sensor. Figure 3-6 (b) shows the response curves for the P-2L sample under 3000 ppm of H₂ at different operating temperatures. During the exposure of H₂, the resistance of sample increased
and reached to a saturation limit. Then, the resistance returned back to its original value in several minutes after stopping the target gas. It can be seen that the response values were high at 175°C and the recovery time was decreased with an increasing of the temperature. This improvement in sensor recovery time can be attributed to high thermal energy of H₂ molecules to react with oxygen molecules. According to the temperature analysis, the highest response was recorded at 175°C, hence this temperature was selected as an optimum temperature for all other gas sensing data.

Figure 3-7 (a) shows the experimental values for sample P-2L for 250 - 3000 ppm of H₂ gas at 175°C. Figure 3-7 (b) shows all sensor responses to H₂ concentrations for 1000, 2000 and 3000 ppm of H₂ in air at 175°C. The response values were increased with an increasing of the concentration of the target gas. The response values at 175°C for 3000 ppm of H₂ in percentage were 54, 68, 37 and 17 for N-2L, P-2L, P-4L and P-6L, respectively. The sample that was prepared with a multi-step coating and annealing method, P-2L, showed the highest response compared to one step annealed sample, N-2L. This can be attributed to a smaller grain size and a higher porosity in the film, P-2L. The surface morphology of these samples also verified our assumption about the grain size and the percentage of the porosity (Figures 3-3 (a) and 3-3 (b)). The specific surface area is an important parameter, which deserves more attention due to porosity and grain size of metal oxide gas sensors. The area of the surface area can be defined using the following equation [112]:

\[
A = \frac{6}{\rho D}
\]  

(3.2)

where, \(D\) is the average grain size of spherical grains and \(\rho\) is the theoretical density of metal oxide. Figure 3-7 (c) shows the gas sensor response as a function of surface area.
under different concentrations of H₂ at 175°C. It can be seen that by increasing the
surface area, the gas sensor response was increased. In general, the gas sensing
performance of metal oxide films can be explained by a diffusion-reacting approach [21,
113]. According to this approach, the gas sensor response was determined by a surface
reaction and a gas diffusion capability in the film. The gas distribution throughout the
film was enhanced by forming a higher porosity and smaller grain size. The surface
morphology analysis of samples in Figure 3-3 shows an increase in the grain size with
increase of the film thickness. With an increase in film thickness from four to six layers,
the response values decreased significantly.
Figure 3-7: (a) Response curves of sensor fabricated with P-2L sample for H₂ concentration of 250-3000 ppm in air at 175°C, (b) Sensor response for NiO samples for different H₂ concentrations at 175°C and (c) Sensor response as a function of surface area.

Figure 3-8 (a) shows the repeatability data for N-2L sample under 2000 ppm of H₂ at 175°C. Repeatability is an important factor for commercial gas sensors [28, 92]. This property is an important factor for commercialized products, which need to work for several thousands of cycles in different ambient conditions [38]. It can be seen that the response and recovery times were almost constant for each cycle of this device. It should be noted that all these gas sensors were tested for more than several times. No significant change was observed in the sensor response, though they were tested for few different occasions in a 6 month period.
Figure 3-8: (a) Repeatability data for N-2L under 2000 ppm of H$_2$ at 175°C, (b) Cross sensitivity responses for two different gas mixture 1000 ppm H$_2$ and 25-75 ppm NH$_3$ at 175°C, (c) Cross responses for 1000 ppm H$_2$ and 1000-3000 ppm CH$_4$ at 175°C and (d) Gas sensor response to different target gases at 175°C.

MOGSs show high response to different target gases, which is normally operated in a mixed gas environment. Therefore, cross sensitivity measurements are important in
the real world applications. The selectivity of a device can be enhanced using different filters, operating at a different temperature, using arrays of sensors to detect a specific gas [98]. In order to study the effect of other gases on the hydrogen gas sensing properties of NiO thin film; the sensors were tested in a presence of other reducing target gases such as NH₃ and CH₄. Figure 3-8 (b) shows the response values of P-2L sample towards individual gas and mixtures of H₂ in the presence of NH₃ gas at 175°C. The response value was increased continuously with increasing of the concentration of NH₃ gas (25-75 ppm) while passing 1000 ppm of H₂. It was observed that the sample showed a higher response to a mixture of gas, which represented that NH₃ molecules competed more to absorb on the surface sites than H₂ gas molecules. Figure 3-8 (c) shows the gas response of P-2L of CH₄ gas in the presence of H₂ gas. It was shown that the sensor had a fast response to the hydrogen gas but on the other hand no significant changes in the gas sensor response was detected after introducing CH₄ gas. Therefore, NiO sensor had a good selectivity towards H₂ gas compared to CH₄ at 175°C. This research group is currently working on a wider range of target gases and different operating temperatures; The result of these studies will be published elsewhere. Figure 3-8(d) shows the gas sensor response for different target gases at 175°C. It can be seen that the sample showed a high response to hydrogen gas compared to CH₄ gas in a same concentration level. The sensor showed high response to NH₃ gas even in a low concentration level. The NH₃ level was selected in this range due to the threshold level value of 25 ppm and limitation in an experimental setup. It can be clearly seen that the sensor had a high response value even in low concentration values.
The effect of humidity on the sensor performance has been studied by different researchers. Water vapor is available in normal humidity conditions and also is a byproduct of all hydrocarbon combustions. Sawaguchi et al. reported that the sensing behavior of the sample was affected by a temperature lower than 60°C in 18-85% humidity [114]. It has been stated that the humidity is less effective at a high operating temperature (>120°C) [115]. Figure 3-9 shows the dynamic gas response for P-2L sample under 3000 ppm of H₂ gas at 175°C in dry and normal air (35% humidity) conditions, respectively. It can be seen that the gas sensing performance of the sample decreased by 5% compared to the dry air environment. Moreover, it can be seen that the recovery time increased in the humid air compared with the dry air, and this phenomenon was in an agreement with other studies reported elsewhere [9].

![Figure 3-9: Dynamic gas response of P-2L sample 3000 ppm of H₂ gas in dry and humid (35%) air at 175°C.](image)
3.4 Conclusions

Nanocrystalline NiO films were successfully deposited by a sol-gel process. Special efforts were made to enhance the porosity of NiO film. The structural, electrical and sensing properties of prepared films were investigated as a function of film fabrication conditions, testing temperature and H₂ concentration. The gas sensor response was temperature dependent and the highest response was observed at a relatively low temperature (175°C) of H₂ gas. It was found that the NiO films had several important sensor characteristics such as repeatability, high response, and fast response/recovery times to H₂ gas. The overall recovery times of the sample were decreased by increasing the operating temperatures >175°C. It was also found that the thickness and porosity of the film were two important parameters, which affect the main gas sensing characteristics of NiO based H₂ sensors. The measurements revealed that the sensor response was decreased by increasing the film thickness. The maximum sensitivity of 68% was measured at 175°C for 3000 ppm of H₂ for multi-step annealed sample. The sample showed a low humidity dependent in a normal humidity condition (35%).
Chapter 4

Enhancement of Hydrogen Gas Sensing of Nanocrystalline Nickel Oxide by Pulsed Laser Irradiation

4.1 Introduction

Monitoring of hydrogen in an ambient condition is important due to its wide range of applications in industries, laboratories and energy storage. Industries are dealing with transport, storage and use of $H_2$ in large scales. Therefore, there is a need for a stable, high sensitive sensor for monitoring and leak detection of $H_2$. Metal oxide gas sensors have been considered as an alternative replacement for current large and expensive analytical techniques such as optical spectroscopy and gas chromatography [17, 18]. Conventional metal oxide gas sensors consist of large poly-crystalline grains where surface and grain boundaries are two causes of limiting their electrical transport phenomena [4, 7, 8]. The gas sensing ability can be intensified with decreasing a grain size to nano scale. In the last few years, nanostructured metal oxide gas sensors (NMOS) such as nickel oxide (NiO), zinc oxide (ZnO) and tin oxide (SnO$_2$) have attracted much attention due to their high sensitivity and fast response and recovery times [97, 116-119].
Modification of metal oxide thin films by a laser has been reported to improve different properties of the sample such as electrical conductivity, carrier mobility, microstructure and crystallinity [3, 7]. A laser irradiation can be used to improve the surface of metal oxide thin film and increase the sensor response [46]. Several appropriate uses of a laser have been introduced such as using a constant or pulsed wave laser with different wavelength to get a desired property. Recent works related to \( \text{H}_2 \) detectors by Stamaki et al. and Brilis et al. reported the response of 15-40\% for 30,000 ppm of \( \text{H}_2 \) at 200\(^\circ\)C for gas sensor, which was fabricated by pulsed laser deposition on a silicon substrate [50, 74].

In this study, a post-fabrication modification by a pulsed laser irradiation of nanocrystalline is introduced to improve \( \text{H}_2 \) sensing of NiO thin films. The NiO samples were irradiated with a pulsed 532 nm wavelength using a Nd:YVO\(_4\) laser beam. The laser power was used to optimize the sensor response as a combination of higher response magnitude and faster response and recovery times. Nanostructured sol-gel samples were selected for this study for several reasons such as, small grain size (20 nm), high surface to volume ratio, and low operational temperature compared to other conventional sensors. High response of these sensors as well as faster response and recovery to \( \text{H}_2 \) exposure can have a significant impact for industrial applications. Laser irradiation offers an additional tool to modify the microstructure of thin film such as crystallinity, grain size, and defects. This study is a continuation of our efforts to investigate and design a better metal oxide gas sensor by using a laser modification of metal oxide surfaces. In an earlier study, this group showed that UV irradiation had an effect on the \( \text{H}_2 \) gas sensing of ZnO [5].
4.2 Experimental

Nanocrystalline p-type NiO thin films were synthesized using a sol-gel technique. Nickel nitrate hexahydrate (Ni(NO$_3$)$_2$·6H$_2$O) was dissolved in isopropanol alcohol and polyethylene glycol 200 to make 0.1 M solution by constant stirring at 25°C. Nano nickel hydroxide particles were produced in the solution by adding dilute ammonia into the stirring solution, in order to eliminate particle agglomeration; Triton X-100 was added to decrease surface tension into the solution. A very thin and uniform layer of solution was spread on a 2×2 cm$^2$ no alkaline glass substrate by a spin coating at 1500 rpm for 20 seconds and 3000 rpm for 10 seconds. After coating of each layer, the samples were heated to 350°C for 5 minutes to remove any organic compound in the film. Two layers were coated on the substrate to gain a proper thickness of the active layer. After coating two layers of sol-gel mixture, they were calcinated at 550°C in a tube furnace for three hours in the air. The calcination process improved the microstructure and produced of the nanocrystalline NiO film.

After the annealing step, the samples were subjected to a laser irradiation using Nd:YVO$_4$ pulsed laser system (pulsed width= 8 ns) with a wavelength of 532 nm using an Osprey-532 laser source, which was equipped and controlled by a X-Y scanner. The laser beam with a window size of 20×20 µm$^2$ irradiated onto the film surface. The pulsing frequency of laser system was fixed at 10 kHz and the scanning speed was kept at 30 cm/s. The scanning pattern was designed and calibrated to yield three values for the laser irradiation of 50, 75, and 100 mJ/cm$^2$. 
The X-ray diffraction (XRD) data were collected with a grazing incidence X-ray diffraction (GID) technique with a chromatized Cu-K$_\alpha$ radiation using 40 mA and 45 kV in a two theta range between 35° and 45° with a low incident angle of 0.9° (PANalytical, X-ray). The GID method preferentially probes the surface layer and it causes an increase in the reflected intensity compared to a regular XRD method. The XRD spectra were used to determine crystallographic phases of samples. The scanning electron microscope (SEM- Hitachi S-4800) was used to study the surface morphology of NiO films before and after the post-laser irradiation step. Fresnel approach was used to theoretically estimate the thickness of films [17]. A program developed using Matlab software to theoretically estimate refractive indices and thicknesses of NiO films based on the experimental values of the reflectance data from bi-layer of NiO/glass substrate. The value of the thickness for NiO films was estimated around 21 ± 3 nm.

The chemical binding energy analysis was performed on the surface of the samples using XPS measurements (Kratos Axis Ultra XPS) with Al K$_\alpha$ at 1486.6 eV and base vacuum of $2\times10^{-10}$ mbar. To minimize a charging effect, a low energy electron gun was used for charge neutralization. Corrections of energy shift, due to the steady state charging were made by assigning 284.6 eV binding energy to the C 1s peak [80].

In order to fabricate sensor devices, the gold electrodes with a thickness of 50 nm were deposited by a vacuum thermal evaporation. Photolithography was used to fabricate electrodes with a comb like structure with a length of 200 µm and a space of 20 µm. The samples were mounted in a custom build Pyrex chamber (200 cm$^3$) which had inlet and outlet to pass the gas above the sample. The samples were placed on a resistive heater, while the temperature was continuously controlled by a thermocouple. The carrier gas
was introduced to the chamber throughout the process. Various concentrations (1000-3000 ppm) of high purity $\text{H}_2$ in dry air were introduced into the chamber using the mass flow meter. The time constant for gas exchange in the test chamber was $\sim$ 15 seconds. The resistance between the electrodes was measured continuously using a Keithley-2001 multi-meter in 1s time intervals.

### 4.3 Results and Discussion

In general, fabricating nano-sized grains in metal oxide is a vital step to gain a high performance sensor with high a response and a fast response and recovery times [73, 120, 121]. In this study, nanocrystalline NiO is fabricated using a sol-gel method.

By implementing an accurate concentration of a solution and an optimum temperature, at the initial steps of preheating of the sample, the random orientation of nuclei initiated on the surface of the glass substrate. Furthermore, these nucleation sites can be converted to very fine NiO grains after the annealing step. During this stage, crystal planes which had lower energy and a higher growth rate stabilized and made the final crystallographic structure of the grains [78, 122].

Figure 4-1 shows the XRD patterns of NiO films irradiated with different laser power levels. Both simple cubic phase and face centered cubic structure have been reported in a literature for sol-gel derived NiO films [72, 123]. The diffraction patterns of our samples revealed two peaks at 37.4° and 43.4°, which corresponded to (111) and (200) planes of simple cubic NiO, respectively. The (002) peak intensity was higher than that of the (111) peak. Moreover, (111) and (200) peaks shifted towards a higher angle as the laser intensity increased (from 50 to 75 mJ/cm$^2$) indicating that the films had a higher
thermal stress induced by high laser power levels [91]. By increasing the laser power to 75 and 100 mJ/cm$^2$, the crystallinity of the sample decreased. By calculating the FWHM (full width at half maximum) for (200) plane at 43.4\textdegree, the average grain size was calculated using Scherer formula to be around 20 nm [124]. However, due to some limiting factors in GID method, the Scherer formula are not suitable to evaluate an accurate crystal size of the sample [125], therefore an additional investigations were carried out with SEM measurements to investigate the surface morphology and the change in grain size of the samples.

![Grazing incidence X-ray diffraction pattern](image)

**Figure 4-1:** Grazing incidence X-ray diffraction pattern of samples before and after laser irradiation.

Figure 4-2 shows the SEM morphology of nanocrystalline NiO samples before and after the laser irradiation. It can be clearly seen that the as-deposited film had a spherical grains with a smooth coverage. As the laser power increased from 50 to 100
mJ/cm$^2$, the surface morphology and the uniformity of thin film were changed. The average grain size of samples estimated using SEM data is 17.8 nm, 29.9 nm, 14.4 nm, and 15.2 nm for as-deposited and 50, 75 and 100 mJ/cm$^2$ irradiated samples, respectively. The surface to volume ratio and a degree of crystallinity are two parameters that play an important role in gas sensing of NiO thin films [23, 126]. The grain size was increased slightly using 50 mJ/cm$^2$, which can enhanced the electrical conductivity throughout the grains [22]. The corresponding XRD pattern in the Figure 4-2 (b) also represents higher peak intensities for the sample. By applying a higher laser power of 75 mJ/cm$^2$, the grain size decreased as shown in Figure 4-2 (c). Moreover, as the laser power was increased to 100 mJ/cm$^2$, the grain size was slightly changed and the degree of crystallinity was degraded significantly as shown in Figure 4-2 (d). The grain size histogram was inserted in the Figure 4-2 to better exhibit the grain size distribution in each sample.

The results from Figures 4-1 and 4-2 show that the power level of the laser beam can be used to optimize the size of the grains and maximize the film uniformity of as-deposited NiO thin films. As the laser intensity ($I$) increased from zero towards a critical threshold ($I_c$) the laser functioned as a heat provider to heal defects in the grains and thus, caused an increase in the size and the uniformity of grains. When $I > I_c$ the laser heat was adequate to start local melting of several NiO layers [127]. For laser intensities greater than $I_c$, crystallinity was completely degraded and an amorphous phase was created. As a result, an optimization of laser power was required to get the best combination of grain size, porosity level and crystallinity of NiO thin film for gas sensing applications.
Figure 4-2: SEM images of nanocrystalline NiO on the glass substrate with different laser power (a) As-deposited, (b) 50 mJ/cm², (c) 75 mJ/cm² and (d) 100 mJ/cm².

The XPS measurement revealed the chemical states of bonded atoms [128]. Figure 4-3(a) and 4-3(b) shows the XPS spectra of as-deposited and 75 mJ/cm² laser irradiated samples, respectively, for the Ni 2p and O 1s ranges. The peaks for as-deposited sample obtained at binding energies of 854.8 eV (Ni 2p$_{3/2}$) and 873.9 eV (Ni 2p$_{1/2}$) suggested the presence of NiO [129]. For 75 mJ/cm² laser powered sample, the Ni 2p$_{3/2}$ peak at 854.7 eV and Ni 2p$_{1/2}$ peak at 874.2 eV indicated the presence of NiO. Satellite peaks appeared at the 861-862 eV (Ni 2p$_{3/2}$) and 879-881 eV (Ni 2p$_{1/2}$) due to shakeup processes [129]. It is clear that the portion of Ni 2p$_{3/2}$ at 856.7 eV, which corresponds to Ni$^{3+}$ is increasing with laser irradiation. Figure 4-3 (b) shows the O 1s spectrum and clearly separated two peaks, which correspond to the binding states of Ni$^{2+}$
(530.2 eV) and Ni$^{3+}$ (532.3 eV) [130]. It is known that a non-stoichiometric NiO, contains Ni$^{2+}$ vacancies and to keep the charge neutral, some Ni$^{2+}$ should be oxidized to Ni$^{3+}$ hence the presence of Ni$_2$O$_3$ conforms the non-stoichiometric of NiO samples [80, 131]. It can be seen clearly that the portion of O 1s from Ni$^{2+}$ was decreasing with a laser irradiation and gives a rise to O 1s peak corresponds to Ni$_2$O$_3$ at 532.3 eV. The concentration of the peak decreased and the intensities of both peaks were in the same level. These results suggested that NiO partially turns to Ni$_2$O$_3$ when the films were laser irradiated.
Figure 4-3: XPS spectra of at the original surfaces of as-deposited and 75 mJ/cm² laser powered samples in the (a) Ni 2p and (b) O 1s ranges.

The electrical properties of NiO thin films were characterized by collecting a change in the resistance with a temperature in the range of 25-250° C.

Figure 5-4 shows a semi-log plot of σ with an inverse of the absolute temperature (T). This monotonic increase in σ with increasing T is a well-known semiconductor behavior [87, 132]. It can be seen that, the conductivity of NiO films increased by a laser irradiation at 50 mJ/cm² and significantly decreased by an increase of laser power to 75 mJ/cm² and 100 mJ/cm². As an example, the values of σ in units of $10^5 \Omega^{-1}.cm^{-1}$ at 100°C are 1.00, 1.34, 0.3 and 0.07 for as-deposited, 50, 75 and 100 mJ/cm² laser power irradiated samples, respectively. A decrease in conductivity with increasing the laser annealing was reported for SnO₂ gas sensor [133]. Activation energies can be obtained from fitting Arrhenius equation to the data in Figure 4-4. The calculated $E_a$ values were
0.38, 0.37, 0.43, 0.45 eV for as-deposited, 50, 75 and 100 mJ/cm² laser power irradiated samples, respectively. It was noticed that for the sample with the laser irradiation at 50 mJ/cm², the activation energy was the lowest. This was in consistent with the structural data shown in Figures 4.1 where the crystallinity increased for 50 mJ/cm² irradiated sample and the crystallinity decreased upon further increase of laser power to 100 mJ/cm². The activation energy has been attributed to the tunneling of charge carriers among NiO grains [24]. The sample with the highest crystallinity had the lowest value for \( E_a \).

![Figure 4-4: Semi-log plot of the conductivity (\( \sigma \)) versus reciprocal of the absolute temperature (1/T) of NiO films before and after laser irradiation.](image)

The \( \text{H}_2 \) gas response of NiO thin films irradiated by different laser power levels were investigated by measuring a resistance versus time over two electrodes for a constant temperature. The samples were tested at different temperatures between 150-225°C. It was found that the best response of NiO for \( \text{H}_2 \) exhibited at 175°C. All data
discussed further were collected at this temperature. After H\textsubscript{2} gas was introduced into the chamber, the sensor resistance was increased to a saturation level and by purging H\textsubscript{2} gas from the chamber the resistance returned to its original value. Same behavior intensified by an exposing the samples to higher H\textsubscript{2} concentrations.

The H\textsubscript{2} sensing mechanism of NiO can be attributed to the non-stoichiometry of percentage of Ni\textsuperscript{+2} and O\textsuperscript{-2} in the prepared samples. Vacancies which are located in cation sites can form holes. Oxygen molecules absorb on the surface of grains and produce oxygen ions \cite{24, 134}. When oxygen ions adsorb on the surface of NiO grains, they act as an acceptor and force electrons to be removed from the grains and produce extra holes in the lattice. As a result of this reaction, the resistance of the samples was decreased by an increasing of hole concentration \cite{35, 135}. By exposing the samples to a reducing gas such as H\textsubscript{2}, the H\textsubscript{2} molecules reacted with adsorbed oxygen and released electrons back to the lattice. Therefore, hole concentration in the lattice decreased and the resistance of the film increases, which was a normal p-type semiconductor behavior \cite{71}. The reaction summaries are \cite{71, 136, 137}:

\begin{equation}
O_{2\text{(adsorbed)}} + 2\overline{e} \leftrightarrow 2O^{-} \tag{4.1}
\end{equation}

\begin{equation}
H_{2} + O_{\text{adsorbed}} \rightarrow H_{2}O_{\text{vapor}} + e \tag{4.2}
\end{equation}

The response of the NiO sample as a function of different H\textsubscript{2} gas concentrations was collected. Figure 4-5(a) shows the sensor response to H\textsubscript{2} concentrations of 1000, 2000 and 3000 ppm in the air for all samples. It can be seen that by increasing the H\textsubscript{2} concentration, the response values increased for all samples. In the sample which irradiated with a low laser power, 50 mJ/cm\textsuperscript{2}, the response decreased due to its larger grain size and a decrease in surface to volume ratio. By further increasing of laser power
to 75 mJ/cm$^2$, the sample possessed the highest response compared to all samples. This phenomenon can be attributed to a smaller grain size and higher uniformity of NiO film irradiated with 75 mJ/cm$^2$. Figure 4-5(b) shows the experimental response values for 1000, 2000 and 3000 ppm of H$_2$ gas at 175°C for 75 mJ/cm$^2$ laser power sample. Furthermore, as the laser power was increased to 100 mJ/cm$^2$, the response decreased as a result of a degradation of crystallinity.
The experimentally measured responses (S) of sensors were fitted with a theoretical model as the first order time step response with exponential rise and fall functions. The equations for the sensor response (S) are given by [84]:

\[
\frac{R}{R_0} = \exp\left(\frac{t}{\tau_1}\right), 0 \leq t \leq t_1,
\]

(4.5)

\[
\frac{R}{R_0} = \exp\left(\frac{t_1}{\tau_1}\right) \times \exp\left(\frac{t-t_2}{\tau_2}\right), t_1 < t \leq t_2.
\]

(4.6)

where, \(R_0\) is the initial resistance of the sensor, \(t_1\) is the time when the gas is turned off, \(t_2\) is the time when the sensor recovers to its original value, and \(\tau_1\) and \(\tau_2\) are transient times for response and recovery processes, respectively. Transient time was defined as the time needed for the sensor to reach to 63% of its initial value. Separate fits to the curve before
and after $t_1$ were done to determine $\tau_1$ and $\tau_2$. Figure 4-6 shows the experimental values for response and first order exponential fit for 1000 ppm of $\text{H}_2$ gas at 175°C of NiO sample irradiated with 75 mJ/cm$^2$ laser power. By comparison of the experimental data and the first order response, it can be seen that the fitted values were within 95% accuracy of experimental values. Figure 4-7 (a) and 4-7 (b) show the fitted data for $\text{H}_2$ gas response of NiO samples for two different $\text{H}_2$ concentrations of 1000 and 3000 ppm at 175°C. Table 4.1 shows the values of $S$, $\tau_1$ and $\tau_2$ for all samples exposed to different $\text{H}_2$ concentration at 175°C. These concentrations, which have a safety factor of 10 (Low explosion limit of $\text{H}_2$, 40000 ppm), were selected for $\text{H}_2$ concentration, in this experiment. The highest response for 1000-3000 ppm of $\text{H}_2$ gas was measured for the 75 mJ/cm$^2$ sample. Moreover, this sample had a response time of $\tau_1= 134$ s which was also the highest of the set for 1000 ppm of $\text{H}_2$ at 175°C. On the other hand, the recovery times decreased monotonically while going from the as-deposited sample to the laser irradiated sample, and decreased further by increasing the laser power. The $\tau_1$ and $\tau_2$ values decreased by increasing the $\text{H}_2$ concentration for all samples and this phenomenon could be described by increasing $\text{H}_2$ molecules and limited available sites on the surface of grains.
Table 4-1: S, τ₁, and τ₂ values for different samples.

<table>
<thead>
<tr>
<th>Sample</th>
<th>H₂ (10³ ppm)</th>
<th>Response, S (%)</th>
<th>Response time, τ₁ (s)</th>
<th>Recovery time, τ₂ (s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>As-deposited</td>
<td>1</td>
<td>26.7</td>
<td>87</td>
<td>788</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>35.8</td>
<td>85</td>
<td>446</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>46.3</td>
<td>81</td>
<td>322</td>
</tr>
<tr>
<td>50 mJ/cm²</td>
<td>1</td>
<td>21.7</td>
<td>87</td>
<td>471</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>25.4</td>
<td>80</td>
<td>225</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>32.3</td>
<td>71</td>
<td>181</td>
</tr>
<tr>
<td>75 mJ/cm²</td>
<td>1</td>
<td>32.4</td>
<td>134</td>
<td>406</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>42.3</td>
<td>128</td>
<td>259</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>57.9</td>
<td>101</td>
<td>187</td>
</tr>
<tr>
<td>100 mJ/cm²</td>
<td>1</td>
<td>7.7</td>
<td>80</td>
<td>229</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>10.2</td>
<td>79</td>
<td>145</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>13.2</td>
<td>67</td>
<td>117</td>
</tr>
</tbody>
</table>

Figure 4-6: Real response and first order exponential fit under 1000 ppm of H₂ gas at 175°C of 75 mJ/cm² laser power NiO sample.
When compared, the as-deposited sample response values improved by about 21% for 1000 ppm of H$_2$ and 24% for 3000 ppm of H$_2$, respectively in the case of this 75 mJ/cm$^2$ sample. The effect of using optimized laser power to improve sensor response
was not a special case for these NiO samples. The same study was done for thicker NiO films doped with lithium and ZnO thin films derived from sol-gel method. In both cases, this group founded similar trends to optimize sensor response for H$_2$ detection with laser irradiation. Detailed results, for these experiments will be reported elsewhere. These data demonstrated the generality of our results for other types of semiconducting oxide films.

The sensing properties of samples are determined by two competing parameters of high conductivity which correlates with a high crystallinity and high surface to volume ratio for a higher adsorption of H$_2$ gas molecules. It can be seen that low laser power decreased response as a result of an increase in the grain size and the crystallinity and therefore a decrease in surface to volume ratio. As a result, the exposed area decreased which was consistent with the SEM observation from the Figure 4-2. However, the rise in crystallinity caused an increase in conductivity as seen in Figure 4-1. By further increasing the laser power to 75 mJ/cm$^2$, the response increased compared to as-deposited sample due to its higher uniformity and smaller grain sizes as evidenced from the SEM images from the Figure 4-2 (c) and lower conductivity (Figure 4-4). By using the laser power of 100 mJ/cm$^2$, the grain crystallinity degraded significantly and the samples show low sensitivity to H$_2$ gas. It is well known that samples with more porosity have higher the sensitivity. Thus, there is a competition between increasing crystallinity decreased the porosity with high laser power. Therefore, there is an intermediate power level (in this case 75 mJ/cm$^2$), which can improve the gas sensing property of NiO samples and decrease the recovery time.

Repeatability is a critical factor for commercial gas sensors which need to work for a long period of time without the need for replacement and recalibration [28, 92].
Figure 4-8 (a) shows the repeatability data for the laser-irradiated sample under 1000 ppm of H₂ gas at 175°C. A high repeatable behavior was observed for the sample. Small deviation can be attributed to small deviation in inserting target gas using mass flow meters. The samples also were tested at different times to address reliability issues. It was found that the samples showed the similar sensing behavior over time. Figure 4-8 (b) shows the response values for different measurements. It is shown that the response values were almost comparable over time.
Figure 4-8: (a) Repeatability of 75 mJ/cm$^2$ laser power sample under 1000 ppm of H$_2$ gas at 175°C and (b) Response values of different test numbers for as-deposited and 75 mJ/cm$^2$ laser powered NiO sample under 1000 ppm of H$_2$ gas at 175°C.
4.4 Conclusion

In summary, a nanocrystalline NiO sensor can be used for H\textsubscript{2} gas detection at a lower temperature than conventional metal oxide gas sensors. This lowering of the sensing temperature can be beneficial in many industrial applications. This oxide has a number of advantages, such as high response, and fast response and recovery. In this study, the pulsed laser irradiation on NiO film was employed to improve its gas sensing properties. Different laser power levels have been tested to understand the effect of laser irradiation on the gas sensing behavior of NiO sample. At an optimal laser power level, the laser-irradiated sample had a higher response and faster response recovery times compared to the as-deposited sample. The results of this investigation suggested that the laser irradiation technique was a general and applicable method for NiO based gas sensors. Furthermore, the authors believe that this study will influence a further improvement of metal oxide gas sensors by laser treatments in the future.
Chapter 5

Cross Sensitivity Performance of Sol-gel Derived Nickel Oxide Gas Sensor

5.1 Introduction

The first section of this chapter is devoted for an analysis of NiO gas sensor for several reducing gases at different temperatures. The second part, describes an effect of Pt coating on the deposited sample. The results were analyzed and compared for gas sensors with and without Pt.

The microstructure and surface properties of as-deposited and Pt decorated NiO films were studied using X-ray diffraction and scanning electron microscope. The gas sensor responses as well as response and recovery times were analyzed to understand the gas sensing mechanism, selectivity and optimal sensing temperature. The cross sensitivity data suggested that this sensor could be used to detect reducing gas selectively in ambient conditions with high repeatability. The Pt decorated sample showed very high response to hydrogen gas even at a low operating temperature (< 175°C).
5.2 Experimental Procedure

The NiO thin films were deposited using a sol-gel technique by dissolving 0.1 M Nickel nitride hexahydrate (Ni(NO$_3$)$_2$·6H$_2$O) into 20 ml of equal amount of isopropanol alcohol and polyethylene glycol 200. The solution was stirred at 25°C for 2 hours to make a green transparent solution. Nickel hydroxide particles were introduced into the solution by adding dilute ammonium hydroxide drop wise to the solution under severe magnetic stirring condition. The resulting solution was stirred for 1 hour. Finally, a light greenish solution was obtained, and was used for the coating step using a spin coating system (Laurell WS-400B-6NPP-LITE). In order to eliminate particle agglomerations, several drops of Triton X-100 were added to the solution to decrease surface tension. NiO films were coated on a non-alkaline glass substrate. The glass substrates were cleaned with acetone and distilled water to remove any organic compounds. The spin coating was performed at a room temperature, with a speed of 3000 rpm for 30 s on the glass substrates (2×2 cm$^2$). After depositing each layer, the films were preheated in the air at 350°C for 5 min to remove organic compounds in the deposited film. The coating steps were repeated for several times to produce a uniform film with a desired thickness. Afterwards, the films were post heated at 550°C for 3 hrs. in the air using a tube furnace. In order to fabricate sensor devices, a thin layer of gold (~75 nm) was coated on the surface of thin film by a thermal evaporation technique. The gas sensor electrodes were patterned by an optical lithography technique. The electrodes with a comb like structure with a length of 200 µm and a space of 20 µm were fabricated on the top of thin film. To fabricate Pt decorated samples, Pt (99.999%) nanoparticles were deposited on the film.
using a thermal evaporation technique. The apparatus was evacuated to a pressure below $10^{-7}$ Torr before the thermal evaporation. The amount of Pt particles on the surface of NiO was controlled by the distance of the evaporation source to the samples.

### 5.3 Results and Discussions

The XRD patterns of as-deposited NiO and Pt-decorated NiO on a glass substrate are given in Figure 5-1 for two theta scans between 30° and 50° using a grazing incidence beam technique. A relative high intensity diffraction peaks at 37.4° and 43.7° were obtained and corresponded to (200) and (111) planes of polycrystalline NiO for both samples. In the case of Pt decorated sample, all the intensities of the peaks were decreased and no specific Pt peaks was identified due to the small fraction of Pt deposited on the surface of the film.

![Figure 5-1: XRD patterns of both NiO and NiO-Pt films on glass substrates.](image)
The surface topography of as deposited and Pt decorated NiO was examined using a scanning electron microscope (Figure 5-2 (a) and 5-2 (b)). The surface observations showed a uniform grain size distribution on the surface of samples. Pt decorated samples showed a slight difference on the surface. Due to the thermal evaporation, a very thin layer of Pt formed on the surface of the grains. Additional EDAX analysis was used to verify the existence of Pt particles on the surface of the sample. The mapping analysis revealed a uniform distribution of Pt on the surface of sample (Figure 5-2 (c) and 5-2 (d)).

Figure 5-2: (a) As deposited NiO sample, (b) Pt decorated NiO, (c) Pt mapping of Pt decorated sample and (d) EDAX analysis of Pt decorated.
Figure 5-3 shows the conductivity dependence of as-deposited and Pt decorated. The NiO samples in the temperature range of 25-250°C. The electrical conductivity was increased with an increase of the testing temperature which indicated a semiconductor behavior. The conductivity of films increased for Pt decorated sample compared to as deposited sample. The activation energy values were calculated using Arrhenius equation. The calculated $E_a$ values for as deposited and Pt decorated sample were 0.38 and 0.32 eV, respectively.

![Figure 5-3: Semi-log plot of the conductivity ($\sigma$) versus reciprocal of the absolute temperature ($1/T$) of as-deposited and Pt decorated NiO thin film.](image)

The gas sensing of film depends on the adsorption/desorption mechanism of target gas molecules on the surface of NiO grains [50]. By introducing reducing gases to the chamber, target gases react with adsorbed oxygen molecules and as a result of this reaction, reaction products are produced and electrons are injected back to the grain.
Therefore, the resistance of the sensor increases. The reaction summaries for all of reducing gases in this study are listed below [18, 34, 35, 138, 139]:

\[
O_{2\text{(gas)}} \rightarrow O_{2\text{(ad)}}^-, \quad (5.1)
\]

\[
O_{2\text{(ad)}} + 2\overline{e} \leftrightarrow 2O^-, \quad (5.2)
\]

\[
H_2 + O_{\text{(ad)}}^- \rightarrow H_2O_{\text{(aq)}} + \overline{e}, \quad (5.3)
\]

\[
CH_4 + 4\overline{O} \rightarrow CO_2 + 2H_2O + 4\overline{e}, \quad (5.4)
\]

\[
2NH_3 + 3\overline{O}^\rightarrow \rightarrow 3H_2O + N_2 + 3\overline{e}. \quad (5.5)
\]

Different tests were collected to evaluate the optimum operating temperature for target gases for as deposited NiO sample. The gas sensor response was collected upon exposure to different target gases under dry air for the operating temperatures from 100 to 225°C. Figure 5-4 shows the sensor response values as a function of the operating temperature for 3000 ppm of CH$_4$ and H$_2$ and 75 ppm of NH$_3$. It can be seen that, the sensor response was the highest at 175°C for H$_2$, and CH$_4$. On the other hand, the sensor exhibited a maximum response at 150°C for NH$_3$. At low operating temperatures the low sensor response can be attributed to the low thermal energy of a target gas to react with the adsorbed oxygen. An increase in the response values was observed for all gases and sensor response reached to a maximum value in the temperature range from 150 to 175°C for all target gases. By further increasing the temperature to 225°C, the response values decreased for all gases which is due to the difficulty of an exothermic reaction at a high temperature and the increase in the desorption rate of adsorbed molecules from the surface of grains [111]. It has been reported that, there is an optimum operating temperature for most of semiconductor metal oxide gas sensors [21, 23, 72, 78].
Therefore, the operating temperature of 175°C was selected for further investigation and all other gas sensing measurements were collected at this operating temperature. It was observed that the sensor exhibited faster response and recovery times at a higher operating temperature, this data was published by this group in another study [140].

Figure 5-4: Gas sensor responses for different operating temperatures under 3000 ppm of $H_2$ and $CH_4$ and 75 ppm of $NH_3$.

Figure 5-5 shows the sensor response under different concentrations of target gases at 175°C. It can be seen that the response values increased with increasing target gas concentration. The NiO showed high response to $H_2$ and $NH_3$ and relatively low response to $CH_4$. The sensor response was satisfactory for 1000-3000 ppm of $H_2$ and $CH_4$, with safety factors of 13 and 5 compared to the other NiO-based gas sensor in its class, respectively [28, 70, 71, 74]. The sensor response was comparatively high under 25 ppm of $NH_3$ in a relatively low operating temperature (<200°C). It was mentioned that the TLV level of $NH_3$ is 25 ppm [18]. Therefore, the response values of 31% under 25
ppm of NH₃ were high enough to promote the NiO thin film as a practical ammonia NH₃ sensor.

Figure 5-5: Gas sensor response of NiO sensor under different concentrations of H₂, CH₄ and NH₃ at 175°C.

Figure 5-6 shows the sensor response for 1000, 2000 and 3000 ppm of H₂ and CH₄ at 175°C. Figure 5-7 (a) and 5-7 (b) show the calculated time constants for response and recovery processes for different concentrations of target gases at 175°C. It can be seen that both τ₁ and τ₂ values decreased with an increase in the concentration of target gas. This decrease in the sensor response time can be attributed to a higher pressure of impinging gas with an increasing of gas concentration [93]. In contrast, the rate of desorption is proportional to the surface coverage of gas molecules. Therefore, both time constant values decreased with increasing the concentration of target gases [141]. The sensor showed the smallest response time constant for H₂ and the longest recovery time constant for NH₃ among studied gases.
Figure 5-6: Dynamic response of NiO thin film for three concentrations of H₂ and CH₄ at 175°C.
Figure 5-7: The time constant values for different gases at 175°C: (a) response constant ($\tau_1$) and (b) recovery constant ($\tau_2$).

Figure 5-8 (a) and 5-8 (b) shows the sensor response for different concentrations of H$_2$ while passing 50 ppm of NH$_3$ and 3000 ppm of CH$_4$ at 175°C. One of the main challenges related to MOGS is designing a highly selective gas sensor [1]. Due to a nature of MOGS, the sensor responds to one or many gases in a gas mixture. For detecting target gas in a mixed environment using a MOGS, the sensor response and recovery speed can be used as effective parameters to detect a target gas. Also, filters can be used to make the sensor more selective in a different gas sensing application [37]. For example, using a SiO$_2$ layer on the top of the sensor allows only H$_2$ molecules to diffuse through the layer [9].

In order to study the effect of mixed gases on the gas sensing behavior of NiO thin film, H$_2$, CH$_4$ and NH$_3$ were selected to study the cross sensitivity measurements. A mixture of CH$_4$ and H$_2$ is used in combustion engines. It can be seen that the NiO sensor
showed a high selectivity towards H$_2$ and the response value increased up to 90% in a NH$_3$-H$_2$ mixture. But on the other hand, sensor response for H$_2$ in CH$_4$-H$_2$ mixture showed a less response (31%). Decrease in the response value can be explained by a decrease in adsorption sites and diffusion speed of gases in CH$_4$-H$_2$ mixture. Figure 5-8 (c) and 5-8 (d) show the gas sensor selectivity for CH$_4$ and NH$_3$. These two gas mixtures are important in gaseous emissions from biological aerobic treatment from piggery slurry and spreading of manure from dairy cows [144, 145]. It can be seen that the gas sensor had a good selectivity towards NH$_3$, but the gas sensor was not selective towards CH$_4$ while passing 75 ppm of NH$_3$. Also, the selectivity of NH$_3$ gas over H$_2$ was reproduced in another study by this group [56]. As mentioned earlier, selectivity is a major challenge in MOGS. Therefore, another observation of data can be used to detect specific gases in a mixture. It was observed that the gas sensor response changes with a change in the operating temperature. The gas sensor response increased for NH$_3$ up to 150°C and decreased with further increasing of a temperature up to 225°C. On the other hand, the gas sensor response to H$_2$ increased with an in the temperature from 150 to 175°C. These observations can be used effectively to further improve the accuracy and selectivity of the MOGS.
Figure 5-8: Cross sensitivity responses under different gas concentration of NiO sample at 175°C (a) H₂ in NH₃ (b) H₂ in CH₄, (c) NH₃ in CH₄ and (d) CH₄ in NH₃.

The gas sensing behavior of Pt decorated sample was studied towards hydrogen gas at different operating temperatures. The ability of the metal oxide gas sensor to detect different target gases depends on the interaction between gas molecules and the surface of the metal oxide grains. As mentioned in the chapter one, the gas sensing performance of
the sensor depended on its elemental composition, doping, and defect structures. It has been reported that the gas sensing performance of the sample can be improved using metal additives, such as Pt to improve the response of a sensor and decrease the operating temperature. The Pt metal improved the gas-semiconductor reaction by a catalytic effect. It has been reported that these noble metals have a higher sticking coefficient to gases compared to metal oxide and dissociate gas molecules over the grains (spillover zones). In the contact areas, the Pt particles acted as a catalyst and shortened the diffusion process of gas molecules; and increase the activity of gas sensing of metal oxide [24, 146].

Figure 5-9 shows the dynamic resistance response to different hydrogen concentrations for the Pt decorated sample at 25°C and 175°C respectively. It can be seen that the sensor clearly showed a Pt catalytic effect on the gas sensing performance of the sample. The Pt acts as a catalytic promoter which improved the reactions on the surface of metal oxide. Figure 5-10 shows the sensor response values for different hydrogen concentrations and the comparison between dynamic responses of the sensor at different operating temperature for 3000 ppm of hydrogen gas. It can be seen that the response values increased significantly at a relatively high operating temperature [146]. As stated in the previous section, the Pt particles were highly dispersed on the surface of NiO. [147]. Therefore, due to higher amount of reactive oxygen ion adsorption, the sensor response increases using a Pt catalyst in this study.
Figure 5-9: Response for 500, 1000, 2000 and 3000 ppm H\textsubscript{2} gas of Pt decorated NiO at (a) 25°C and (b) 175°C.
Figure 5-10: (a) Response to 1000, 2000 and 3000 ppm of H$_2$ for NiO-Pt sample as a function of working temperature and (b) Response and recovery graphs for 3000 ppm H$_2$ at different working temperatures.
5.4 Conclusions

In conclusion, NiO semiconductor metal oxide gas sensors were successfully fabricated using NiO films coated by a sol-gel process. The highest response was recorded in the range of 150-175°C for H₂, NH₃ and CH₄. The concentration dependence of the gas sensor response indicated that the NiO can be used to monitor the leakage of the hydrogen gas in the ambient conditions. The highest response was detected at 175°C for the H₂ gas. The gas sensor response was collected for different target gases and it was found that the gas type could be identified by using NiO based sensors. The cross sensitivity data also showed that the sample had a high selectivity towards NH₃ and low selectivity to CH₄. Furthermore, the sensor showed a high repeatability for a wide range of gas concentrations, such as H₂, CH₄ and NH₃. The Pt decorated sample was tested for different hydrogen gas concentrations at different operating temperatures. The Pt decorated sample showed significant higher response compared to as deposited sample at a different operating temperature. It was reported that Pt decorated sample could be used in a room temperature for hydrogen gas sensor applications.
Chapter 6

Conclusions and Recommendations

This chapter is devoted to conclusions and main findings of this research project and future recommendations for this investigation.

6.1 Conclusions

NiO thin films were fabricated by a sol-gel coating technique on a non-alkali glass substrate. The microstructure of the film was characterized by XRD, SEM, TEM techniques. The electronic and gas sensing properties indicated that the NiO film had a p-type conductivity with a low thermal activation energy. Also, the band gap of the materials was within the values reported in the literature. The sensor response was depended on the concentration and testing temperatures. Therefore, all parameters could be optimized to manufacture a gas sensor to monitor H₂, ammonia, methane and other reducing gases in the air at a low operating temperature. Here, it was demonstrated that the H₂ gas could be detected in a wide range of concentrations. The gas sensing properties of NiO sensors indicated that the gas sensors could be operated below 200°C.
with reasonably fast response and recovery times. The concentration of H\textsubscript{2} below 0.1 % in an ambient condition can be easily detected with NiO thin film-based sensors.

Special efforts were made to enhance the porosity of the NiO films. The structural, electrical and sensing properties of the prepared film were investigated as a function of film fabrication method, testing temperature, and H\textsubscript{2} concentration. The gas sensor response was temperature dependent, and the highest response was observed at 175°C for H\textsubscript{2} gas. It was found that the NiO films had several important sensor characteristics, such as repeatability, high response, and fast response/recovery times to H\textsubscript{2} gas. The overall recovery times of the sample were decreased by increasing operating temperatures >175°C. It was also found that the thickness and porosity of the film were two important parameters, which affected the main gas sensing characteristics of NiO based H\textsubscript{2} sensors. The measurements revealed that the sensor response decreased by increasing the thicknesses of films. The maximum sensitivity of 68% was measured at 175°C for 3000 ppm of H\textsubscript{2} for a multi-step annealed sample. The sample showed low humidity dependence in a normal humidity condition (35%).

In another study, pulsed laser irradiation on NiO film was employed to improve the gas sensing properties. Different laser power levels were tested to understand the effect of laser irradiation on the gas sensing property of NiO films. At an optimal laser power level, the laser-irradiated sample showed higher response and faster recovery times than the as-deposited sample. The result of this investigation suggests that the laser irradiation technique is a general and applicable method for NiO based gas sensors. Furthermore, the authors believe that this study will influence further improvement of metal oxide gas sensors by laser treatments in future.
The cross sensitivity measurements were carried out to investigate the gas sensing performance of the NiO gas sensor in a mixed gas environment. The highest response was observed in the operating temperature range of 150-175°C for H₂, NH₃ and CH₄. The concentration dependence of gas sensor response indicated that the NiO could be used effectively to monitor target gases quantitatively. The gas sensor response was collected for different target gases, and it was found that the gas type could be identified by using NiO based sensors. The cross sensitivity data also showed that the sample had a high selectivity towards NH₃ and low selectivity to CH₄. Furthermore, the sensor characteristics indicated good repeatability for different target gases. The Pt decorated sample was tested for different hydrogen gas concentrations at different operating temperatures. The Pt decorated sample showed significant high response towards H₂ gas compared to as deposited sample at different operating temperature. It was reported that the Pt decorated sample could be used at room temperature for hydrogen gas sensor applications.

6.2 Future Works

It is suggested that several main properties can be investigated in detail. First, the gas sensor behavior of the device should be studied for more target gases and the sensor response should be recorded for each gas in wider temperature ranges. Second, an array of sensors can be designed and used to collect data at several different operating temperatures. These data can be analyzed and compared with reference gases to identify each target gases. The technique is called electronic nose. This method can improve the selectivity of the gas sensor in a mixed gas environment. Third, the sensor performance
can be improved by doping different elements to investigate the effect of doping agent on the gas sensing performance of NiO thin film. Fourth, several arrays of sensors operating in different operating temperatures can be used to improve the selectivity of the sensor.

Finally, industrial and economic considerations in designing and fabricating different metal oxide thin films should be considered.
References


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