بسم الله الرحمن الرحيم

STRUCTURE AND ELECTRIC BASED GAS SENSING IN ANTIMONY DOPED ZnO MICRO-WIRES

بنية و حساسية أسلاك النانو المصنعة من أكسيد الزنك والمطعمة بعنصر الأنتيموني اتجاه الغازات

by

Alaa Ali Ismaeel Gezzawi

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This Thesis was submitted in partial fulfillment of the requirements for the Master's Degree in physics from the Faculty of Graduate Studies at Birzeit University, Palestine

2020

Advisor: Dr. Khalid F. Eid

Member: Dr Hazem Abu Sara

Member: Prof. Wael Karain

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Decleration

I, Alaa Ali Ismaeel Gezzawi, declare that this thesis titled, ‘Structure And Electric Based Gas Sensing in Antimony Doped ZnO Micro-Wires’ and this work presentedin it are my own

Dr. Khalid F. Eid (supervisor)

Prof. Wael Karain (Member)

Dr. Hazem Abu Sara (Member)

ABSTRACT

STRUCTURE AND ELECTRIC BASED GAS SENSING IN ANTIMONY DOPED ZnO MICRO-WIRES

By Alaa Ali Ismaeel Gezzawi

This thesis discusses the effect of Oxygen, Hydrogen and Nitrous Oxide gases on the electric conductance of Sb-doped ZnO micro-wires. The micro-wires have a ZnO core and a Sb-rich ZnO shell. The resistance of these wires is quite sensitive to light, temperature and gas environment. The three parameters seem to affect the conductance of the micro-wire through the same mechanism This electric conductance of ZnO:Sb micro-wires has a rich behavior that can be utilized in sensing applications because it is sensitive to different kinds of gases. The latter allows the use of these wires as gas sensors. This thesis will focus on studying the gas-sensing properties of ZnO:Sb towards H_2, O_2 and N_2O gases as well as the structure of these Sb doped ZnO micro-wires. The conduction mechanism depends on simple potential divider circuit connected to a (My DAQ). The DAQ is connected to a LabVIEW program to measure the voltage of the sample and calculate its resistance using a simple equation. DAQ is also used to measure the temperature on a second channel. To provide Nitrous gas we get it from a jar with a regulator. Hydrogen and Oxygen gases were performed by electrolysis of water. Then we used thin tubes to provide these gases to the sample.

ملخص

بنية و حساسية أسلاك النانو المصنعة من أكسيد الزنك والمطعمة بعنصر الأنتيموني اتجاه الغازات

بواسطة آلاء علي اسماعيل غزاوي

تتناول أطروحة هذه الرسالة تأثير غازات الأكسجين والهيدروجين وأكسيد النيتروس على التوصيل الكهربائي لأسلاك المايكرو المصنوعة من أكسيد الزنك. هذه الأسلاك تتكون من أكسيد الزنك في مركز السلك ومحاط بطبقة من نفس الأكسيد المطعم بالأنتيموني . مقاومة هذه الأسلاك حساسة للغاية للضوء ودرجة الحرارة والغاز المحيط . هذه العوامل الثلاثة تؤثر على موصلية هذا السلك من خلال نفس الآلية. هذا التوصيل الكهربائي لأسلاك أكسيد الزنك المطعم بالأنتيموني له سلوك مهم ولافت يمكن استخدامه في تطبيق أجهزة استشعار لأنه حساس لأنواع مختلفة من الغازات. حيث يمكن استخدام هذه الأسلاك كجزء من أجهزة استشعار الغاز. ستركز هذه الرسالة على دراسة حساسية أسلاك المايكرو المصنوعة من أكسيد الزنك المطعم بالأنتيموني اتجاه غازات H_2 و O_2 و N_2O وكذلك البنية التفصيلية لهذه الأسلاك، ولحساب مقاومة سلك أكسيد الزنك المطعم بالأنتيموني، يتم وصلها مع دارة تقسيم جهد ، ويقوم جهاز (My DAQ) بقياس فرق الجهد بين طرفي السلك، ومن ثم حساب مقاومته بواسطة معادلة رياضية بسيطة، ويقوم أيضا بقياس درجة الحرارة في نفس الوقت على قناة أخرى. ويتم تزويد العينة بغاز النيتروس من خلال جرة معبأة به، أما بالنسبة لغاز الأكسجين والهيدروجين فقد حصلنا عليهما من خلال تحليل الماء. ثم استخدمنا أنابيب رفيعة لتوصيل الغاز الى العينة.

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To my lovely husband, Mahmood

And my sweet daughters Donia and Khlood

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1 INTRODUCTION

1.1 Introduction to ZnO

Many metal oxides are suitable for detecting flammable, toxic, reducing or oxidizing gases by conductive measurements. Metal oxides such as Mn_2O_3, CdO, TeO_2 Co_3O_4, NiO, SrO, TiO_2, In_2O_3,WO_3 and ZnO - the sensor which is the subject of my thesis - attracted much attention in recent years because of their low cost, high sensitivity , easy fabrication methods, and simplicity of their use[1]. The performance of the sensor towards a specific gas depends on the materials, morphology and fabrication process. It also depends on the surface properties and electronic structure, so the base such as Zn, Ti or Te materials in metal oxide will change the factor influencing the surface reaction (such as chemical components, surface modification, temperature, and humidity)[1,2].

1.2 Surface Conduction and oxygen vacancies

It is demonstrated that the electrical properties of high resistivity of ZnO material are dominated by the surface [3], But, The mechanism through which the surface of ZnO:Sb and other metal oxides conduct electricity is still debatable. Two prime suspects causing the higher surface conductivity are oxygen vacancies and unintentional hydrogen doping [4,5]. Oxygen vacancies are the most likely invisible agents of oxide surfaces, where the conductivity of semiconducting metal oxides seems to come from the adsorption and desorption of O_2 molecules, and that the adsorbed O_2 molecules diffuse across the surface to find a vacancy -which is a fingerprint of the oxide electronic structure-, where they fill that vacancy producing an O atom adsorbed on the nearest metal atom. The color, the conductivity, the strength, or any other properties of the conductor are controlled by faults, defects or dislocations in the structure. The oxygen vacancy is one of the most important and relevant defects in many oxides. Depending on the material, defects can change the structure and properties of oxygen vacancies and are often elusive species, highly diluted and difficult to detect so that experiments should be made to study their effects [6].

1.3 Properties of ZnO and some of its potential uses

Before discussing acceptor-doped ZnO, we should enumerate the electrical and optical characteristics of undoped ZnO. It is a transparent semiconducting metal oxide [1] with a direct band gap (Eg=3.37 eV) and a large excitation binding energy (60 meV)[7] which permits excitonic emission at room temperature and above[8]. ZnO is a promising material for electronic and optoelectronic devices due to its fascinating physical properties (e.g., wide band gap, high excitonic binding energy, high saturation velocity, good conductivity, large piezoelectric field and exhibiting near UV emission) and its ability to grow into nanostructures (e.g., nano-rods[9], nano-tubes[10], nano-fibers[11], nano-wires [12] nano-belts[13] and other nano-structures.

Nanostructures of ZnO have attracted the researchers' attention because of their high surface to volume ratio, minimal power consumption, low weight, low toxicity, good thermal and chemical stability, good oxidation resistibility, good biocompatibility and high electron mobility [14].

ZnO can be used in different types of sensors (i.e., biosensors, pH sensors, UV sensors, and gas sensors). It is sensitive to reductive (H_2 [15], NH_3[16], CH_4, CO[17], CO_2,H_2S), oxidative (NO_2, NO[18], N_2O[19],O_3 and O_2) and volatile organic compounds (VOCs)(i.e.; methanol, ethanol, acetone, butane,..) [20]- Organic gases are also considered reductive gases -.

A major problem with ZnO is that it is typically an n-type material. It is difficult to achieve reliable, stable and low- resistivity p-type doping in ZnO. Yet, such p-type doping can be made under a set of experimental conditions like vacuum or darkness [3,21,22].

1.4 Antimony-doped ZnO

Antimony-doped ZnO can be grown using a simple thermal evaporation process of ZnO and Sb_2O_3, In this work, ZnO:Sb fiber was grown in an alumina crucible by a catalyst-free, low-cost thermal evaporation process. [23]. Hot probe measurements of single micro-wires show a stable n-type behavior for Sb-doped ZnO[24]. Figure 1.1 shows SEM images of as-grown ZnO:Sb wires.

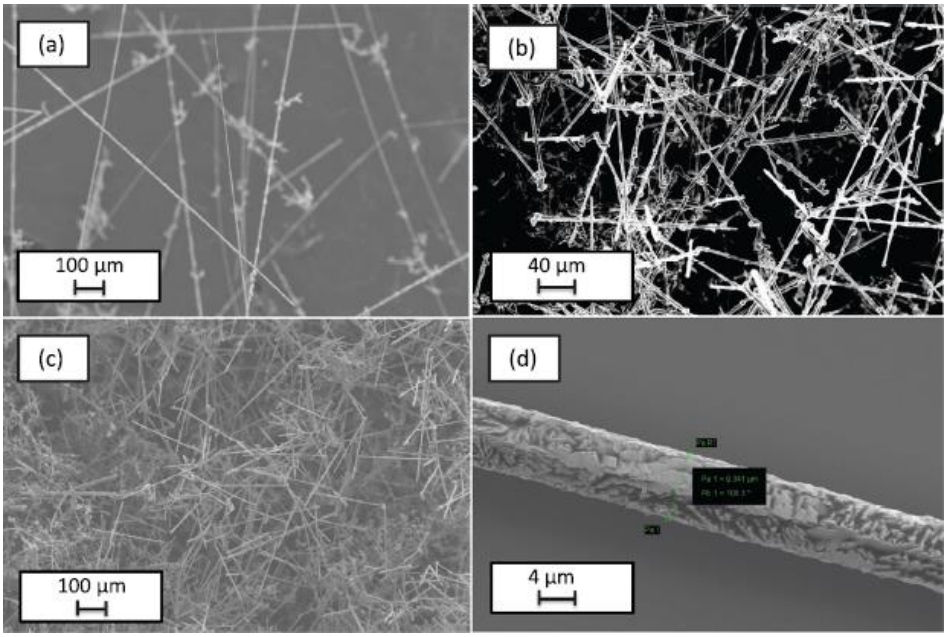


Figure 1.1 SEM images of the as grown ZnO:Sb wires: (a)about 2 cm long wires and a diameter of 5-8 micrometer, (b) about 5mm long wires and diameter of 3-5 micrometer, (c) about 2 mm long wires and a diameter of 0.1-1 micrometer, and (d) high-magnification SEM image for individual wire[24].

1.5 ZnO:Sb wire

Each ZnO:Sb wire contains between 5 and 7 at. % Sb relative to ZnO, indicating chemically stable ZnO:Sb wires , the fibers were consists of two portions: The Sb-rich part and the Zn-rich part. The Zn-rich part with about 4-5 at.% of Sb is Sb doped ZnO .The Sb rich part exists as small crystals at the surface of the Zn stem and consists of two compounds: ordonezite ($ZnSb_2O_6$) and zinc antimony oxide ($Zn_7Sb_2O_{12}$) [25,26].

Zn atoms have 41-43 at. % while O atoms have about 51-53 at. % of the total composition. So Sb atoms have likely occupies Zn sub-lattice sites in ZnO:Sb nano- and micro-wires[26,27,28].

1.6 Nitrous oxide

1.6.1 N_2O chemical properties

Nitrous oxide (N_2O), also known as dinitrogen monoxide and laughing gas, is a colorless toxic non-flammable gas with an asymmetrical linear structure (N =N =O).It has a boiling point of (-88.5^{o} C) , a molecular weight of 44.01 g.mol^{-1}

[29] ,is an endothermic compound ($\Delta_f H_{o298}$ = +82.05KJ.mol^{-1}) [30], and is one of the most important oxidizing agents[31].

1.6.2 N_2O uses and emission sources

N_2O emissions come from three main sources: 1) The most common source is nitrification and denitrification processes by fertilizers used in agriculture.2) Biological sources of digestion and decomposition. 3) Industrial production, including medical use and diesel motor vehicles equipped with catalytic converters [32].Medical use of N_2O was a new era in dentistry, as it removes pain, so it was used as anesthetic for many years. Although medical N_2O emission contributes less than 0.05% to the total greenhouse emission per year, anesthetists and all should be aware of its pollution effects and its toxicity. For personal health, it was found that nitrous oxide interacts with vitamin B_{12} and folate cycle, which affects methionine synthase. Methionine synthase directly affects DNA manufacturing; so long term exposure to nitrous oxide causes bone-marrow depression and central peripheral neuropathy. Besides, nitrous oxide is one of the main gases causing global warming through its conversion to nitric oxide in the stratosphere which contributes to ozone destruction [30]. For these two reasons, nitrous oxide should be detected especially in the anesthesia room. So far, analytical instruments based on infrared spectrophotometry and photoacoustic spectroscopy have been available for the detection of N_2O, but those instruments are expensive. Instead an inexpensive N_2O sensor, if possible would be better.

1.7 Motivation

These situations motivated us to study the sensing characteristics of ZnO:Sb towards N_2O, H_2 and O_2 gases. For many years ZnO has been extensively studied theoretically and experimentally, while ZnO:Sb also showed some success making both of them promising candidates for future electronic and optoelectronic devises. Different experiments on metal oxide-based sensors were made. Pure ZnO shows high sensitivity to N_2O [18], In this thesis, my experiment tests the sensitivity of Sb-doped ZnO individual micro-wires towards N_2O and O_2 gases (oxidizing gases) , as well as H_2 gas (reducing gas). I will study their effect on the resistance of this micro-wire, hoping that will help manufacturing new and inexpensive gas sensors.

2 Theoretical background

Temperature, light illumination, and the ambient gas composition/abundance affect the resistance of ZnO:Sb. ZnO nanostructures are a promising material for chemical gas sensors due to high chemical stability and the simplicity of its preparation. It has been prepared by different methods such as sol-gel [33] radio frequency (RF) sputtering [34], and oxidation of Zn metal [35]. This chapter presents a theoretical background about the mechanisms that control these changes on ZnO and Sb doped ZnO.

2.1 ZnO conductivity

It is proposed that holes from hole electron pairs discharge lattice oxygen ions at the surface, producing a surface excess of zinc and an electron enrichment layer in which conduction occurs, and the conductivity is associated with the surface[36]

Different theories have been developed to explain the surface conductivity of ZnO. Scientists showed that there is an inverse relationship between conductivity and the presence of oxygen; this would suggest that V_O (oxygen vacancy) or excess Zn is responsible for this conductivity. V_O has been ruled out as a major shallow donor, although Zn_I (interstitial Zn) complexes have not[37], other experiments showed that V_O is a deep donor that cannot cause n-type conductivity in ZnO, and that native acceptors influence electrical conductivity through compensation[38], Alternatively, SIMS measurements suggest an accumulation of group Ⅲ donors may instead be the cause of the surface conductivity [37].More recently, a first-principles investigation based on density functional theory puts forward an evidence of hydrogen (H donors, particularly the form of H_O) as a responsible factor for the conductivity of ZnO [37,39,40,41]. In contrast to the other semiconductors where interstitial hydrogen has been found to act as an amphoteric impurity (an impurity that prevents hydrogen acting as a source of conductivity) hydrogen acts as a shallow donor in ZnO [39,42],

2.2 Photoconduction and surface effect

When a ZnO:Sb micro-wire is exposed to visible light (or any light wavelength) its resistance decreases rapidly for the first few seconds and then continues to decrease at a slower pace, where it finally attains a stable value. This behavior of ZnO:Sb wires

attempting to remain in a high conductance state after the removal of light illuminating source is a clear indication of persistent photoconductivity. after turning off the light source the resistance gets back its original value in a very slow manner, the energy of any visible light is enough to free oxygen atoms from the surface and impact the resistance to the same level regardless of the actual wavelength since the light energy is much larger than the energy bond for the atoms [42].

In the dark a depletion layer of low conductivity appears near the surface, because the adsorbed oxygen captures an electron and becomes negatively charged. When light absorbed near the surface it discharges the oxygen ions and the adsorbed oxygen layer is desorbed releasing electron. Then the depletion layer is destroyed and the consequent increase in conductance results F.or a single crystal, it seems that hydrogen reduces the crystal surface to give zinc atoms [36]. It is possible that atomic hydrogen is the reason behind reducing the resistance of the micro-wire when exposed to light.

In an n-type semiconductor, such as ZnO, A negative charge at the surface causes the conduction band near the surface to bend upward away from the Fermi level and reduces the electron concentration. This region is called the depletion layer. A positive charge on the surface bends the conduction band down toward the Fermi level and for ZnO increases the electron concentration producing an enrichment space-charge layer. The photolysis can occur when the holes, from hole-electron pairs generated by light, discharge surface lattice oxygen ions leaving an excess of zinc at the surface (see fig 3.1). The conductivity so produced is similar to that resulting from the adsorption of zinc atoms from the vapor. The dependence of the rate and magnitude of the change in conductivity on the ambient conditions clearly indicates the importance of surface effects [36]. Under illumination two components of photo-response are observed: (i) usual photo-conductance caused by photo-carrier generation; (ii) conductance caused by accumulation of electrons in depletion layer due to oxygen photo-desorption [43].

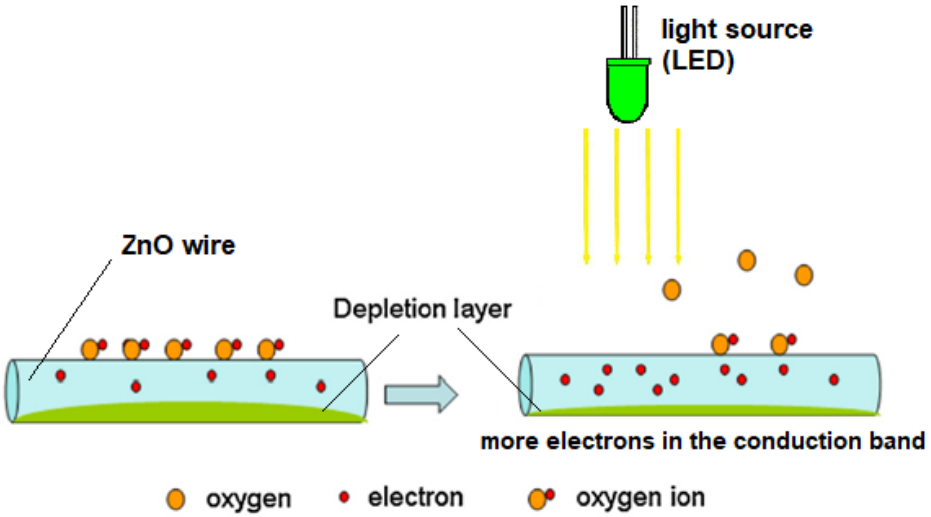


Figure 2.1: effect of light illumination on ZnO wire

2.3 Temperature dependence of photoconductivity of single ZnO micro-wires

The resistance of the micro-wire decreases significantly when the temperature rises. Both temperature and resistance took some time to attain stable values see (Figure 4.2). Once the temperature stabilized, the resistance also became stable. The cause behind this significant reduction of resistance of ZnO:Sb micro-wire with the increase of temperature is desorption of oxygen from the surface of the wire. Since the value of thermal energy at 150 °C for example, (i.e. KBT= 0.0365 eV) is far less than the bandgap energy of ZnO:Sb (3.4 eV), there is no possibility of transferring electrons from the valence band to conduction band due to thermal energy itself. The mechanism of freeing adsorbed oxygen atoms is the only plausible explanation of this behavior. When the wire is heated, the thermal energy causes the loosely adsorbed oxygen atoms to desorb from the surface so, more electrons become free and available for conduction, leading to a decrease in resistance [42].

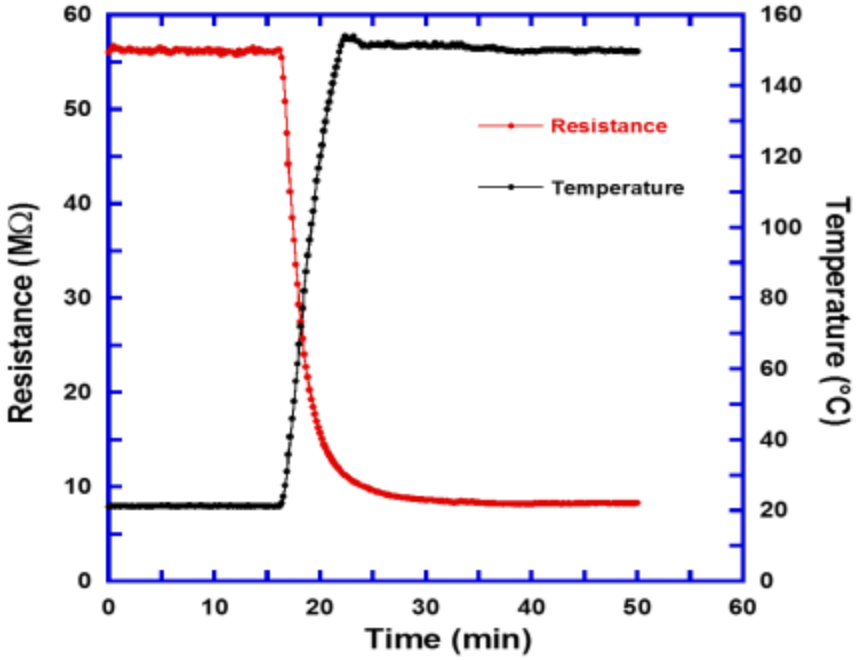


Figure 2.2: Resistance variation of a single ZnO:Sb micro-wire as the temperature rose from 20 oC to 150 oC in the absence of light[42].

2.4 Combined effects of temperature and light illumination

It is found that persistent photoconductivity exists and it decreases with decreasing temperature, the photosensitivity is found to be linear with the applied voltage, and it increases with decreasing temperature [44]. Under light illumination, a slight decrease in the resistance of the wire occurs with increasing temperature, while a much stronger dependence occurs at the absence of light. Furthermore, the resistance drop associated with light exposure is the same as that due to raising the temperature. The desorption of oxygen from the wire surface is the mechanism that impacting the resistance in both cases [42]. However, the light illumination immensely affects the surface conductivity of ZnO:Sb wire at room temperature but its effect is insignificant at 200℃ or above. This might be because the thermal energy already saturates the same phenomena that the light illumination causes so that there is nothing more to do by the visible light at 200℃[42].

2.5 ZnO and gas sensing

ZnO is a metal oxide semiconductor that is hypersensitive to gases; the sensing mechanism depends on the change of the resistance of the semiconductor in the presence of the gas under test, for oxidative gases such as oxygen, the adsorption of the gas lead to an electron transfer between the ZnO surface and the adsorbed oxygen. The oxygen molecule from the ambient atmosphere are initially at the ZnO surface follows by the extraction of electron from the conduction band of the ZnO material, the oxygen molecule is then converted to a single or double oxygen ion and become ions adsorbed on the surface. This leads to a decrease in the electron concentration in the ZnO surface and consequently the increase in the resistance. The reaction of these gases such as Hydrogen or hydrocarbons or any reduction gases with the adsorbed oxygen will result in the release of the captured electrons back to the conduction band thereby increasing the electron concentrations, which in turn decreasing the resistance (see Fig 3.3 and Fig 3.4)[45].

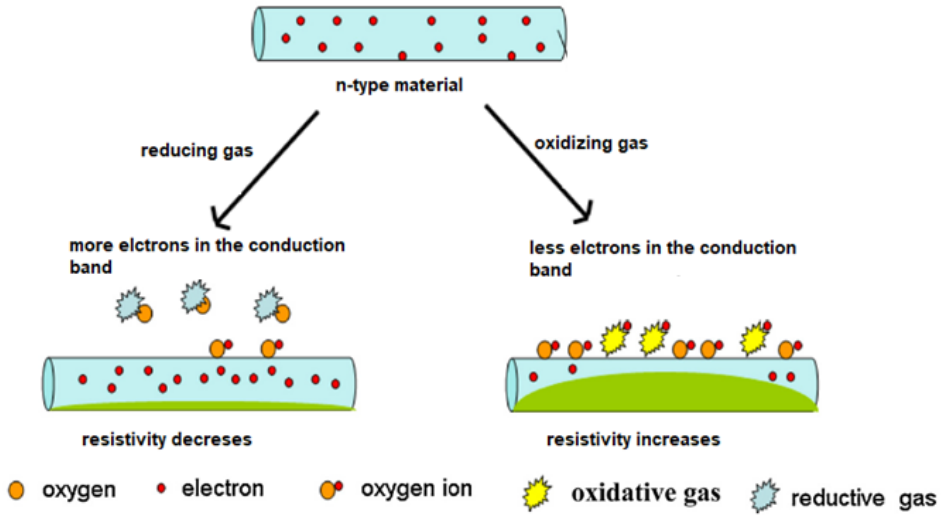


Figure 2.3: Effect of chemo-sorption of oxidizing and reducing gases on the n-type semiconductor material

As mentioned earlier, the ZnO gas sensor adsorbed oxygen from the surrounding atmosphere on its surface and extracts electrons from its conduction band to form O^{2-} species on the surface, and depending on the surface temperature of the sensor these oxygen molecules converted to one of the following ions [46, 47]:

$O_2(gas) \Leftrightarrow O_2(adsorbed)$

$O_2(adsorbed) + \bar{e} \Leftrightarrow O_2^-$

$O_2^- + \bar{e} \Leftrightarrow 2\bar{O}$

which lead to the increase in the resistance. on the other hand, when a reducing gas (R) like Hydrogen is introduced, it reacts with the adsorbed Oxygen to form RO, which supposed to release the electrons from the oxygen ion to the conduction band of ZnO, leading to the reduction in the resistance of the micro-wire (see fig 3.3 and Fig 3.5). This could be expressed as following [47, 48]:

$R + O2- \Rightarrow RO + 2\bar{e}$

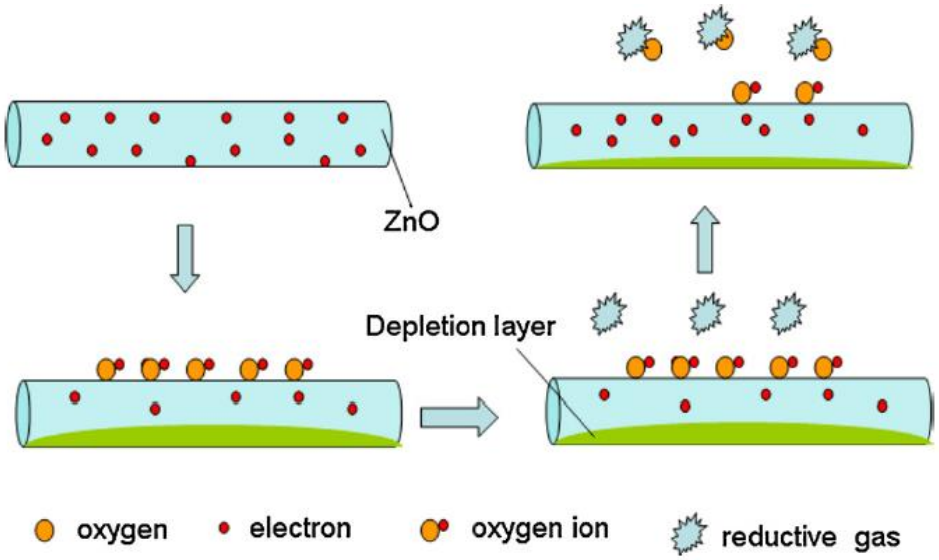


Figure 2.4: The schematic image of the reductive gas ZnO sensor [13].

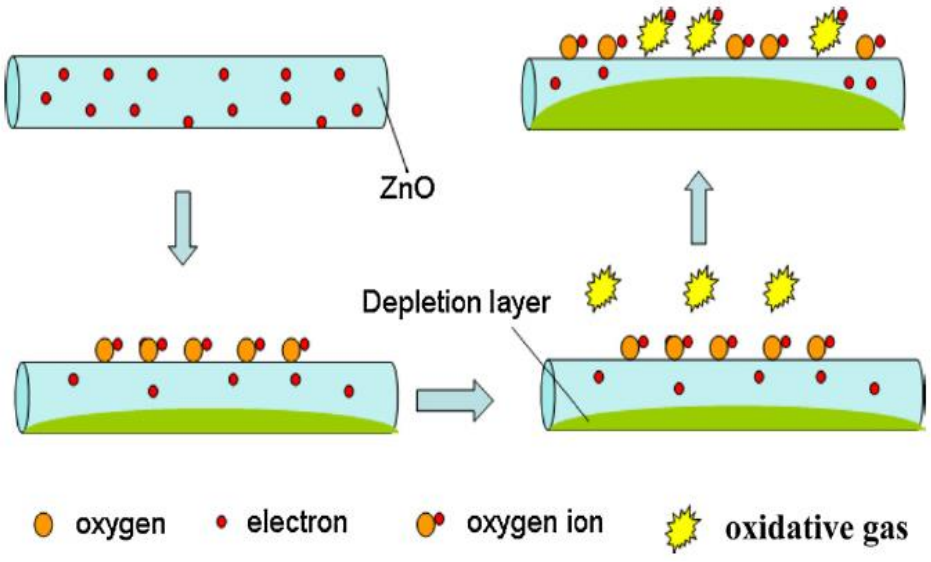


Figure 2.5: The schematic image of the oxidative gas ZnO sensor [13].

The morphology of ZnO can vary from nano-rods, nano-tubes and nano-needles to nano-injector, nano-helixes and nano-disks. So that ZnO nanostructures can be based upon to construct functional devices as gas sensors, chemical sensors, biosensors, UV sensors, pH sensors and other sensors with different sensing mechanisms. However, high selective response still remains a great challenge, and a sensor should pass many tests to be sorted as an efficient sensor, and the parameters of sensors are [13]:

1) The sensitivity of a sensor: is defined as the ratio of the change amplitude of a sensor signal to the original amplitude, which is defined as:

$$S = \frac{\Delta R}{R} \times 100\%$$

Where ΔR is the change amplitude of the sensor signal, and R is the amplitude of the original signal. The signal could be the resistance, current, voltage or conductance, etc.

2) Response time and recovery time:

Response time is the time taken by a sensor to achieve 90% of the total signal change.

Recovery time is the time taken by a sensor to achieve 90% of its original signal state.

3) Detection limit: is the lowest amount of the object which the sensor could have a response to.

4) Selectivity: it means how well it responses to a certain gas compared to other gases. The pure ZnO has poor selectivity. But defects and the introduction of certain functional groups to affect the adsorption processes can improve its selectivity.

5) Stability and reproducibility: is the change of sensing behavior after numerous times of switching between ‘ON’ state and ‘OFF’ state.

3 EXPERIMENTAL DEITAILS

3.1 Sb-doped ZnO micro-wires

The Sb-doped ZnO micro-wires used in this thesis were grown previously at Miami University, USA using a simple thermal evaporation process [23,50]. While Sb-dopant has been predicted to produce a p-type behavior of ZnO, hot probe measurements showed clear n-type conduction in all of them[24]. One main problem we faced is that the micro-wires that were grown at Miami were mostly destroyed on the way to Birzeit. While these wires were as long as 3 centimeters initially, the longest fragments of wires are only 1mm in length when they arrived. Nonetheless, we were able to connect several wires and study them successfully. Each wire was connected in series to a 1.5V battery and an external resistance to form a voltage divider used to measure the electric resistance of the wire. The process to connect and study these wires

3.2 Connecting single Sb-doped ZnO micro-wire

A. The sample of Sb-doped micro-wires was connected from both sides to a very thin copper wire using silver conductive adhesive epoxy. Chemtronics cw2400; conductive epoxy, (shown in Fig. 2.1). The epoxy application and curing process was as follows:

Figure 3.1 Silver conductive adhesive epoxy: A 2 part electrically conductive silver epoxy for general purpose prototype, repair and rework applications. That is quick to set, and has excellent electrical conductivity.

1. We first mixed one drop from the two parts(A and B) of the conductive epoxy on a piece of aluminum foil and saved it for later steps (it should be consumed before it dries)
2. A thin copper wire with a very small drop of our mix was used as a carrier to the ZnO micro-wire.
3. A sample of the micro-wires were placed under the lens of microscope
4. One micro-wire was chosen and transmitted using the copper wire and placed on a piece of glass.
5. This micro-wire was connected from both sides with two thin copper wires using the epoxy mix made before.
6. The sample was annealed at T= 50℃ for 10 minutes.
7. Now the sample (the micro-wire) is connected from both sides to thin copper wires as shown below in Fig. 2.2 and ready to be connected to other parts of the circuit.

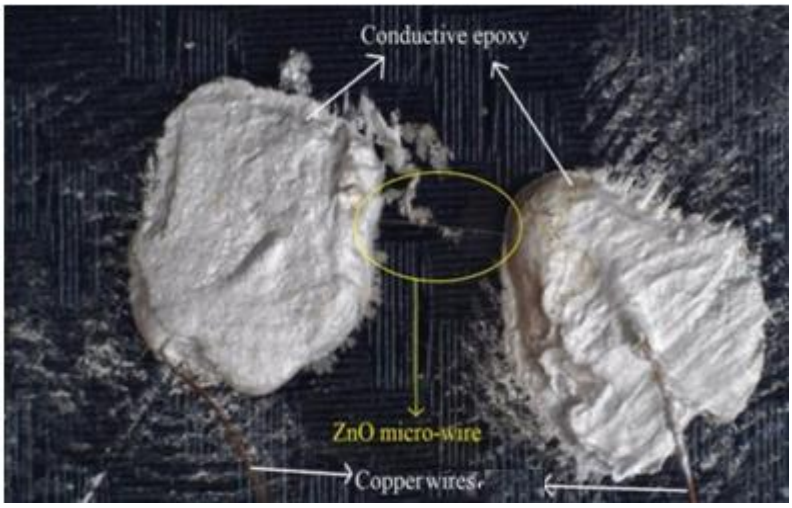


Figure 3.2 An individual ZnO:Sb : two copper wires connected to the ZnO:Sb on a glass substrate using conductive epoxy.

B. The wire was then connected to a 1.1 MΩ resistor and a D-cell battery to form a simple potential divider circuit (see Figure 2.3). The voltage drop of the sample V_{out} was measured using a National Instruments Data Acquisition (My DAQ) unit and a LabVIEW program - it is organized to collect a rate of 100 points per second-, which was

controlled by a PC in order to find the resistance of the micro-wire . If a resistance R_1 is connected in series with the ZnO micro-wire with a DC voltage source (ε), the unknown resistance of the ZnO wire could be found using the equation

$$R_{ZnO} = R_1 \times (\frac{V_o}{\varepsilon - V_o}).$$

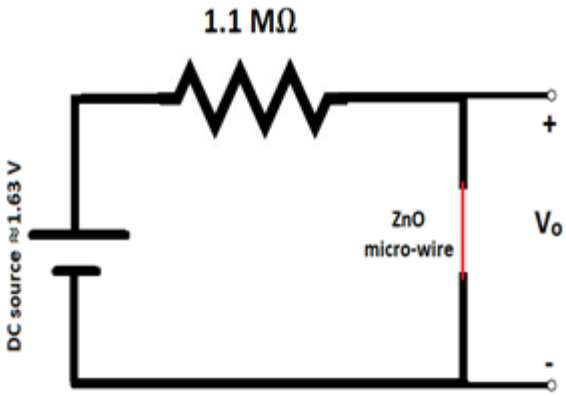


Figure 3.3 A cartoon of the potential divider circuit for the electrical resistance measurement of individual ZnO:Sb micro-wires.

3.3 LabVIEW program

The Labview program was used to perform the measurement and the analysis is shown in appendix A.

3.4 Setup

The sample was put in a tightly-closed glass container (see Fig 2.5)

1. All the wires were inserted in the glass container through small holes on its side.
2. KOSOO excellent insulating heavy wall heat shrink material was used to cover the wires that might meltdown (it is shown in Figure. 2.4).

Figure 3.4 KOSOO material:

This provides maximum reliability for insulation and protection to cable joints and te rminations.

3. The entire set up was covered with aluminum foil to keep the sample in darkness (Figure 2.6).
4. The gas was injected inside the container through a small hole with an inlet in the side of the container, (see Figure 2.5).

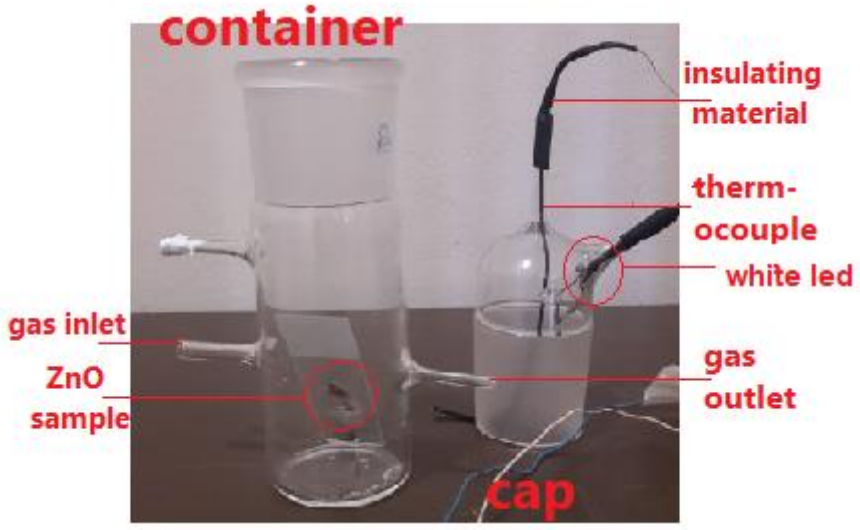


Figure 3.5: the glass container and its cap next to it: We have the ZnO sample inside the container and a hole designed to get gas inside the container, a gas outlet thermocouple and a LED.

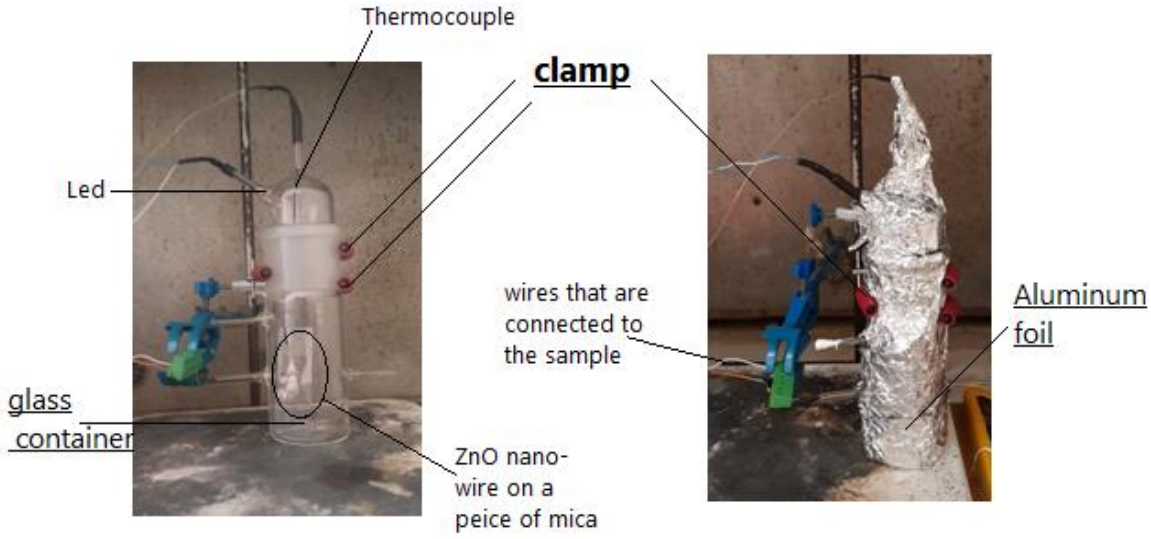


Figure 3.6: During the experiment: Left: ZnO micro-wire inside a glass container. Right: the glass container covered with aluminum foil.

3.5 Supplying oxygen and hydrogen

Hydrogen and Oxygen gases were produced using electrolysis of water to separate hydrogen from oxygen and we made two designs to provide them to the sample: A plastic model and a glass model.

3.5.1 Plastic Model

The plastic model is shown in Figure 2.7:

a. The set was made from two plastic bottles, opened and connected with a plastic tube.
b. Two graphite electrodes were inserted at the bottom of each bottle.
c. The two electrodes were connected with wires outside the bottles with a DC source. (The larger the voltage applied the larger amount of Oxygen and Hydrogen provided).
d. The bottles were filled with a solution of water and sodium chloride (table salt).
e. When a DC voltage was applied, the separation of Oxygen and Hydrogen started.

f. Oxygen will gather in the bottle where the positive electrode was inserted (the anode)
g. Hydrogen will gather in the bottle where the negative electrode was inserted (the cathode).
h. A thin tube was used to transfer Oxygen to the ZnO sample, and another tube to transfer Hydrogen.

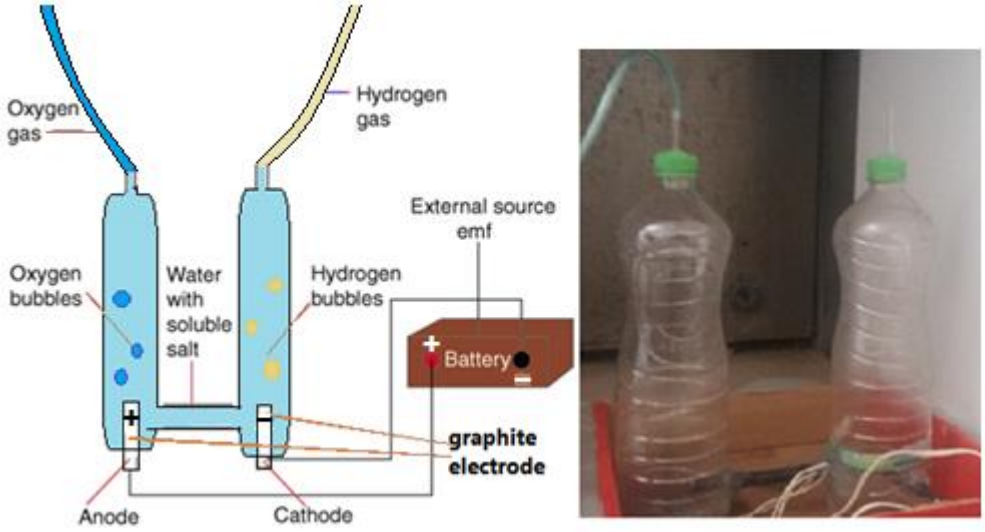


Figure 3.7: water electrolysis: Hydrogen gas gathers at the cathode and Oxygen gas gathers at the anode. This is the plastic design.

3.5.2 Glass Model

When the experiment got not expected results, as we will see in chapter3, we made a new design for electrolyses made of glass (see Figure 2.8), to make sure that plastic did not affect our result. However, we got the same results for both designs.

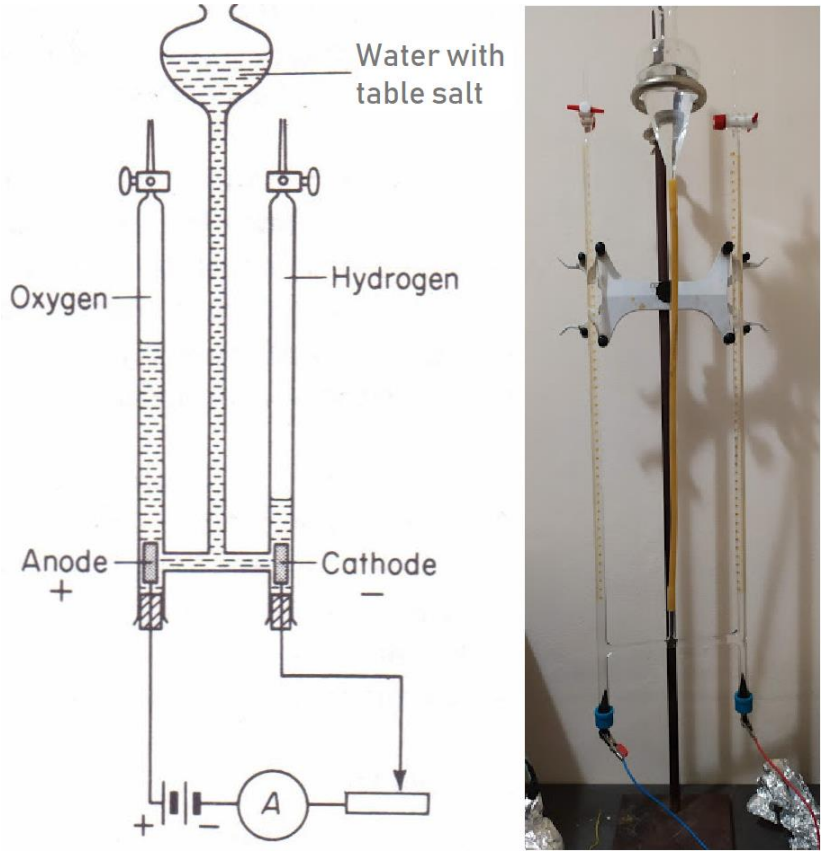


Figure 3.8: Hofmann design for electrolysis: Hydrogen gas gathers at the cathode and Oxygen gas gathers at the anode. This is the glass design.

My Hofmann design consists of two graduated tubes fitted with taps and provided with graphite electrodes. The tubes are connected near the bottom by a short cross tube which has an upright tube and reservoir.

In order to start the electrolysis of water, the taps are opened, and water to which few amount of table salt have been added is poured in until the graduated tubes are both full. The taps are then closed and current is passed through the setup from a 20 V battery. The current is adjusted to give a stream of bubbles from the electrodes. When sufficient gas has collected it was transferred to the sample using a thin tube

3.6 Light Illumination

Super LEDs were used to control the light exposure on the sample, they were added at the top left of the glass container, (see Fig 2.4). Different colors of LEDs were used, (see Figure 2.9).

Figure 3.9: Different LED colors.

3.7 Heat Source

The entire setup was placed on a hot plate to change the temperature of the sample; a thermocouple is inserted from the top hole (see fig 2.4) to measure the temperature inside the container. The thermocouple was connected to the second channel of the DAQ to measure the resistance and temperature at the same time.

3.8 Nitrous Oxide

Finally, to provide Nitrous oxide to the sample, a nitrous oxide jar was connected with a regulator then to a thin tube connected with the glass container (See Figure 2.10). The regulator was used to control the flow of N_2O gas that is going inside the container.

Figure 3.10: the N_2O gas jar and the regulator.

3.9 The complete Setup

The complete setup is shown in (Figure 2.11).

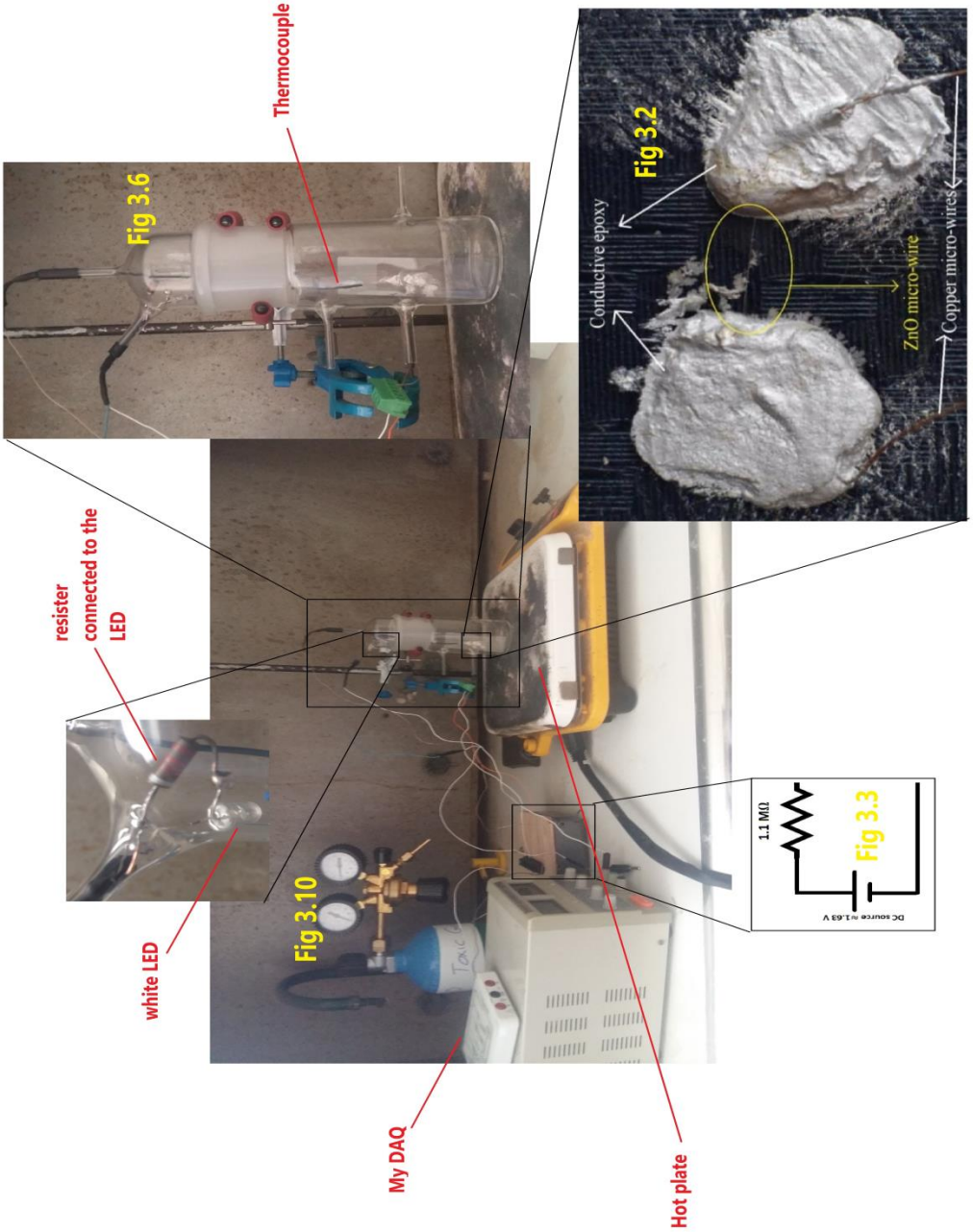


Figure 3.111: The complete setup of the experiment
All parts of my setup are shown in this figure and labeled as it appeared in the context, some parts are magnified to show its details.

4 DATA AND RESULTS

4.1 The effect of light

4.1.1 LEDs

To study the effect of light, different LED colors were used, for the first time blue led was used, the effect is clear, turning on the light reduces the resistance at 50 % approximately in a sharp way, and when turning off the LED the resistance rises again in a slow manner that took several days to attain the start point (see Figure 3.1) .

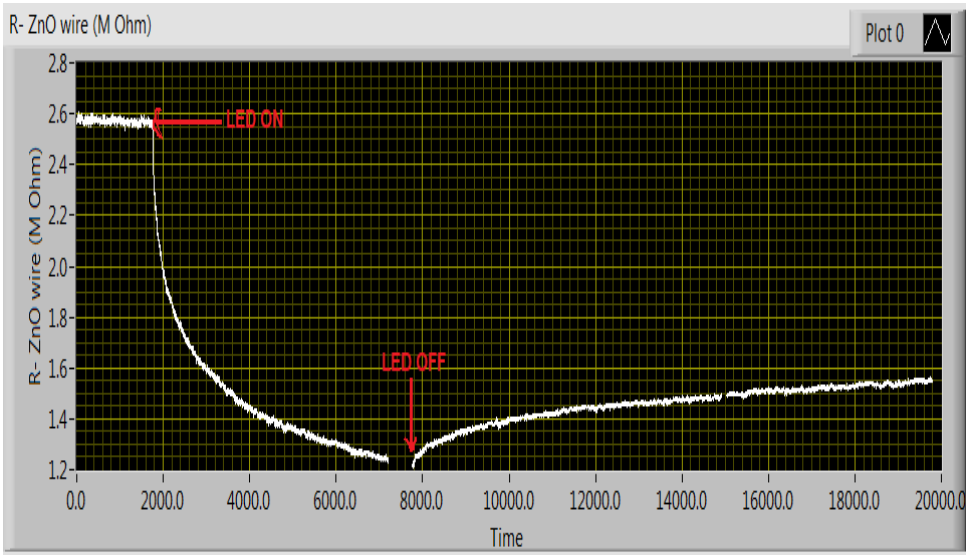


Figure 4.1: The effect of blue LED,The LED was turned on at 1990 sec and off at 8000 sec

A second experiment was made with green color led, the resistance also reduce to approximately 40 % of its original value, and it took long time to attain its start point resistance again, see Figure 3.2 .

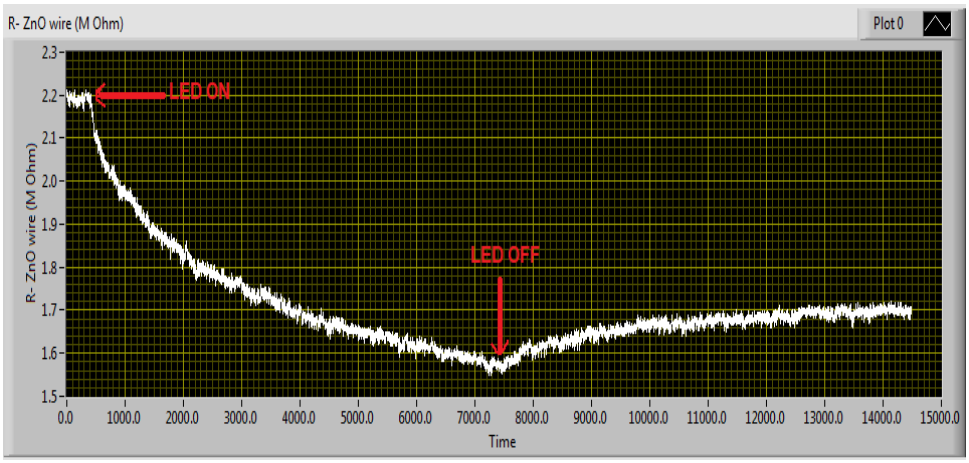


Figure 4.2: The effect of green LED, The LED was turned on at 400 sec and off at 7400 sec

After that a red LED was used , the resistance reduced to approximately 80% of its original value , it did not reduced as much as green and blue LEDs because it has very low intensity compared to them, see Figure 3.3 .

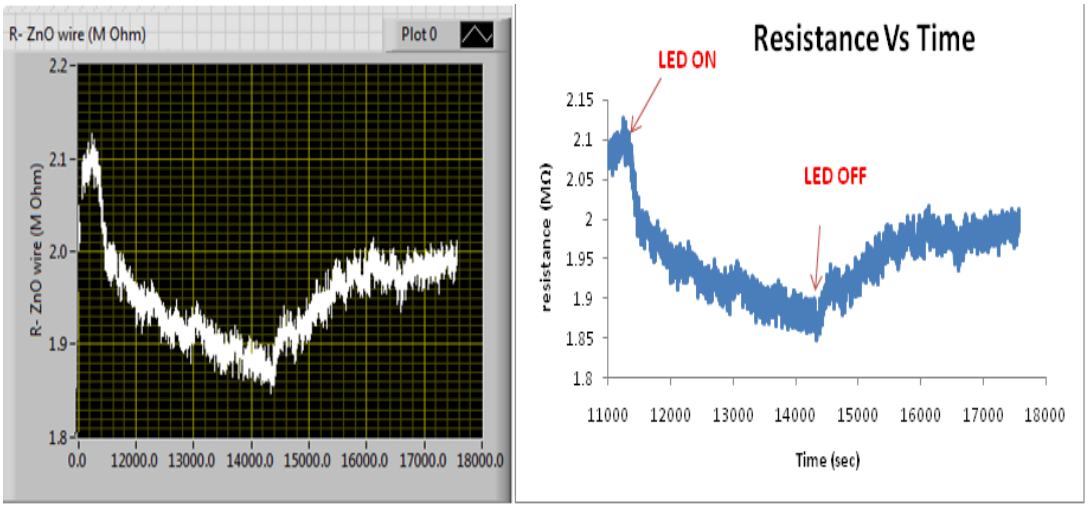


Figure 4.3: The effect of red LED, The LED was turned on at 11000 sec and off at 14400 sec, Left: the result from LabView, Right; the result drown with excel.

This is consistent with the natural response of the ZnO, and it was discussed in details in chapter 2.

4.1.2 UV

UV response is very similar to colored light that come from LEDs, the resistance falls rapidly under UV and it recovers slowly (see Figure 3.4).

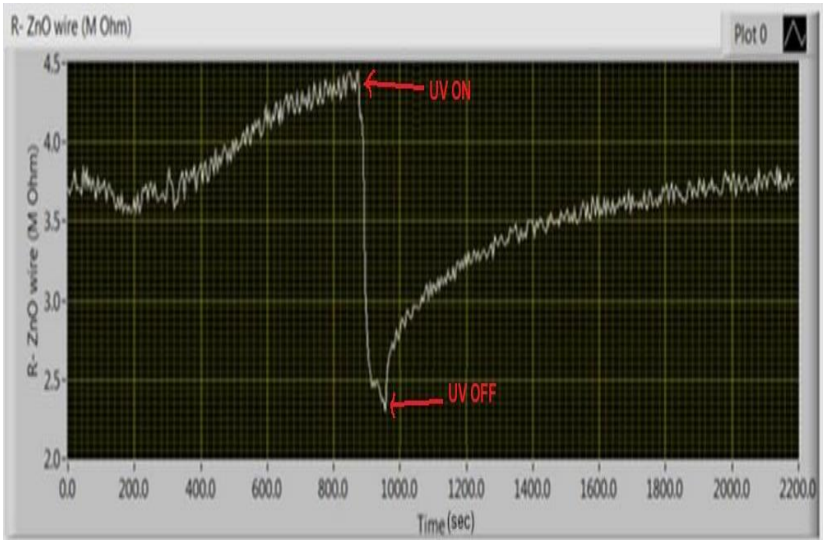


Figure 4.4: The effect of UV, The UV lamp was turned on at 860 sec and off at 960 sec.

4.2 Heating the sample

Before heating the sample the resistance was around 8.9MΩ, then when it was heated to approximately 150 ° C, the resistance falls to o.816MΩ, the drop in the resistance is consistent and in the same time as the temperature rises, after three days the resistance stayed at the same value o.816 MΩ, and did not return to its original value.

It was not expected that the resistance would stay at its minimum value after leaving it for three days, so oxygen gas was supplied to the micro-wire (see Figure 5.5),

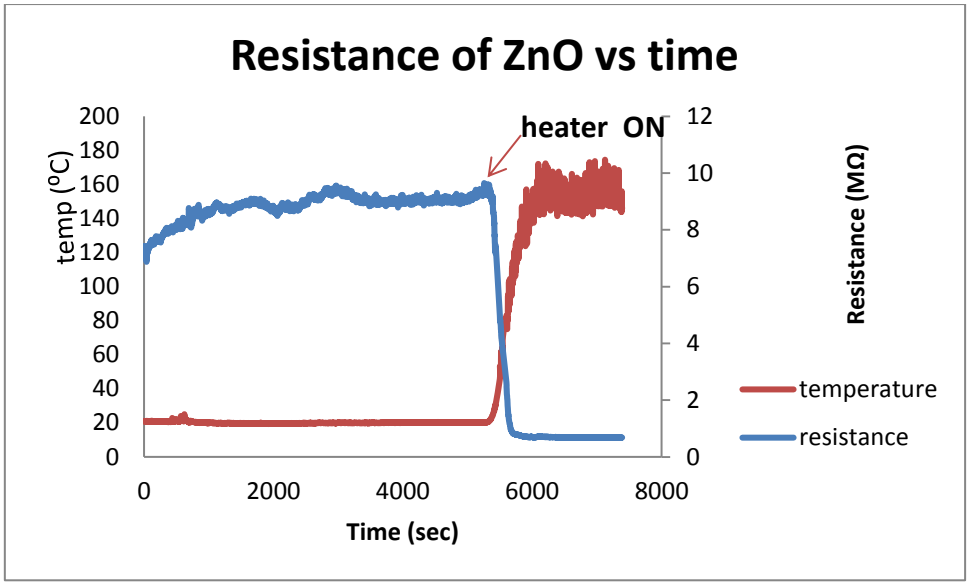


Figure 4.5: Resistance variation of a single ZnO:Sb microwire as the temperature rose from 20℃ to 150℃ in the absence of light. The sample was kept inside the small glass container with the cap of the container being closed.

After supplying oxygen gas the resistance of the ZnO micro-wire increased to approximately 0.85M Ω (see Figure 3.6) and it never returned to its start value before heating. So I used different sample to complete the experiment.

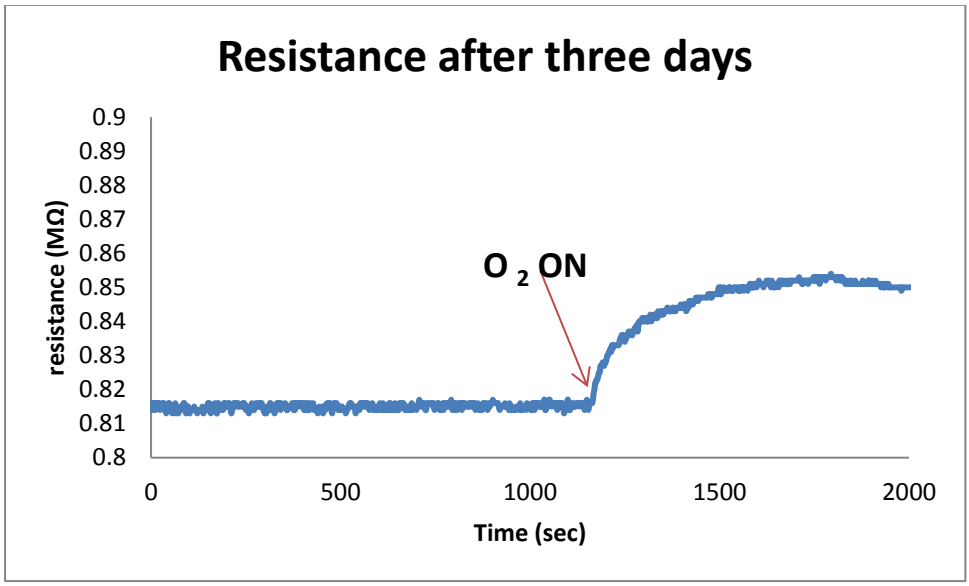


Figure 4.6: Resistance after three days
Resistance at room temp. after three days of being heated to 150C° for 1 hour, its resistance did not rise until supplying Oxygen gas, and it never returns to its start point resistance.

4.3 Gas Effect

The third part of the experiment was to test the effect of Hydrogen, Oxygen and N_2O gas on ZnO:Sb micro-wires.

4.3.1 The Effect of Oxygen

Many experiments were made previously to test the effect of Oxygen gas on the resistance of many metal oxides including ZnO and Sb doped ZnO , it is also known that supplying O_2 gas to the atmosphere around ZnO:Sb micro wire increases the resistance, and that exactly what happened to our sample (see Figure 3.7)

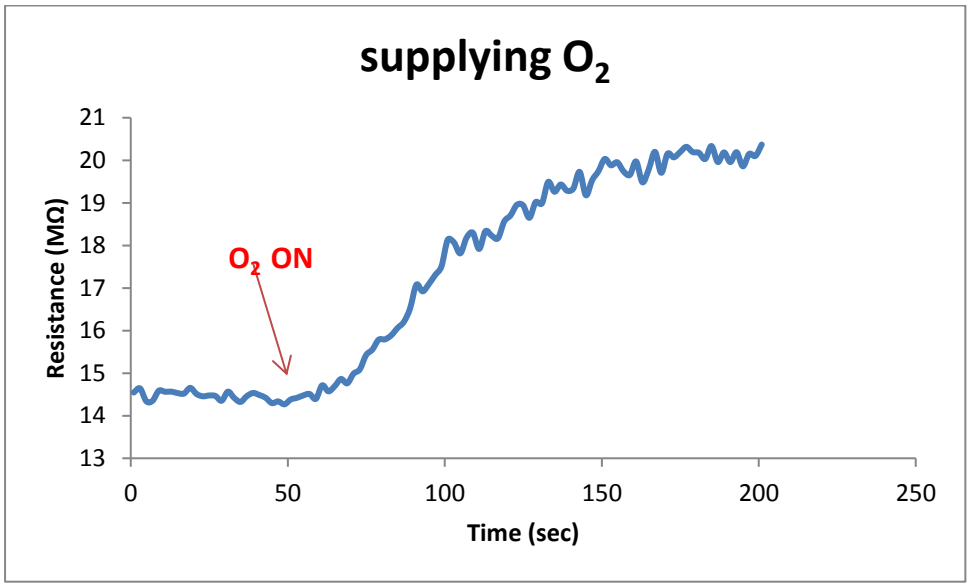


Figure 4.7: Time variation of the resistance of an individual ZnO:Sb micro-wire at 20°C due to oxygen gas flow.

4.3.2 The effect of Nitrous gas

N_2O gas was the first gas to be tested (see Figure 3.8). Turning the LED on decreased the resistance of the ZnO micro-wire, which was expected. However, it was surbrizing that the resistance of the ZnO micro-wire also decreased when N_2O gas was supplied, and it increased when N_2O gas was stopped. This was not expected because N_2O is a highly oxidizing gas and it is supposed to increase the resistance of the ZnO micro-wire.

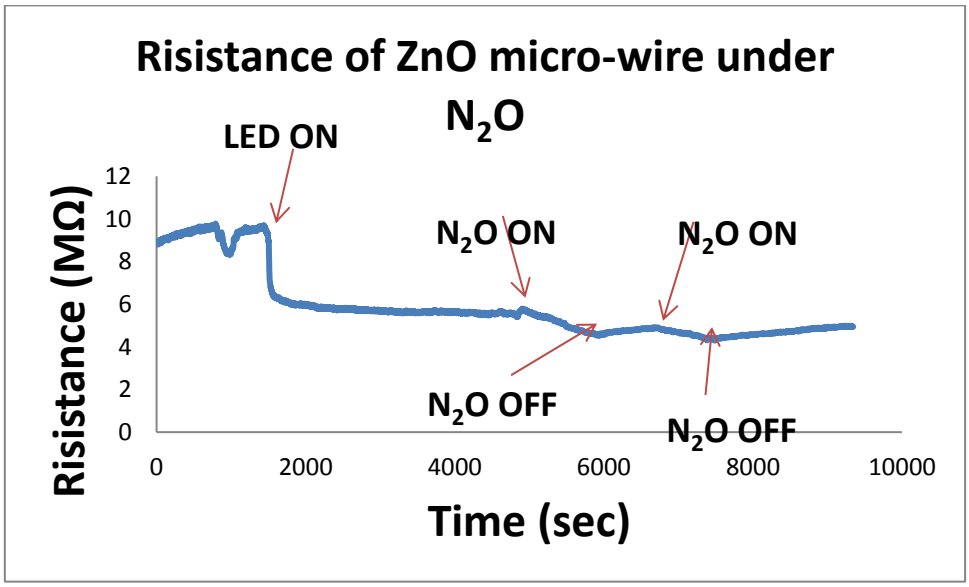


Figure 4.8: Time variation of the resistance of an individual ZnO:Sb micro-wire at 200°C due to nitrous gas flow.

A closer look at the chart (Figure 3.9) will show that when supplying N_2O gas the resistance is reduced from 5.5MΩ to 4.5MΩ within 15 min , and it rises again to around 5MΩ within 10 min after we stop supplying the gas. It then falls again when supplying the gas, and it rises another time with the gas in the same manner.

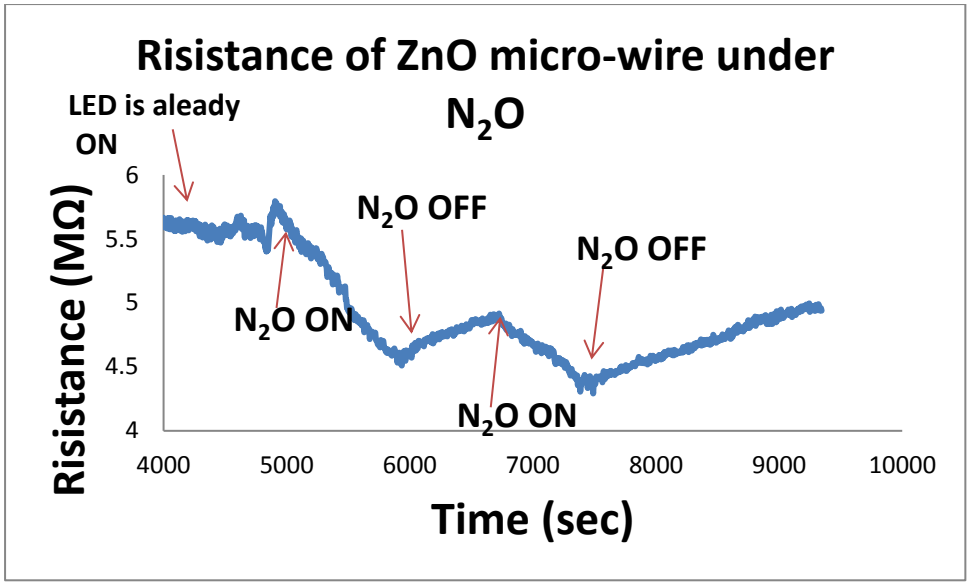


Figure 4.9:A closer look at Figure 3.8
Time variation of the resistance of an individual ZnO:Sb microwire at 20°C due to nitrous gas flow

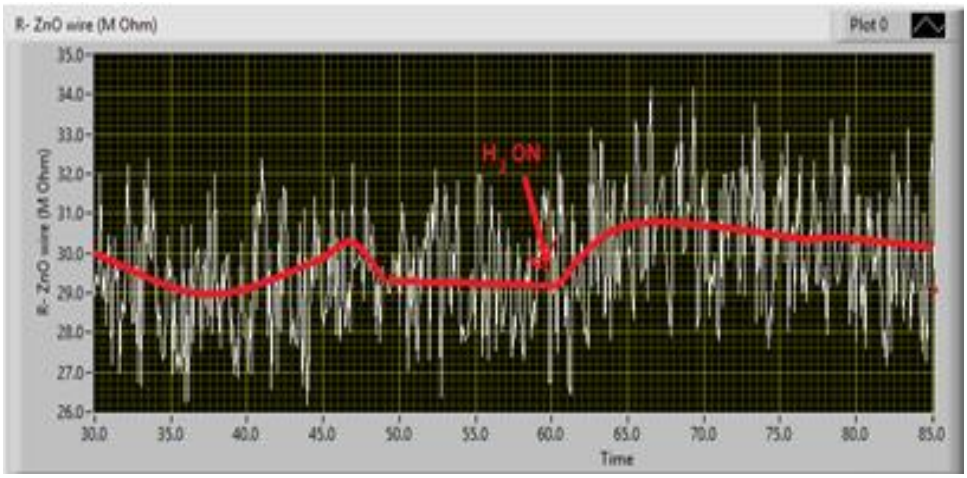
4.3.3 The effect of Hydrogen

In this part Hydrogen gas was tested using the same setup, and as said before Hydrogen gas is a reducing gas, and its effect was really unexpected. This forced us to repeat the experiment many times and using two different ways of water electrolysis to separate hydrogen and oxygen (explained in chapter 2), it was a surprising result, supplying hydrogen raised the resistance of the ZnO:Sb micro-wire in a small value.

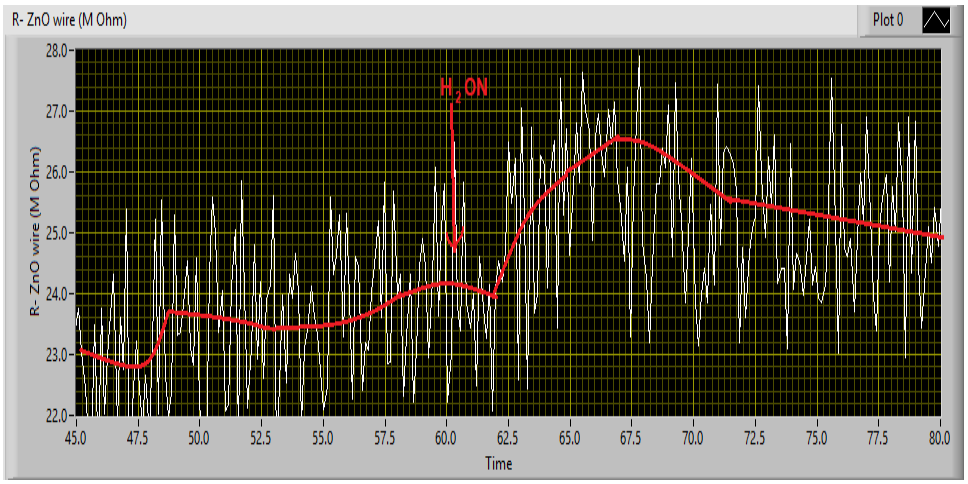
In darkness and at room temp.

In the first trial the sample was in darkness at room temperature, the resistance of ZnO:Sb micro-wire showed a very small response to Hydrogen (see Figure 3.10) the red line showing the average value of the resistance, one can see that it rises a little under Hydrogen gas Figure 3.10 a), b), and c) show the effect of hydrogen under the same conditions.

a)



b)



c)

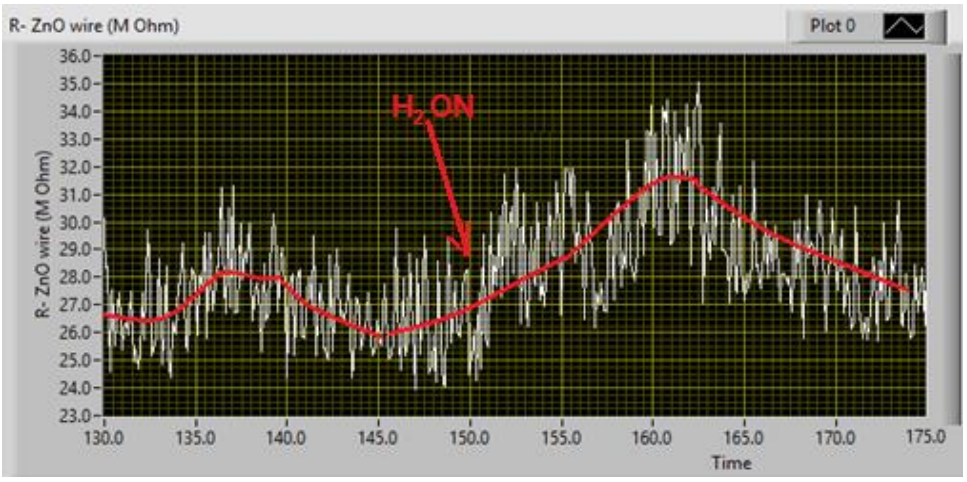


Figure 4.10: Time variation of the resistance of an individual ZnO:Sb micro-wire at 20°C due to hydrogen gas flow
a)10 ml of H_2 was on at 60 sec for approximately 10 sec. b) 15 ml of H_2 was on at 60 sec for approximately 13 sec. c) 15 ml of H_2 was on at 150 sec for approximately 13 sec.

Hydrogen Gas with Heat

This time the sample was heated to 100ºC, and the effect of Hydrogen on the resistance is clearer (see Figure 3.11), the resistance rises from 2.4MΩ to 2.5MΩ.

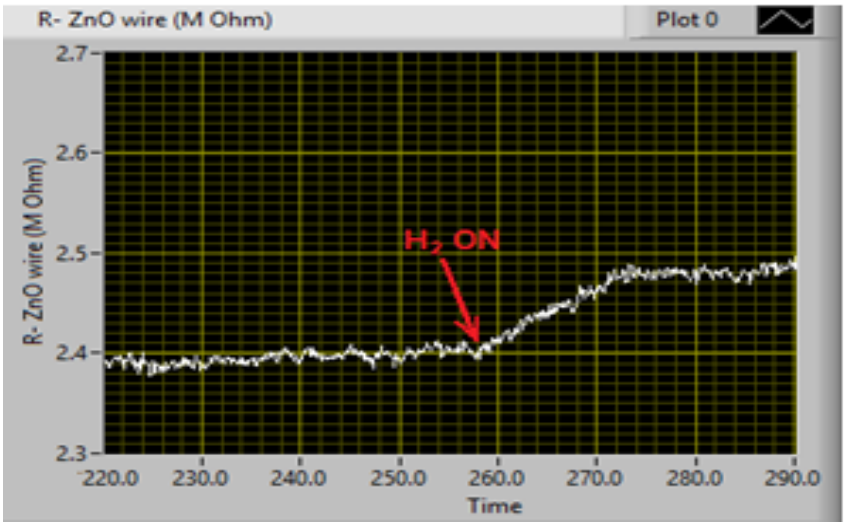


Figure 4.11: Time variation of the resistance of an individual ZnO:Sb micro-wire at 100°C due to hydrogen gas flow.

4.3.4 Supplying Hydrogen and Oxygen to the sample

To check the previous result, Oxygen was switched with Hydrogen several times, see Figure 3.12.

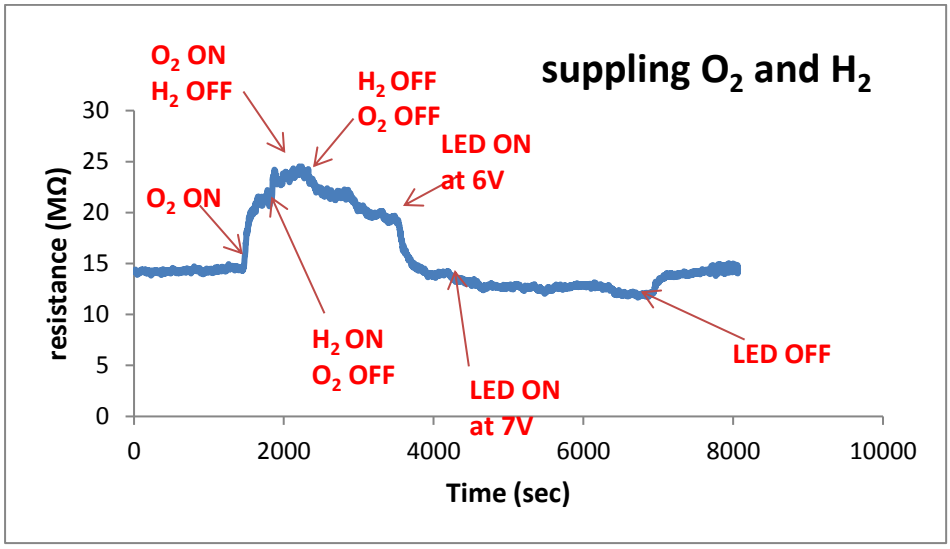


Figure 4.12: Time variation of the resistance of an individual ZnO:Sb micro-wire at 20°C due to switching between oxygen and hydrogen gas flow
First , when oxygen gas was on, The resistance increases ,then I turned off oxygen gas and turned hydrogen gas on, the resistance continued to increase , then I repeated these two steps and no effect occurs, after that , both gases were turned off, and the resistance decreases.

Oxygen is the first one, and it raised the resistance in a fast manner to approximately 1.5×the starting resistance, then Hydrogen was supplied, it also raised the resistance but in a slower manner, Oxygen was supplied again, the resistance increased a little, at last both Hydrogen and Oxygen are switched off, the resistance decreased, as a final step , a white LED was used to test the sample, its resistance fall in a fast manner as usual, so we can say that this micro-wire still attain its properties. Figure 3.13 shows a closer look to Figure 3.12.

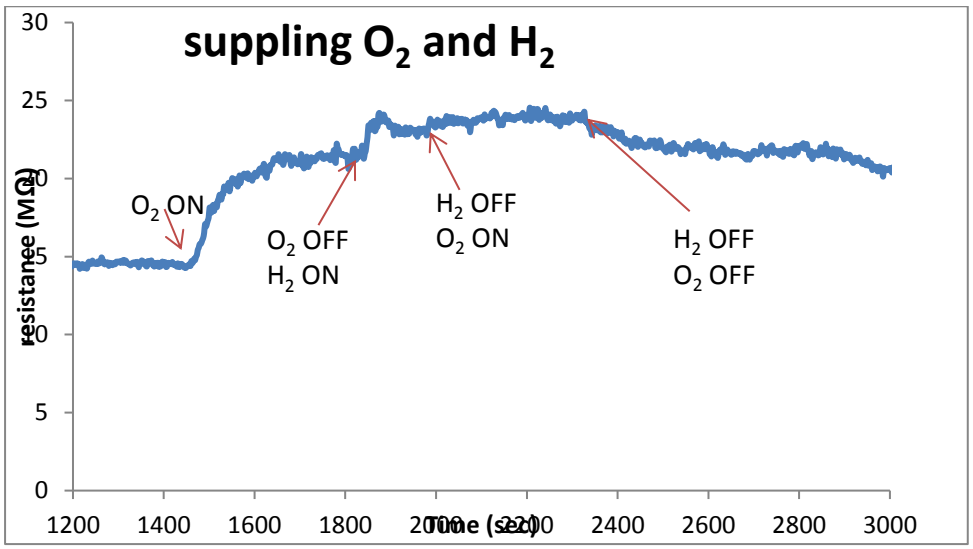


Figure 4.13: a closer look to Figure 3.12

4.4 UV and Hydrogen

When UV was ON the resistance falls as expected, the hydrogen gas was supplied for 15 sec and it raised the resistance of the wire (see Figure 3.14).

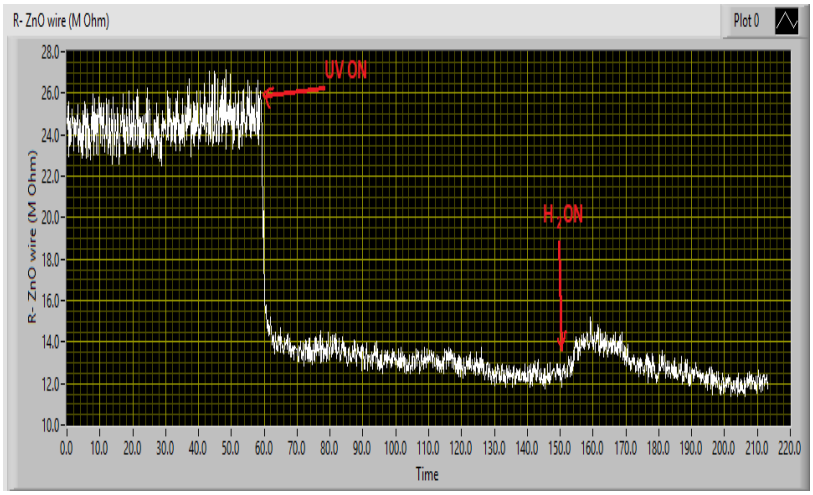


Figure 4.14: Time variation of the resistance of an individual ZnO:Sb micro-wire at 20°C due to hydrogen gas flow under UV illumination.

5 CONCLUSIONS AND FUTUER WORK

In this thesis, we systematically studied the effects of light illumination, temperature variation, and oxygen gas flow on the electrical resistance of ZnO:Sb micro-wires. On the basis of the results of the experiments done so far, we conclude that all these three parameters: light illumination, ambient temperature and abundance of oxygen, hydrogen and N_2O impact the electrical resistance. However, we found unexpected results. Not all oxidizing gases increase the resistance of ZnO:Sb such as N_2O gas, and not all reducing gases do the opposite just like Hydrogen gas.

Still, despite the large body of work associated with native defects in ZnO, many questions remain regarding the optical and electronic properties of these centers. In my experiment things takes another direction. N_2O gas reduced the resistance of the ZnO:Sb micro-wire, and hydrogen gas raised it, so things must be explained and some new assumptions should be found.

We recommend that future studies assess the response of these ZnO:Sb wires to other oxidizing and reducing gases. Furthermore, meticulous studies of the response time, recovery time and efficiency of these micro-wires to oxygen gas will improve the possibility of their utilization in sensor devises.

6 APPENDIX A

To measure the voltage in order to calculate the resistance using LabVIEW program you need a block diagram (shown in Figure 6.1) and you need front panel window like the one shown in Figure 6.2.

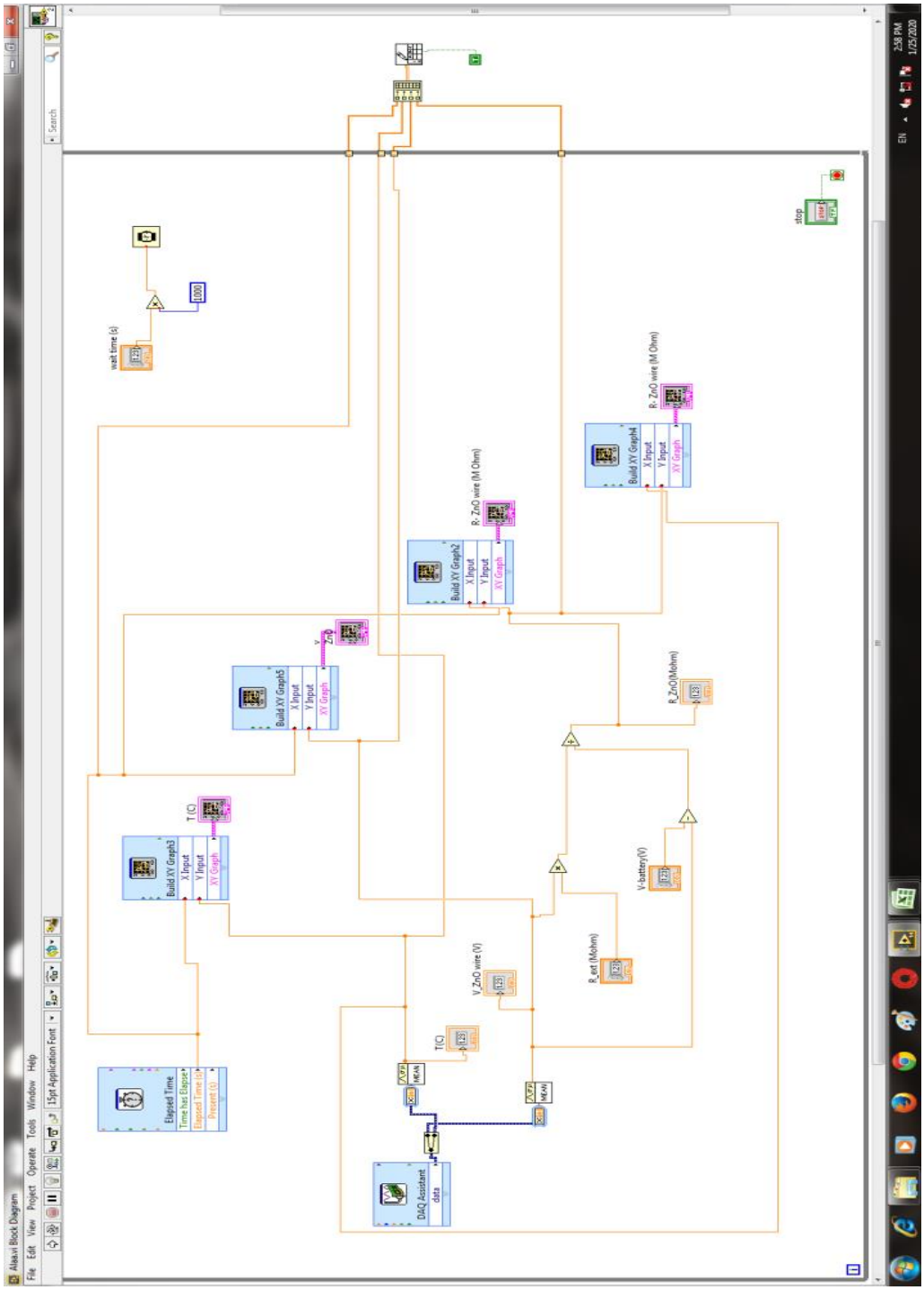


Figure 6.1: The block diagram of the LabVIEW program.

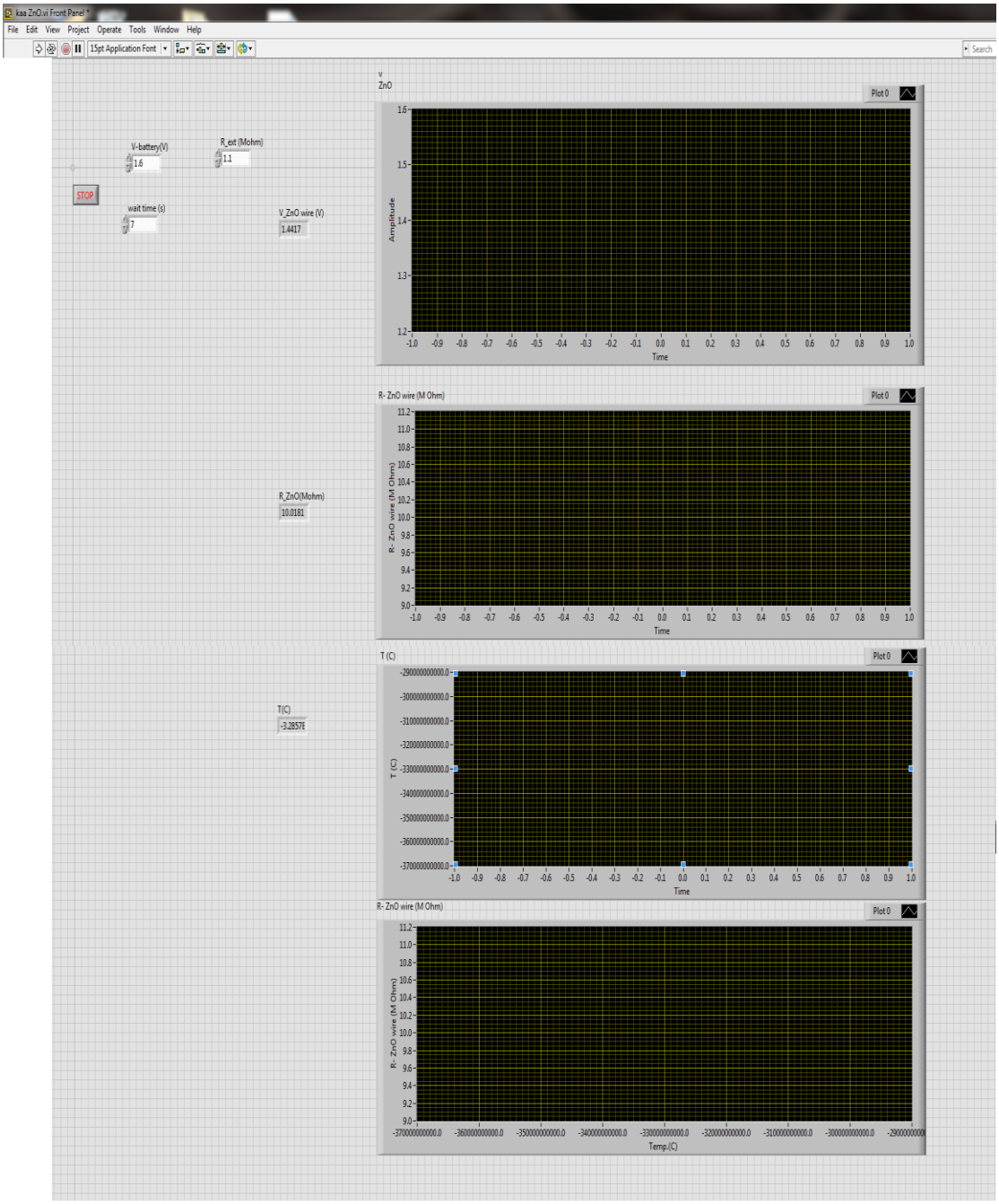


Figure 6.2: Front panel window.

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